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AMINO TRI-LOWER ALKYLIDENEPHOSPHONIC ACID BUILDERS FOR SYNTHETIC DETERGENTS

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14 Claims. (Cl. 252-137)

This is a continuation-in-part of application Ser. No. 221,308, filed Sept. 4, 1962, now abandoned.

This invention relates to improved builders for synthetic detergents and more particularly to the use of amino tri-lower alkylidenephosphonic acids and their salts as builders for synthetic anionic, nonionic, and/or amphoteric surface active compounds which are suitable as detergents in aqueous solutions.

As used herein, the term "builder" means a substance used with or in a detergent to aid in cleansing.

The use of builders in detergents is well known today with one class in particular, the polyphosphates, being extensively used. The polyphosphates, e.g., sodium triphosphate and tetrasodium pyrophosphate, are used primarily because they are relatively inexpensive and they exert, when used in moderate amounts, a synergistic effect on relatively low percentages of the surface active compounds. However, the susceptibility of the polyphosphates to hydrolysis or degradation in aqueous solutions is well known, being primarily dependent on pH and temperature conditions. Because of this limitation, it is believed apparent, therefore, that a "hydrolytically stable" builder having building properties comparable to the polyphosphates would represent an advancement in this art.

Of particular note is the suitability of a "hydrolytically stable" builder for use in liquid detergents in order to provide a relatively long shelf life or remain stable under various storage conditions. In addition, such a builder could be used advantageously with dry detergents for improved handling and storage characteristics, especially when the detergent is in an aqueous solution ready for use. Also, in processing dry detergents where a spray-drying operation is employed, much higher temperatures could be used with a "hydrolytically stable" builder. The foregoing is by no means the extent to which the builders may be used, but are noted only as representative areas and it can, therefore, be appreciated that "hydrolytically stable" builders could be used advantageously in many and varied applications.

Therefore, it is an object of this invention to provide an improved builder for synthetic surface active compounds.

Another object of this invention is to provide a "hydrolytically stable" builder for synthetic anionic, nonionic and/or amphoteric surface active compounds which are suitable for use as detergents in aqueous solutions.

Another object of this invention is to provide an improved washing composition having incorporated therein a "hydrolytically stable" builder.

Another object of this invention is to provide an improved washing composition of a synthetic anionic, nonionic and/or amphoteric surface active compounds and a "hydrolytically stable" builder.

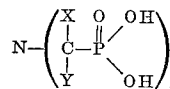
A still further object of this invention is to provide an improved liquid washing composition of a synthetic anionic, nonionic and/or amphoteric surface active compounds and a "hydrolytically stable" builder.

Other objects will become apparent from the detailed description and the claims.

It has been found that amino tri-lower alkylidenephos-

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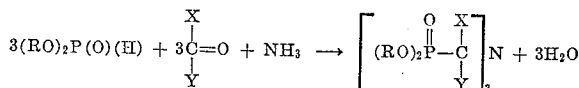
phonic acids, or a salt thereof, said acids being of the following formula:



wherein X, Y or both represent hydrogen or a lower alkyl group (1-4 carbon atoms), exhibit improved building properties in detergents as will be more fully discussed hereinafter.

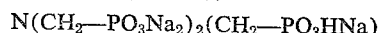
Compounds illustrative of the invention are: amino tri(methylphosphonic acid), amino tri(ethylidenephosphonic acid) and amino tri(isopropylidene phosphonic acid), amino mono(methylphosphonic acid) di(ethylidene phosphonic acid) and amino tri(butylidenephosphonic acid).

Amino tri-lower alkylidenephosphonic acids and their salts may be prepared by various means, one of which comprises as a first step the preparation of the corresponding ester by the following general reaction:



The free amino tri-lower alkylidenephosphonic acids and their salts may be readily prepared by hydrolysis of the esters using strong mineral acids such as hydrochloric acid and the like.

By the term "hydrolytically stable," as used herein, is meant a substantial resistance by the builder to hydrolysis or degradation under various pH and temperature conditions. For example, a 20 gram sample of pentasodium amino tri(methylphosphonate),



was dissolved in 100 ml. of water. A 25 ml. portion of the solution was added to a 25 ml. portion of 12 M HCl to give a 10% solution of the builder in HCl. Another 25 ml. portion of the solution was added to a 25 ml. portion of 10% NaOH to give a 10% solution of the builder in a 5% solution of NaOH. The foregoing 10% solutions were boiled for a period of four hours, at the end of which both solutions exhibited no change in physical properties. Nuclear magnetic resonance spectra showed the two 10% solutions to be identical with a fresh 10% solution of the builder in water, thereby establishing the resistance of the builder to hydrolysis or degradation under severe temperature and pH conditions. It should be noted that all known polyphosphates, whether in the acid, salt or ester form, would hydrolyze or degrade completely under the foregoing conditions. Another sample, in this instance 2 grams of the anhydrous penta sodium amino tri(methylphosphonate), a dry powder, was heated on a thermogravimetric balance. Below a temperature of 300° C. less than 1% weight loss resulted. X-ray diffraction patterns of the heated sample and an unheated sample were identical. As is believed apparent from the foregoing, the builder of the instant invention is "hydrolytically stable" and by exhibiting building properties comparable to the polyphosphates can be used advantageously in many various detergents building applications.

Generally stated, this invention relates to the use of amino tri-lower alkylidenephosphonic acids and their salts as builders for synthetic anionic, nonionic and/or amphoteric surface active compounds to provide improved cleansing agents, and, in addition, to the resulting detergent compositions formed therefrom.

It is to be understood that although the sodium salts of amino tri-lower alkylidenephosphonic acids are preferred, and in particular the penta sodium salt, other alkali metal salts, such as potassium, lithium and the

like, as well as mixtures of the alkali metal salts, may be substituted therefor. In addition, any water-soluble salt, such as the ammonium salt and the amine salts, which exhibit the characteristics of the alkali metal salt may be used to practice the invention. In particular, amine salts prepared from low molecular weight amines, i.e., having a molecular weight below about 300, and more particularly the alkyl amines, alkylene amines and alkanol amines containing not more than 2 amine groups, such as, ethylamine, diethylamine, propylamine, propylenediamine, hexylamine, 2-ethyl hexylamine, N-butylethanolamine, triethanolamine and the like, are the preferred amine salts. Since most of the synthetic detergent compositions are used in alkaline aqueous systems, amino tri-lower alkylidenephosphonic acid may be used by adjusting the pH, if required, of the detergent composition or the resulting aqueous solution to the desired alkaline pH condition. In view of the foregoing, it is preferred that the pH of the detergent composition or the aqueous medium be such as to result in an aqueous washing solution having at least a pH of 9 or above when the detergent composition is used in amounts to give effective cleansing action.

It has been found that penta sodium amino tri(methylphosphonate)hexahydrate particles are non-hygroscopic and free flowing and, therefore, exhibit improved handling properties which make them especially suited for use as a builder. The hexahydrate penta sodium salt may readily be prepared by humidifying the anhydrous salt form under about 30-90% relative humidity and room temperature conditions for about 30 minutes. The anhydrous penta sodium amino tri(methylphosphonate) may readily be prepared by dissolving the acid form in an aqueous solution containing a stoichiometric amount of NaOH, evaporating and drying at about 120° C.

As previously mentioned, the improved builder may be used with any of the conventional detergents classed as synthetic non-soap anionic, nonionic and/or amphoteric surface active compounds which are suitable as cleansing agents. Anionic surface active compounds can be broadly described as compounds which contain hydrophilic and lyophilic groups in their molecular structure and which ionize in an aqueous medium to give anions containing the lyophilic group. These compounds include the sulfated or sulfonated alkyl, aryl, and alkyl aryl hydrocarbons and alkali metal salts thereof, for example, sodium salts of long chain alkyl sulfates, sodium salts of alkyl naphthalene sulfonic acids, sodium salts of sulfonated abietenes, sodium salts of alkyl benzene sulfonic acids particularly those in which the alkyl group contains from 8-24 carbon atoms; sodium salts of sulfonated mineral oils and sodium salts of sulfosuccinic acid esters such as sodium dioctyl sulfosuccinate.

Advantageous anionic surfactants include the higher alkyl aryl sulfonic acids and their alkali metal and alkaline earth metal salts such as for example sodium dodecyl benzene sulfonate, sodium tridecyl benzene sulfonate, magnesium dodecyl benzene sulfonate, potassium tetradecyl benzene sulfonate, ammonium dodecyl toluene sulfonate, lithium pentadecyl benzene sulfonate, sodium dioctyl benzene sulfonate, disodium dodecyl benzene disulfonate, disodium di-isopropyl naphthalene disulfonate and the like as well as the alkali metal salts of fatty alcohol esters of sulfuric and sulfonic acids, the alkali metal salts of alkyl aryl (sulfothioic acid) ethers and the alkyl thiosulfuric acid, etc. Preferred anionic organic surface active agents are, as noted hereinbefore, sodium salts of alkyl benzene sulfonic acids and particularly preferred sodium salts of alkyl benzene sulfonic acids are those in which the alkyl group or radical contains 10 to 18 carbon atoms in a straight (i.e. unbranched) chain.

Nonionic surface active compounds can be broadly described as compounds which do not ionize but acquire hydrophilic characteristics from an oxygenated side chain, usually polyoxyethylene, while the lyophilic part of the

molecule may come from fatty acids, phenols, alcohols, amides or amines. Examples of nonionic surfactants include products formed by condensing one or more alkylene oxides of 2 to 4 carbon atoms, such as ethylene oxide or propylene oxide, preferably ethylene oxide alone or with other alkylene oxides, with a relatively hydrophobic compound such as a fatty alcohol, fatty acids, sterol, a fatty glyceride, a fatty amine, an aryl amine, a fatty mercaptan, tall oil, etc. Nonionic surface active agents also include those products produced by condensing one or more relatively lower alkyl alcohol amines (such as methanolamine, ethanolamine, propanolamine, etc.) with a fatty acid such as lauric acid, cetyl acid, tall oil fatty acid, abietic acid, etc. to produce the corresponding amide.

Particularly advantageous nonionic surface active agents are condensation products of a hydrophobic compound having at least 1 active hydrogen atom and a lower alkylene oxide (for example the condensation product of an aliphatic alcohol containing from about 8 to about 18 carbon atoms) and from about 3 to about 30 mols of ethylene oxide per mol of the alcohol, or the condensation product of an alkyl phenol containing from about 8 to about 18 carbon atoms in the alkyl group and from about 3 to about 30 mols of ethylene oxide per mol of alkyl phenol. Other advantageous nonionic detergents include condensation products of ethylene oxide with a hydrophobic compound formed by condensing propylene oxide with propylene glycol.

Amphoteric surface active compounds can be broadly described as compounds which have both anionic and cationic groups in the same molecule. Such compounds may be grouped into classes corresponding to the nature of the anionic-forming group, which is usually carboxyl, sulfonic acid or sulfuric ester. Examples of such compounds include sodium N-methyl taurate, sodium N-coco beta amino, propionate, sodium N-tallow beta amino dipropionate, sodium N-lauryl beta iminodipropionate and the like.

Other typical examples of these categories of the anionic, nonionic and/or amphoteric surface active agents are described in Schwartz and Perry "Surface Active Agents," Interscience Publishers, New York (1949), and the Journal of American Oil Chemists Society, volume 34, No. 4, pages 170-216 (April 1957).

The amount of builder necessary to be used with the surface active compound (active) may vary depending upon, inter alia, the end use, type of active employed, pH conditions and the like. It should be noted that the builder of the instant invention may be used in conjunction with the conventional polyphosphate builders (alkali metal polyphosphates, i.e., sodium tripolyphosphate, tetrasodium pyrophosphate, tetrapotassium pyrophosphate, disodium pyrophosphate and the like). It has been found that a builder containing a ratio by weight of sodium tripolyphosphate and penta sodium amino tri(methylphosphonate) within 1:10 and 10:1 in some instances functions better as a builder than either when used individually. The new builders can be employed with detergents as above described in any desired proportions. The optimum active/builder ratio depends upon the particular active employed and the end use for which the mixture is intended but most generally will fall within the range of an active/builder weight ratio 4:1 to 1:4, which is, therefore, the preferred range to practice the invention.

The resulting detergent composition, that is, the active and builder, of the present invention is generally effective when used in aqueous systems in conventional amounts such as is normally used with detergent compositions containing known builders (e.g., polyphosphates) and which is generally about 0.2% concentration or below.

The invention is not to be limited to any particular method of mixing the builder and the detergent. The builder may be mechanically mixed in, crushed in the detergent

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in the form of a slurry, or dissolved in a solution of the detergent. In addition, the builder may be admixed with the detergent in any of the forms in which the detergent is manufactured in, as well as being added simultaneously or separately to an aqueous solution. In any event, the builder is intended to be used with the detergent at the time of application as a cleansing agent.

To illustrate the invention, the following examples are presented.

Example I

In this example, penta sodium amino tri(methylphosphonate) was compared under carefully controlled conditions with sodium tripolyphosphate for building properties in hot water. The conditions of the test were: hardness—150 p.p.m., total detergent concentration—0.2%; temperature—60° C.; pH—adjusted to tabulated value in 60° C. solution prior to testing; active—dodecylbenzene sodium sulfonate. The tests were made in a Launder-Ometer machine on standard soiled fabric specimens. The following are the tabulated results with various active/builder ratios expressed in percent of an industry standard: sodium lauryl alcohol sulfate.

TABLE 1

pH	Active/builder ratio	Detergency, A ¹	Percent standard B ²
9.....	0/100	52	56
9.....	20/80	59	76
9.....	40/60	86	92
10.....	0/100	62	67
10.....	20/80	73	81
10.....	40/60	95	95
11.....	0/100	67	72
11.....	20/80	95	101
11.....	40/60	110	112

¹ A=penta sodium amino tri(methylphosphonate).

² B=sodium tripolyphosphate.

The above results indicated that the builder of the instant invention compares very favorably in hot water with sodium tripolyphosphate, a widely used builder. Note that especially at higher pH values and higher active/builder ratios they exhibit no material differences in their building properties. Therefore, it can be appreciated that the new hydrolytically stable builders of this invention exhibit building properties comparable to conventional widely-used builders and can advantageously be used in many applications where the conventional builders are not suitable.

Example II

In this example, penta sodium amino tri(methylphosphonate) was compared under carefully controlled conditions with sodium tripolyphosphate and tetra potassium pyrophosphate for building properties in cold water. The conditions of the test were: hardness—150 p.p.m.; total detergent concentration—0.2%; temperature—77° F.; pH—10; active—sodium dodecylbenzene sulfonate. The tests were made in a Launder-Ometer machine. The following are the tabulated results with various active/builder ratios expressed in percent soil removal based on a standard soiled fabric specimen.

TABLE 2

Active/builder ratio	Percent soil removal		
	A ¹	B ²	C ³
20/80.....	23	20	24
40/60.....	22	23	27

¹ A=penta sodium amino tri(methylphosphonate).

² B=tetra potassium pyrophosphate.

³ C=sodium tripolyphosphate.

From the above tests results, it can be observed that the builder of the instant invention compares equally to two of the most widely used builders, namely, sodium tripolyphosphate and tetra potassium pyrophosphate. As can be appreciated, the builders of the instant invention can be used advantageously in situations where the con-

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ventional polyphosphates are not suitable especially in situations which require a hydrolytically stable builder.

It should further be noted that the penta sodium salt of amino tri(methylphosphonic acid) exhibits a markedly greater solubility in water than either sodium tripolyphosphate or tetra sodium pyrophosphate. For example, at room temperature penta sodium amino tri(methylphosphonate) is soluble in water to the extent of 44%, whereas sodium tripolyphosphate is soluble to the extent of 13% and tetra sodium pyrophosphate is soluble to the extent of 16%. It is, therefore, believed appreciated that because the builder of the instant invention is hydrolytically stable and exhibits good water solubility, it is extremely suitable for use in liquid detergents.

While a detergent composition in accordance with this invention need contain only a detergent active of the class described and amino tri-lower alkylidenephosphonic acids and their salts, it will be appreciated that the incorporation in the mixture of additional ingredients commonly used with cleansing agents, such as perfume, anti-redeposition agents (e.g., carboxymethylcellulose), brightening agents (e.g., fluorescent dyes) and the like, is contemplated as being within the invention.

The following detergent compositions in which the percentages are by weight are presented as being illustrative of the present invention:

I

	Percent
30 Sodium dodecyl benzene sulfonate	20
Pentasodium amino tri(methylphosphonate)	50
Sodium carboxymethylcellulose	1
Sodium silicate	10
35 Sodium sulfate	19

II

Nonionic condensate (dodecyl alcohol-ethylene oxide on a 1:10 molar ratio basis)	20
40 Tetrapotassium pyrophosphate	30
Pentasodium amino tri(methylphosphonate)	49
Sodium carboxymethylcellulose	1

III

Sodium N-methyl taurate	20
45 Dipotassium amino tri(isopropylidenephosphonate) ..	50
Sodium carboxymethylcellulose	1
Sodium sulfate	29

All of the foregoing detergent compositions are effective for cleaning textiles, hard surfaces such as dishes, walls and the like when used in concentrations of about 0.2% in water.

What is claimed is:

1. A new washing composition comprising a non-soap, organic synthetic detergent selected from the group consisting of anionic, nonionic, and amphoteric surface active compounds and, as a builder, a compound selected from the group consisting of amino tri-lower alkylidenephosphonic acids containing substituents on the carbon atom of the N—C—P linkages selected from the group consisting of hydrogen and lower alkyl groups, containing from 1 to 4 carbon atoms and their water soluble salts selected from the group consisting of alkali metal salts, ammonium salts and low molecular weight alkyl, alkylene and alkanol amine salts; said detergent and said builder being by weight within a ratio of 1:4 to 4:1.

2. A new liquid washing composition comprising water, a non-soap, organic synthetic detergent selected from the group consisting of anionic, nonionic and amphoteric surface active compounds and, as a builder, a compound selected from the group consisting of amino tri-lower alkylidenephosphonic acids containing substituents on the carbon atom of the N—C—P linkages selected from the group consisting of hydrogen and lower alkyl groups containing from 1 to 4 carbon atoms and their water

soluble salts selected from the group consisting of alkali metal salts, ammonium salts and low molecular weight alkyl, alkylene and alkanol amine salts; said detergent and said builder being by weight within a ratio of 1:4 to 4:1 and in a concentration in said water greater than about 0.2% by weight.

3. A new washing composition comprising a non-soap, organic synthetic detergent selected from the group consisting of anionic, nonionic, and amphoteric surface active compounds and, as a builder, a compound selected from the group consisting of amino tri-lower alkylidene-phosphonic acids containing substituents on the carbon atom of the N—C—P linkages selected from the group consisting of hydrogen and lower alkyl groups containing from 1 to 4 carbon atoms, and their water soluble alkali metal salts, said detergent and said builder being by weight within a ratio of 1:4 to 4:1.

4. A new washing composition comprising a non-soap, organic synthetic detergent selected from the group consisting of anionic, nonionic and amphoteric surface active compounds and, as a builder, an admixture of an inorganic alkali metal polyphosphate and a compound selected from the group consisting of amino tri-lower alkylidenephosphonic acids containing substituents on the carbon atom of the N—C—P linkages selected from the group consisting of hydrogen and lower alkyl groups containing from 1 to 4 carbon atoms, and their water soluble alkali metal salts, said detergent and said builder admixture being by weight within a ratio of 1:4 to 4:1, and said alkali metal polyphosphate and said builder compound being by weight within a ratio of 1:10 to 10:1.

5. A new washing composition comprising an anionic non-soap, organic synthetic detergent and, as a builder, a compound selected from the group consisting of amino tri-lower alkylidenephosphonic acids containing substituents on the carbon atom of the N—C—P linkages selected from the group consisting of hydrogen and lower alkyl groups containing from 1 to 4 carbon atoms, and their water soluble sodium salts, said detergent and said builder being by weight within a ratio of 1:4 to 4:1.

6. A new washing composition comprising an anionic non-soap, organic synthetic detergent and, as a builder, amino tri(methylphosphonic acid), said detergent and said builder being by weight within a ratio of 1:4 to 4:1.

7. A new washing composition comprising an anionic non-soap, organic synthetic detergent and, as a builder, pentasodium amino tri(methylphosphonic acid), said detergent and said builder being by weight within a ratio of 1:4 to 4:1.

8. A new washing composition comprising sodium dodecyl benzene sulfonate and, as a builder, a compound selected from the group consisting of amino tri(methylphosphonic acid) and its water soluble alkali metal salts, said sodium dodecyl benzene sulfonate and said builder being by weight within a ratio of 1:4 to 4:1.

9. A new washing composition comprising sodium dodecyl benzene sulfonate and, as a builder, penta sodium amino tri(methylphosphonate), said sodium dodecyl benzene sulfonate and said builder being by weight within a ratio of 1:4 to 4:1.

10. A new washing composition comprising a non-soap, organic synthetic detergent selected from the group consisting of anionic, nonionic, and amphoteric surface active compounds and, as a builder, a compound selected from the group consisting of amino tri(methylphosphonic acid) and its water soluble alkali metal salts, said detergent and said builder being by weight within a ratio of 1:4 to 4:1.

11. A new washing composition comprising an anionic non-soap, organic synthetic detergent and, as a builder, an admixture of sodium tripolyphosphate and a compound selected from the group consisting of amino tri(methylphosphonic acid) and its water soluble alkali metal salts, said anionic synthetic detergent and said builder admixture being by weight within a ratio of 1:4 to 4:1, and said sodium tripolyphosphate and said builder compound being by weight within a ratio of 1:10 to 10:1.

12. A new aqueous washing system comprising water, a non-soap, organic synthetic detergent selected from the group consisting of anionic, nonionic and amphoteric surface active compounds and, as a builder, a compound selected from the group consisting of amino tri-lower alkylidenephosphonic acids containing substituents on the carbon atom of the N—C—P linkages selected from the group consisting of hydrogen and lower alkyl groups containing from 1 to 4 carbon atoms and their water soluble alkali metal salts, said synthetic detergent and said builder being by weight within a ratio of 1:4 to 4:1 and being present in said water in effective cleansing amounts below a total of about 0.2% concentration, and said aqueous washing system having at least a pH of 9.

13. A method for cleaning articles comprising washing said articles with an aqueous washing system as defined in claim 12.

14. A new washing composition comprising, as an anionic, non-soap, organic synthetic detergent, a sodium salt of an alkylbenzene sulfonic acid in which the alkyl group contains from 10 to 18 carbon atoms and, as a builder, a compound selected from the group consisting of amino tri(methylphosphonic acid) and its sodium salts, said detergent and said builder being by weight within a ratio of 1:4 to 4:1.

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