ABSTRACT OF THE DISCLOSURE

A heavy duty detergent composition consisting essentially of a surface active agent selected from the group consisting of anionic, nonionic, and amphoteric synthetic detergents and mixtures thereof and, as a builder, a composition consisting essentially of (a) from about 3% by weight to about 16% by weight of certain organic sequestering agents, (b) from about 30% by weight to about 80% by weight of sodium tripolyphosphate, and (c) from about 15% by weight to about 55% by weight of an alkali metal salt, said percents by weight being based upon the total weight of the builder composition; the weight ratio of the surface active agent to the builder composition in the detergent composition being from about 2:3 to about 1:5.

This invention relates to builder compositions which impart improved cleaning efficiency to detergents. More particularly it relates to improved heavy duty detergent compositions employing novel builder compositions. Heavy duty detergents are one of the general types of detergents on the market and are particularly suited for difficult laundering problems, such as cleaning of heavily soiled clothes. They are normally comprised of an active, that is, a surface active agent of the anionic, nonionic or amphoteric type or mixtures of those and a polyphosphate as a builder to increase the cleaning efficiency of the active. Sodium tripolyphosphate is the most commonly used polyphosphate builder for heavy duty detergents; however, sodium tripolyphosphate suffers several serious handicaps. For example, sodium tripolyphosphate is known to be hydrolytically unstable and degrades in aqueous solutions. As another example, certain algen in bodies of water, are believed to be aided in their growth by the degraded products of tripolyphosphate. Excessive algal growth in streams, lakes and the like, have created problems, as for example, by detracting from the appearance of the water and limiting activities thereon, and it is sometimes necessary to use costly chemical treatment or physical removal treatments. Because of problems, such as the foregoing, considerable research effort has been directed toward finding a builder which would impart equal or better cleaning efficiency to an active for heavy duty synthetic detergent applications and would reduce, minimize or obviate the handicaps of sodium tripolyphosphate. A number of builders and builder compositions have been proposed or tried in the past; however, those which exhibit good building action are relatively expensive and thus would add appreciably to the cost of the heavy duty detergent if employed as a replacement for sodium tripolyphosphate. Thus, sodium tripolyphosphate is believed to be unrivaled as a builder for heavy duty detergent, especially on a price-performance basis.

As can be appreciated, therefore, an economical builder composition which imparts a better cleaning efficiency to detergents than the commonly used builder, sodium tripolyphosphate, and which reduces, minimizes or obviates the handicaps of sodium tripolyphosphate would be a significant advancement in the art.

It is therefore an object of this invention to provide a builder composition which imparts improved cleaning efficiency to detergents.

It is another object of this invention to provide an improved heavy duty detergent composition employing a novel builder composition.

It is a further object of this invention to provide an improved heavy duty composition containing a novel builder composition which imparts a better cleaning efficiency to detergents than the commonly used, builder, sodium tripolyphosphate.

It is still another object of this invention to provide an economical builder composition for heavy duty detergents which reduces, minimizes or obviates the handicaps of the commonly used builder, sodium tripolyphosphate.

These and still further objects of the present invention will become readily apparent to one skilled in the art from the following detailed description.

The present invention, comprising (a) an organic sequestering agent, (b) sodium tripolyphosphate and (c) an inorganic alkali metal salt, provides compositions useful for imparting improved builder action to synthetic surface active agents of the anionic, nonionic and amphoteric types and mixtures of the actives when the foregoing components of the builder composition are combined in proper amounts; all of which will be more fully discussed hereinafter. The builder composition of this invention when compared to the commonly used heavy duty detergent builder, sodium tripolyphosphate, has been found to exhibit not only superior performance and at present prices superior performance on a price-performance basis, but also to reduce, minimize or obviate many of the limitations of sodium tripolyphosphate. Organic sequestering agents and the inorganic alkali metal salts used in this invention are hydrolytically stable, and do not degrade in aqueous solutions. Since in the practice of this invention the organic sequestering agent and inorganic alkali metal salt can be used in amounts up to 70% by weight of the builder, the promotion of algae growth that is attributed to the use of sodium tripolyphosphate as a builder can be reduced. As can be appreciated, a composition comprised of the foregoing components which include as a substitute for a portion of sodium tripolyphosphate a relatively inexpensive alkali metal salt and with the components exhibiting a synergistic action to yield a builder which gives performance superior to sodium tripolyphosphate is believed to be totally unexpected.

The organic sequestering agents useful in practicing this invention are the amino polycarboxylic acids, the amino tri (lower alkylidenephosphonic) acids, the alkyene diphosphonic acids, the water soluble salts of the foregoing acids and mixtures thereof.

Amino polycarboxylic acids are represented by the general structure:

\[
CH_2\text{COOH} \quad N\text{CH}_2\text{COOH} \quad R
\]
where R is a member selected from the group consisting of the radicals

\[ \text{CH}_2-\text{N}-\text{CH}_2-\text{COOH} \]

and

\[ \text{CH}_2-\text{N}-\text{CH}_2-\text{COOH} \]

where R₁ is a member selected from the group consisting of hydrogen, lower alkyl (1-4 carbon atoms), hydroxy substituted lower alkyl, phenyl and hydroxy substituted phenyl, and R₂ is a member selected from the group consisting of hydrogen lower alkyl (1-4 carbon atoms), and hydroxy substituted lower alkyl.

Compounds illustrative of the amino polycarboxylic acids include nitrilo triacetic acid, ethylenediameine tetra-acetic acid, diethylentriamine penta-acetic acid, 1:2-diamino cyclohexane tetra-acetic acid, hydroxyethyl amino diacetic acid, hydroxyethyl ethylene diamine tricetic acid, ortho hydroxyl phenyl ethylene diamine triacetic acid, anthranilic-N-N-diacetic acid, tri (hydroxy methyl) diethylene triamine diacetic acid, c-dibutyl-nitrico triacetic acid and \( \text{C}_{12} \text{H}_{25} \text{N}-\text{CH}_2-\text{COOH} \).

Amino tri (lower alkylidenediphosphonic acids) are represented by the general structure

\[ \text{N} \left( \begin{array}{c} \text{X} \\ \text{O} \\ \text{O} \\ \text{OH} \\ \text{Y} \end{array} \right) \]

where X and Y are members selected from the group consisting of hydrogen and lower alkyl group (1-4 carbon atoms).

Compounds illustrative of amino tri (lower alkylidenediphosphonic acids) include:

- amino tri (methylene phosphonic acid)
- amino tri (ethylenediphosphonic acid)
- amino tri (isopropylenediphosphonic acid)
- amino tri (butylenediphosphonic acid)
- amino tri (propylenediphosphonic acid)
- amino tri (tart-amylidenediphosphonic acid)
- amino tri (isamyldienediphosphonic acid)
- amino tri (sec butylidenediphosphonic acid)

Alkyiene diphosphonic acids are represented by the general structure

\[ \text{HO} \left( \begin{array}{c} \text{O} \\ \text{P} \\ \text{X} \\ \text{O} \\ \text{Y} \end{array} \right) \text{OH} \]

where X is a member selected from the group consisting of hydrogen and lower alkyl group (1-4 carbon atoms), Y is either hydrogen, hydroxyl, a halogen, especially chlorine, bromine and fluoride, or lower alkyl group (1-4 carbon atoms), and n is an integer from 1 to 6.

Compounds illustrative of alkyene diphosphonic acids include:

- methylenediphosphonic acid
- ethylenediphosphonic acid
- 1 hydroxyl, ethylenediphosphonic acid
- hexamethylenediphosphonic acid
- isopropylenediphosphonic acid
- butylenediphosphonic acid

hydroxymethylene diphosphonic acid
1 hydroxyl, propylenediphosphonic acid
amyldienediphosphonic acid
tri (2-hydroxy, 3 methyl, 4 bromo 4 hexylidene) diphosphonic acid
pentamethylenediphosphonic acid
penta (propylenedine) diphosphonic acid
tetra (1-hydroxyethylene) diphosphonic acid
tetra (3-hexylidene) diphosphonic acid
tri (2-hydroxy, 3 amyldiene) diphosphonic acid
tetra (2-amylidene) diphosphonic acid
di (2 methyl, 3 hexylidene) diphosphonic acid
tetra (4 octylidene) diphosphonic acid
penta (2 propyldiene) diphosphonic acid
tri (2-hydroxy, 3 methyl, 4 chloro, 4 butylidene) diphosphonic acid

It is to be understood that although the sodium salts of the amino tri (lower alkylidenediphosphonic acids), alkylidenediphosphonic acids, and aminopolycarboxylic acids are preferred, other water soluble salts such as potassium, lithium, and the like, as well as mixtures of the alkali metal salts may be substituted therefor. In addition, the ammonium salts, as well as amine salts, may be used to practice this invention.

Compounds illustrative of these salts include the following:

- Aminopolyacrylates
  - monopotassium nitrolitratetrate
  - pentasodium diethylentriamine penta-acetate
  - diammonium ethylenediaminetetra-acetate
  - dimethylamino diethylenetriaminetetraacetate
  - trilithium nitrolitratetrate
  - disodium diethylenetriamine penta-acetate
  - tripotassium ethylenediaminetetraacetate
  - dipotassium nitrolitratetrate
  - pentapotassium diethylenetriamine penta-acetate
  - monosodium nitrolitratetrate
  - tetrasodium ethylenediaminetetraacetate

- Amino tri (lower alkylidenediphosphonic acids)
  - disodium amino tri (methylphosphonate)
  - dipotassium amino tri (methylphosphonate)
  - diammonium amino tri (methylphosphonate)
  - Pentasodium amino tri (methylphosphonate)
  - dilithium amino tri (ethylenediphosphonate)
  - diammonium amino tri (ethylenediphosphonate)
  - pentapotassium amino tri (butylenediphosphonate)
  - phosphonium amino tri (isopropylenediphosphonate)
  - disodium amino tri (butylenediphosphonate)
  - diethylamine amino tri (methylphosphonate)
  - dimethylamine amino tri (ethylenediphosphonate)

- Alkylenediphosphonates
  - monolithium methylenediphosphonate
  - dipotassium methylenediphosphonate
  - diethylamine methylenediphosphonate
  - triammonium methylenediphosphonate
  - tetrasodium methylenediphosphonate
  - trisodium 1 hydroxy ethylenediphosphonate
  - trisodium tri (2 hydroxy, 3 amyldiene) diphosphonate
  - monopotasium ethylenediphosphonate
  - dimethylamine ethylenediphosphonate
  - tripotassium amylidenediphosphonate
  - tetrasodium butylenidiphosphonate
  - diammonium isopropylenediphosphonate
  - monosodium amylidenediphosphonate
  - tripotassium ethylidenediphosphonate

The builder composition of this invention may be used with any of the anionic, nonionic or amphoteric type synthetic surface active agents and mixtures of these surface active agents.

Anionic synthetic surface active agents, that is non-soap detergents, are generally described as those com-
pounds which contain hydrophilic and lyophilic groups in their molecular structure and ionize in an aqueous medium to give anions containing both the lyophilic group and hydrophilic group. The alkyl aryl sulfonates, the alkyl sulfates and the sulfated oxethylated alkyl phenols are illustrative of the anionic type of surface active compounds.

The alkyl aryl sulfonates are a class of synthetic anionic surface active agents represented by the general formula

$$(R_2)n_1 + (R_3)Ar^- + (SO_3)M$$

where $R_2$ is hydroxy or a straight or branched chain hydrocarbon group of from 1 to 4 carbon atoms; $R_3$ is a straight or branched chain hydrocarbon radical having from about 1 to about 24 carbon atoms, at least one $R_3$ having at least 8 carbon atoms; $n_1$ is from 1 to 3; $n_2$ is from 1 to 2; $Ar$ is a phenyl or a naphthal radial and $M$ is either hydrogen, an alkali metal, such as sodium, potassium and the like; ammonium, or an organic amine such as entanol amine, diethanol amine, triethanol amine and hexylamine and the like. $R_2$ can be for example, methyl, ethyl, propyl, isopropyl, butyl, isobutyl and the like. $R_3$ can be for example, methyl, ethyl, hexyl, octyl, tert-cotyl, iso-octyl, nonyl, decyl, dodecyl, octadecyl and the like.

Compounds illustrative of the alkyl aryl sulfonates include sodium dodecylbenzene sulfonate, sodium decylbenzene sulfonate, ammonium dodecylbenzene sulfonate, sodium octadecylbenzene sulfonate, sodium nonylbenzene sulfonate, sodium dodecyl-naphthalene sulfonate, sodium heptadecylbenzene sulfonate, potassium eicosyl naphthalene sulfonate, ethylamine undecyl-naphthalene sulfonate and sodium decosyl-naphthalene sulfonate.

The alkyl sulfates are a class of synthetic anionic surface active agents represented by the general formula

$$RSO_3M$$

where $M$ is either hydrogen, an alkali metal, such as sodium, potassium and the like, ammonium or an organic amine, such as ethanolamine, diethanolamine, triethanolamine, ethylenediamine and diethylenetriamine, and the like; and $R$ is a straight or branched chain saturated hydrocarbon radical, such as octyl, decyl, dodecyl, tetradecyl and hexadecyl, as well as the mixed alkyl radicals derived from fatty oils, such as coconut oil, tallow, cottonseed oil and fish oil. $R$ usually has from 8 to 18 carbon atoms.

Compounds illustrative of alkyl sulfate class of anionic surface active agents include sodium octadecyl sulfate, sodium hexadecyl sulfate, sodium dodecyl sulfate, sodium nonyl sulfate, ammonium decyl sulfate, potassium tetradecyl sulfate, diethanolamino octyl sulfate, triethanolamino octadecyl sulfate and ammonium nonyl sulfate.

The sulfated oxethylated alkyl phenols are a class of synthetic anionic surface active agents represented by the general formula

$$R - A - [CH(2CH2)nCH2O] - CH2O - SO3M$$

where $R$ is a straight or branched chain saturated hydrocarbon group having from about 8 to about 18 carbon atoms, such as a straight or branched group, such as octyl, nonyl, decyl, dodecyl and the like; $A$ is either oxygen, sulfur, a carbonamide group, thiocarbonamide group, a carboxylic group or thio-carboxylic ester group, $x$ is an integer from 3 to 8 and $M$ is either hydrogen, or an alkali metal such as sodium, potassium and the like, or ammonium, or an organic amine, such as ethanalamine, diethanolamine, triethanolamine, ethylene diamine and the like.

Compounds illustrative of the sulfated oxethylated alkyl phenol class of anionic surface active agents include

- Sodium dodecylbenzene sulfonate, sodium cetylbenzene sulfonate, sodium dodecyl dodecylamino methyl sulfonate.
- Potassium cetyl dodecylamino methyl sulfonate, potassium cetylhexadecyl dodecylamino methyl sulfonate, potassium cetylhexadecyl dodecylamino methyl sulfonate and potassium cetylhexadecyl dodecylamino methyl sulfonate.
- Also, the C-alkyl substitutated, N-cycloalkyl substituted, amino alkyl sulfonates are illustrative of the amido alkane sulfonates. Compounds illustrative of these include: sodium C-dodecyl N-benzene amido methyl sulfonate, sodium C-hexadecyl N-benzene amido methyl sulfonate, sodium C-hexadecyl N-benzene amido methyl sulfonate and ammonium C-tetradecyl N-naphthyl amido methyl sulfonate.

Illustrative of these synthetic nonionic surface active agents are the products obtained from the reaction of ethylene oxide with an aliphatic alcohol having from 8 to 20 carbon atoms, such as butyl, dodecyl, octyl, dodecyl, dodecyl, tetradeccyl and the like; and with an alkyl phenol in which the alkyl group contains between 4 and 20 carbon atoms, such as butyl, dibutyl, amyl, acetyl, dodecyl, tetradeccyl and the like; and with an alkyl amine in which the alkyl group contains between 1 to 8 carbon atoms.

Compounds illustrative of synthetic nonionic surface active agents include the products obtained from condensing ethylene oxide or propylene oxide with the following: propylene glycol, ethylene diamine, diethylene glycol, dodecyl phenol, nonyl phenol, tetradeccyl alcohol, N-tetradecyl diethanolamide, and N-dodecyl mono-ethanolamide.

Amphoteric surface active compounds can be broadly described as compounds which have both an anionic and cationic group in their structure. Illustrative of the amphoteric compounds are the amido alkane sulfonates which are represented by the general formula

$$R - CO - N - (CH(2)CH2)nSO3M$$

where $M$ is either hydrogen, an alkali metal, such as sodium, potassium, and the like, or ammonium, is an integer from 1 to 5, $R$ is an alkyl radical with from 8 to 18 carbon atoms, and $R_2$ is a member selected from the group consisting of hydrogen, alkyl, aryl or alicyclic radicals.

For example, the C-alkyl substitutated, N-alkyl substituted, amido alkyl sulfonates are illustrative of the amido alkane sulfonates. Compounds illustrative of these include: sodium C-pentadecyl N-methyl amido ethyl sulfonate; sodium C-tridecyl, N-methyl amido ethyl sulfonate; amonium C-decyl, N-dodecyl amido pentyl sulfonate; potassium C-hexadecyl, N-propyl amido propyl sulfonate; and potassium C-tridecyl N-hexyl amido methyl sulfonate.

In addition the C-alkyl substitutated, N-aryl substituted, amido alkyl sulfonates are illustrative of the amido alkane sulfonates. Compounds illustrative of these include: sodium C-dodecyl N-benzene amido methyl sulfonate; potassium C-octyl N-naphthalamido ethyl sulfonate; sodium C-hexadecyl N-benzene amido pentyl sulfonate and ammonium C-tetradecyl N-naphthalamido amido methyl sulfonate.

Also, the C-alkyl substituted, N-cycloalkyl substituted, amino alkyl sulfonates are illustrative of the amido alkane sulfonates. Compounds illustrative of these include: sodium C-dodecyl, N-cyclopropyl amido methyl sulfonate; potassium C-tetradecyl, N-cyclohexyl amido ethyl sulfonate; ammonium C-decyl, N-cyclopropyl amido ethyl sulfonate.
butyl sulfonate and sodium C-octyl, N-cyclohexyl amido methyl sulfonate and the like. Detergent composition, employing an anionic, nonionic, amphoteric type synthetic surface active agent and mixtures of these and the builder composition of this invention in weight ratios of active to builder of from about 2:3 to about 1:5, give excellent cleaning efficiency when used in aqueous solutions in conventional weight concentrations of about 0.2% or below. It has been found that the ranges or parts by weight of the components in the builder composition of this invention are important and the following ranges in parts by weight in the builder should be followed: (a) from about 3 parts to about 16 parts of an organic sequestering agent, (b) from about 30 parts to about 80 parts by weight of sodium tripolyphosphate and (c) from about 15 parts to about 55 parts of an alkali metal inorganic salt selected from the group consisting of sodium sulfate, sodium carbonate, potassium sulfate, potassium carbonate and mixtures thereof.

The invention is not to be limited to any particular method of preparing a detergent containing the builder composition of the present invention and the surface active agent as described herein. The builder composition can be cranked in the active in form of a slurry and the active agent as described herein. The builder composition can be cranked in the active in form of a slurry and the active and builder dried together by any conventional means of drying, such as spray drying. The active and builder can both be dissolved in an aqueous solution and dried together, such as by drum drying and the like, to form the detergent composition. In addition, the active and builder composition can be mixed together in the solid form by any conventional means of mixing solids such as mills, ribbon mixers and the like. Still another means of mixing the active and builder compositions is to dry one or two of the components of the builder composition along with the active by any of the before mentioned drying methods and mix the remaining component or components to the resulting solid.

An additional method of using the builder and active to achieve the desired cleaning results is to add each component of the detergent, the active and the three components of the builder, to form an aqueous solution of desired concentration. In any event the builder is intended to be used in conjunction with the active at the time the resulting detergent composition is used as a cleaning agent. In addition, the sodium tripolyphosphate can be incorporated into the detergent by using sodium tripolyphosphate and sodium hydroxide which reacts in the cranking step to form sodium tripolyphosphate. A suitable method for the use of sodium tripolyphosphate and sodium hydroxide is shown in Example IV.

A detergent composition in accordance with this invention need only contain a surface active agent of classes described and a builder composition as hereinbefore described. However, incorporating additional additives, such as antiredeposition agents, brightening agents, corrosion inhibitors, perfume and the like, is contemplated as being within this invention. These additives are generally used in amounts of up to about 10% by weight of the detergent composition. Compounds such as sodium carboxymethyl cellulose and methyl cellulose are generally classified as antiredeposition agents and are normally found in amounts of below about 2% by weight in the detergent composition. Some heavy duty detergent compositions contain from about 1 to about 7% by weight of a corrosion inhibitor such as sodium silicate. Other additives for specific purposes such as brightening agents, perfume and the like are normally below about 1% by weight in the detergent composition.

To illustrate the invention the following examples are presented. All parts and percentages are by weight unless otherwise indicated.

EXAMPLE I

Ten detergent compositions were prepared by admixing 20 parts by weight of sodium dodecylbenzene sulfonate and 80 parts by weight of various builders. The various builder ingredients in weight percentages are given below.

<table>
<thead>
<tr>
<th>Builder</th>
<th>STP</th>
<th>ATMP</th>
<th>EDTA</th>
<th>NTA</th>
<th>NaSO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Builder 1</td>
<td>10</td>
<td>11</td>
<td>8</td>
<td>39</td>
<td>10</td>
</tr>
<tr>
<td>Builder 2</td>
<td>75</td>
<td>10</td>
<td>39</td>
<td>11</td>
<td>10</td>
</tr>
<tr>
<td>Builder 3</td>
<td>45</td>
<td>29</td>
<td>58</td>
<td>55</td>
<td>10</td>
</tr>
<tr>
<td>Builder 4</td>
<td>45</td>
<td>17</td>
<td>58</td>
<td>55</td>
<td>10</td>
</tr>
<tr>
<td>Builder 5</td>
<td>45</td>
<td>17</td>
<td>58</td>
<td>55</td>
<td>10</td>
</tr>
<tr>
<td>Builder 6</td>
<td>10</td>
<td>11</td>
<td>8</td>
<td>39</td>
<td>10</td>
</tr>
<tr>
<td>Builder 7</td>
<td>10</td>
<td>11</td>
<td>8</td>
<td>39</td>
<td>10</td>
</tr>
<tr>
<td>Builder 8</td>
<td>10</td>
<td>11</td>
<td>8</td>
<td>39</td>
<td>10</td>
</tr>
<tr>
<td>Builder 9</td>
<td>10</td>
<td>11</td>
<td>8</td>
<td>39</td>
<td>10</td>
</tr>
<tr>
<td>Builder 10</td>
<td>10</td>
<td>11</td>
<td>8</td>
<td>39</td>
<td>10</td>
</tr>
</tbody>
</table>

Legend: STP—Sodium tripolyphosphate; ATMP—Pentasodium salt of amion tri(methylphosphonate) acid; EDTA—Disodium salt of ethylene diamine tetracetic acid; NTA—Trisodium salt of mtributyl triacetic acid; NaSO₄—Sodium sulfate.

EXPERIMENT II

In five tests (A, B, C, D and E), the ten detergent compositions prepared in Example I were tested. In each test a control detergent comprising 20 parts by weight of sodium dodecylbenzene sulfonate and 80 parts by weight sodium tripolyphosphate was tested under the same conditions as the indicated detergents. The tests were made in a Launder-Ometer machine on standard soil fabric specimens under the following controlled conditions: hardness—150 p.p.m.; total detergent concentration—0.2%; temperature—60° C.; pH—adjusted to 10 at 60° C. prior to testing.

In each test the cleaning efficiency of the control detergent (using as a builder, sodium tripolyphosphate above) and the indicated detergent compositions were compared using as a basis, an industry standard, Duponol WA (sodium lauryl sulfate) in 50 p.p.m. hardness. In each test the cleaning efficiency of the control detergent (using as a builder, sodium tripolyphosphate alone) was rated as 100. The "Comparative Cleaning Efficiency" given in the following tabulated results indicates the cleaning efficiency of the indicated detergent compositions using the indicated builder prepared in Example I as compared to the control detergent as a basis.

<table>
<thead>
<tr>
<th>Builder</th>
<th>Comparative Cleaning Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>Control 1</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>105</td>
</tr>
<tr>
<td>3</td>
<td>103</td>
</tr>
<tr>
<td>4</td>
<td>107</td>
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<tr>
<td>5</td>
<td>98</td>
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<tr>
<td>6</td>
<td>96</td>
</tr>
<tr>
<td>7</td>
<td>94</td>
</tr>
<tr>
<td>8</td>
<td>92</td>
</tr>
<tr>
<td>9</td>
<td>90</td>
</tr>
<tr>
<td>10</td>
<td>88</td>
</tr>
</tbody>
</table>

1 Control—Detergent composition comprising 20% by weight sodium dodecylbenzene sulfonate and 80% by weight sodium tripolyphosphate.

The results of the above tests dramatically illustrate that a builder composition comprising an organic sequestering agent, sodium tripolyphosphate and an alkali metal salt when used in proper amounts, imparts an excell‘"nt cleaning efficiency to detergents which is totally unexpected. In addition, the results show that the building properties of the builder composition of this invention are superior to sodium tripolyphosphate.

More particularly, the detergent compositions using builder compositions 1, 2, 3 and 4, illustrative of the builder compositions of this invention, exhibited appreciably better cleaning efficiency than the control deter-
gent composition using sodium tripolyphosphate as is shown by the results of Tests A, B, C, and D. The results of these tests further show that the improved cleaning efficiency imparted to the detergents by the builder composition of this invention would not be predicted. More importantly, the results show that sodium sulfate either alone or in combination with sodium tripolyphosphate does not exhibit building properties equal to sodium tripolyphosphate alone. For example, the detergents using builders 6, 7 and 8 had less cleaning efficiency in Test C than the control detergent using sodium tripolyphosphate as a builder. Builders 6 and 7, using sodium sulfate and sodium tripolyphosphate together, range from 92% to 99% as effective as a builder as sodium tripolyphosphate. Further, sodium sulfate alone in only 65% as effective as a builder as sodium tripolyphosphate alone, as is illustrated by the cleaning effectiveness of the detergent using Builder 8 in Test C. Also, the builder compositions with an organic sequestering agent in combination with either sodium sulfate or sodium tripolyphosphate does not have building properties equal to sodium tripolyphosphate. For example, in Test E, Builder 10, a combination of pentasodium amino tri (methylene phosphonate) and sodium sulfate, was only 78% as effective as a detergent builder as sodium tripolyphosphate alone. Similarly, in Tests 9, Builder 9, with pentasodium amino tri (methylene phosphonate) and sodium tripolyphosphate, was only 97% as effective as a detergent builder as sodium tripolyphosphate. From the results of the tests of Builders 6, 7, 8, 9 and 10, one would predict that a builder comprising an organic sequestering agent, sodium tripolyphosphate and sodium sulfate would be inferior to sodium tripolyphosphate alone. It is therefore completely unexpected that a builder appreciably superior to sodium tripolyphosphate is produced by combining the three components of this invention in proper amounts.

In addition, the results of these tests show that it is necessary to have the proper proportions of an organic sequestering agent, sodium tripolyphosphate and an inorganic alkali metal salt in the builder to achieve the improved building efficiency. For example, the results of Test B show that Builder 5 was only 95% as efficient as a builder as sodium tripolyphosphate while Builders 1 and 2 were 104% and 105% as efficient as sodium tripolyphosphate. Therefore, to achieve the benefits of increased builder efficiency it is necessary to control the amounts of each component within the ranges specified herein. More particularly, it is necessary to have a weight percentage range of an organic sequestering agent in the builder from about 3% to about 16%, a weight percentage range of sodium tripolyphosphate in the builder from about 30% to about 80%, and a weight percentage range of an inorganic alkali metal inorganic salt in the builder from about 15% to about 55%.

EXAMPLE III

Six hundred parts of sodium tripolyphosphate, 50 parts of trisodium nitrito triacetate, 200 parts sodium dodecyl sulfate, 150 parts sodium sulfate and 1000 parts of water are charged into a conventional detergent crutcher. The resulting mixture is stirred for 10 minutes and then pumped continuously through a heat exchanger where steam is used to heat the mixture to above 85° C. The slurry is then pumped to a conventional spray drying tower where it is heat dried to form a heavy duty detergent of the following composition.

Ingredients:

| Active—Sodium dodecyl sulfate      | 20 Parts |
| Builder                           | 20 Parts |

Composition of builder:

| Sodium tripolyphosphate | 75 Percent |
| Trisodium nitrito triacetate | 6.25 |
| Sodium sulfate           | 18.75 |

The above detergent gives good cleaning results when used in concentrations of about 0.2% by weight in aqueous solutions in conventional automatic washing machines for laundering clothes and the like.

Other comparable detergent compositions can be prepared in the same manner as described above by replacing trisodium nitrito triacetate with similar amounts of other organic sequestering agents useful in practicing this invention and in like manner, that is, using similar amounts, other alkali metal alkyl sulfates can be substituted for sodium dodecyl sulfate. For example, disodium ethylene diamine tetra-acetate, pentasodium amino tri (methylene phosphonate), trisodium methylene diphosphonate and pentasodium diethylenetriamine pentaoacetate can be substituted for trisodium nitrito triacetate in the foregoing builder composition and sodium octadecyl sulfate, sodium hexadecyl sulfate, potassium monn sulfate, potassium decyl sulfate can be substituted for sodium dodecyl sulfate, and the resulting detergent compositions give good results when used for laundering clothes under the same conditions as the detergent compositions of this example.

EXAMPLE IV

Four thousand parts of water, 1800 parts of sodium dodecylbenzene sulfonate, 1200 parts of sodium dodecyl sulfate, 2000 parts of sodium sulfate, 3200 parts of sodium trimetaphosphate, 400 parts of tetrasodium methylene diphosphonate and 60 parts of sodium carboxymethyl cellulose are charged into a conventional mixing vessel to form a slurry and the resulting slurry is heated to 80° C. The reaction is charged into the slurry. The heat from the reaction evaporates most of the water in addition to converting the sodium trimetaphosphate into sodium tripolyphosphate. After completing the drying by using heated air, a heavy duty detergent is formed having the following composition.

Ingredients:

| Active—Sodium dodecylbenzene sulfonate; sodium dodecyl sulfate | 25.6 Percent |
| Builder | 73.8 |
| Sodium tripolyphosphate (anhydrous basis) | 72.3 Percent |
| Sodium sulfate | 23.2 |
| Tetrasodium methylene diphosphonate or sodium diposphonate | 4.5 |
| Additive—Sodium carboxymethyl cellulose | 0.6 |

The above detergent gives good cleaning results in home clothes laundering applications using conventional automatic washing machines when used in concentrations of about 0.2% by weight in aqueous solutions.

Other comparable detergent compositions can be prepared in the same manner as described above by replacing tetrasodium methylene diposphonate with similar amounts of other organic sequestering agents useful in practicing this invention. For example, similar amounts of disodium ethylene diamino tetra-acetate, trisodium nitrito triacetate, pentasodium diethylenetriamine pentaoacetate, pentasodium amino tri (methylene phosphonate), dipotassium trimethylene phosphonate and dipotassium methylphosphonate can be substituted for tetrasodium methylene diphosphonate in the foregoing builder composition and the resulting detergent composition gives good results when used for home clothes laundering under the same conditions as the detergent composition of this example.

EXAMPLE V

A builder composition comprising 680 parts sodium tripolyphosphate, 40 parts nitroliotrlecic acid, 30 parts sodium carbonate and 370 parts sodium sulfate is prepared by admixing the four anhydrous compounds in a conventional ribbon mixer.
EXAMPLE VI

A detergent composition is prepared by admixing in a conventional ribbon mixer 300 parts sodium c-pentadecyl N-methyl amido ethyl sulfonate, 750 parts sodium tripolyphosphate, 105 parts pentasodium amino tri(methylene phosphonate) and 345 parts sodium sulfate. Admixing of the four anhydrous components results in a 20 duty detergent of the following composition.

Ingredients: Parts
Active 33
Builder 67 25

1 Composition of builder:
Sodium tripolyphosphate 62.5
Pentasodium amino tri (methylphosphinate) 2.75
Sodium sulfate 28.75

The above detergent composition gives good cleaning results in conventional automatic washing machines when used in concentrations of about 0.2% by weight in aqueous solution for laundering soiled clothes.

Other comparable detergent compositions can be prepared in the same manner as described by substituting similar amounts of other amphoteric surface active agents useful in practicing this invention. For example, similar amounts of potassium c-tridecyl N-methyl amido ethyl sulfonate, sodium c-tetradecyl amido ethyl sulfonate, sodium c-tridecyl amido ethyl sulfonate, potassium c-tetradecyl N-cyclohexyl amido ethyl sulfonate and potassium c-pentadecyl, N-methyl amido ethyl sulfonate and the resulting detergent composition gives good results when used in the same manner as the detergent composition of this example.

EXAMPLES VII TO XV

The following detergent compositions are prepared by admixing the anhydrous components in the proportions given in a conventional ribbon mixer. These detergents readily remove soil from clothes when used in concentrations of about 0.2% in aqueous solutions in automatic washing machines.

EXAMPLE VII

Ingredients: Percentages
Active—Sodium tetradecyl sulfate 20
Builder 80

1 Composition of builder:
Sodium tripolyphosphate 60
Potassium sulfate 20
Diamine ethylene diamine tetra-acetate 10

EXAMPLE VIII

Ingredients: Percentages
Active—The product obtained from condensing 10 moles of ethylene oxide per 1 mole of nonylphenol 30
Builder 70

1 Composition of builder:
Sodium tripolyphosphate 60
Ethylene diamine tetra-acetate 10
Potassium carbonate 5

EXAMPLE IX

Active—Sodium dodecyl benzene sulfonate 20
Builder 80

1 Composition of builder:
Sodium tripolyphosphate 40
Trisodium hydroxy ethylenediamine diphosphonate 5
Trisodium nitritotriacetate 5
Sodium sulfate 40

EXAMPLE X

Active—Sodium dodecyl benzene sulfonate 20
Builder 80

1 Composition of builder:
Sodium tripolyphosphate 60
Trisodium hydroxy ethylenediamine diphosphonate 5
Trisodium nitritotriacetate 5
Sodium sulfate 30

EXAMPLE XI

Active 30
Builder 70

1 Composition of active:
Sodium dodecyl benzene sulfonate 40
Sodium dodecyl naphtalene sulfonate 20
Potassium nonyl sulfate 20
Product obtained from condensing 10 moles of ethylene oxide per 1 mole of dithylene glycol 20
Potassium c-tetracetyl, N-cyclohexyl amido ethyl sulfonate 20

2 Composition of builder:
Sodium tripolyphosphate 60
Diamine ethylene diamine tetra-acetate 8
Tetra sodium methylamino diphosphonate 30
Sodium sulfate 10

EXAMPLE XII

Active 25
Builder 75
Additives 2

1 Composition of active:
Sodium dodecyl benzene sulfonate 60
Product obtained from reacting 10 moles of ethylene oxide per 1 mole of N-dodecyl monononohexadecyl amide 20
Sodium dodecyl sulfate 20
Sodium hexadecyl sulfate 10

2 Composition of builder:
Sodium tripolyphosphate 70
Tetrasodium amino tri (ethylenediamine phosphonate) 15
Potassium sulfate 10

3 Composition of additives:
Sodium carboxymethyl cellulose 0.70
Perfume 0.23

EXAMPLE XIII

Active—Sodium dodecyl benzene sulfonate 25
Builder 65

1 Composition of builder:
Sodium tripolyphosphate 60
Pentasodium diethylenetriamine pentacetate 10
Sodium sulfate 30

EXAMPLE XIV

Active—The sodium salt of the sulfuric acid esters of the reaction product of 1 mole lauryl alcohol per 3 moles of ethylene oxide 20
Builder 80

1 Composition of builder:
Sodium tripolyphosphate 60
Trisodium nitritotriacetate 10
Sodium carbonate 30

EXAMPLE XV

Active—The product obtained from the reaction of 5 moles of propylene oxide and 1 mole of ethylene diamine 25
Builder 75

1 Composition of builder:
Sodium tripolyphosphate 70
Peru sodium amino tri (methylphosphonate) 10
Sodium sulfate 15

What is claimed is:
1. A heavy duty detergent composition consisting essentially of an active selected from the group consisting of anionic, nonionic and amphoteric synthetic detergents and mixtures thereof, and a three component synergistic builder composition consisting essentially of (a) from about 3% by weight to about 16% by weight...
in said builder composition of an organic sequestering agent selected from the group consisting of amino tri(lower alkylidene phosphonic acids) of the formula

$$\text{N}^{\text{C}}\text{C}^{\text{OH}}\text{O}$$

where X and Y are selected from the group consisting of hydrogen and lower alkyl groups containing from 1 to 4 carbon atoms, alkylene phosphonic acids of the formula

$$\text{HO}^{\text{C}}\text{C}^{\text{OH}}\text{O}$$

where X is selected from the group consisting of hydrogen and lower alkyl groups containing from 1 to 4 carbon atoms, Y is selected from the group consisting of hydrogen, hydroxyl, halogen and lower alkyl groups containing from 1 to 4 carbon atoms, and n is an integer from 1 to 6, amino polycarboxylic acids of the formula

$$\text{CHCOOH}$$

$$\text{N}\text{-CHCOOH}$$

where R is selected from the group consisting of

$$\text{C}^{\text{OH}}\text{O}$$

$$\text{H}^{\text{O}}\text{C}^{\text{OH}}\text{O}$$

and

$$\text{CHCOOH}$$

$$\text{CHCOOH}$$

$$\text{CHCOOH}$$

where R1 is selected from the group consisting of hydrogen, lower alkyl groups containing from 1 to 4 carbon atoms, hydroxy substituted lower alkyl groups containing from 1 to 4 carbon atoms, phenyl and hydroxy substituted phenyl, and R2 is selected from the group consisting of hydrogen, lower alkyl groups containing from 1 to 4 carbon atoms and hydroxy substituted lower alkyl groups containing from 1 to 4 carbon atoms, the water soluble salts selected from the group consisting of alkali metal, ammonium and amine salts of said acids and mixtures thereof, (b) from about 30% by weight to about 80% by weight in said builder composition of sodium tripolyphosphate and (c) from about 15% by weight to about 55% by weight in said builder composition of an alkali metal salt selected from the group consisting of sodium sulfate, sodium carbonate potassium sulfate, potassium carbonate and mixtures thereof, and the weight ratio of said active to said builder composition is from about 2.3 to about 1.5 respectively.

2. The detergent composition of claim 1, wherein the organic sequestering agent is a sodium salt of said amino tri(methylene phosphonic acid).

3. A heavy duty detergent composition according to claim 1, wherein said organic sequestering agent is selected from the group consisting of said amino tri(lower alkylidene phosphonic acids), said water soluble salts of said acids and mixtures thereof.

4. A heavy duty detergent composition according to claim 4, wherein said organic sequestering agent is selected from the group consisting of said alkylene phosphonic acids, said water soluble salts of said acids and mixtures thereof.

5. The detergent composition of claim 1, wherein the organic sequestering agent is a sodium salt of said methylene diphenyl phosphonic acid.

6. The detergent composition of claim 1 wherein the organic sequestering agent is a sodium salt of 1 hydroxy ethylenediphosphonic acid.

7. A heavy duty detergent composition according to claim 4, wherein said organic sequestering agent is selected from the group consisting of amino polycarboxylic acids, said water soluble salts of said acids and mixtures thereof.

8. The detergent composition of claim 1, wherein the organic sequestering agent is a sodium salt of said ethylene diamine tetra-acetic acid.

9. The detergent composition of claim 1, wherein the organic sequestering agent is a sodium salt of nitrilo tri-acetic acid.

10. A heavy duty detergent composition consisting essentially of, as an active, sodium tetradeceyl benzene sulfonate; and a three component synergistic builder consisting essentially of (a) from about 5% by weight to about 16% by weight in said builder composition of trisodium nitroacetate, (b) from about 30% by weight to about 80% by weight in said builder composition of sodium tripolyphosphate and (c) from about 15% by weight to about 55% by weight in said builder composition of sodium sulfate and the weight ratio of said active to said builder composition is from about 2.3 to about 1.5 respectively.

11. A heavy duty detergent composition consisting essentially of, as an active, sodium tetradeceyl sulfate; and a three component synergistic builder composition consisting essentially of (a) from about 3% by weight to about 16% by weight in said builder composition of trisodium nitroacetate, (b) from about 30% by weight to about 80% by weight in said builder composition of sodium tripolyphosphate and (c) from about 15% by weight to about 55% by weight in said builder composition of sodium sulfate; and the weight ratio of said active to said builder composition is from about 2.3 to about 1.5 respectively.

12. A heavy duty detergent composition consisting essentially of as an active containing from about 5 parts by weight to about 95 parts by weight of sodium tetradeceyl benzene sulfonate from about 5 parts by weight to about 95 parts by weight of sodium tetradeceyl sulfate; and a three component synergistic builder, a composition consisting essentially of (a) from about 3% by weight to about 16% by weight in said builder composition of trisodium nitroacetate, (b) from about 30% by weight to about 80% by weight in said builder composition of sodium tripolyphosphate and (c) from about 15% by weight to about 55% by weight in said builder composition of sodium sulfate; and the weight ratio of said active to said builder composition is from about 2.3 to about 1.5 respectively.

13. A heavy duty detergent composition consisting essentially of as an active, an alkyl polyoxyethylene ether wherein said alkyl group contains from 8 to 18 carbon atoms; and a three component synergistic builder, a composition consisting essentially of (a) from about 3% by weight to about 16% by weight in said builder composition of trisodium nitroacetate, (b) from about 30% by weight to about 80% by weight in said builder composition of sodium tripolyphosphate and (c) from about 15% by weight to about 55% by weight in said builder composition of sodium sulfate; and the weight ratio of said active to said builder composition is from about 2.3 to about 1.5 respectively.

14. A heavy duty detergent composition consisting essentially of as an active, an alkyl phenol polyoxyethylene ether wherein said alkyl group contains from 4 to 20 car-
bon atoms; and a three component synergistic builder, a composition consisting essentially of (a) from about 3% by weight to about 16% by weight in said builder composition of trisodium nitriloacetate, (b) from about 30% by weight to about 80% by weight in said builder composition of sodium tripolyphosphate and (c) from about 15% by weight to about 55% by weight in said builder composition of sodium sulfate; and the weight ratio of said active to said builder composition is from about 2:3 to about 1:5 respectively.

15. The detergent composition of claim 9, wherein the active is an anionic synthetic detergent selected from the group consisting of alkyl aryl sulfonates, alkyl sulfates, alkyl phenol polyoxyethylene ether sulfates and mixtures thereof.

16. The detergent composition of claim 15, wherein the anionic synthetic detergent is an alkyl aryl sulfonate.

17. The detergent composition of claim 15, wherein the anionic synthetic detergent is an alkyl sulfate.

18. The detergent composition of claim 9, wherein the active is an alkyl polyoxyethylene ether.

19. The detergent composition of claim 9, wherein the active is an alkyl polyoxyethylene ether.

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