United States Patent [19]

Cheng

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[54] **CARBONATE BUILT DETERGENTS**

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[58] **Field of Search** ..... 252/175, 180, 181, 110, 252/117, 526, 545, DIG. 11; 210/58

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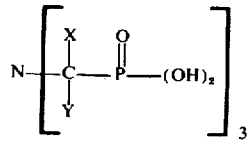
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[57] **ABSTRACT**

A non-polyphosphate built laundry composition utilizing a mixture of sodium carbonate with builder compound selected from the group consisting of amino tri(lower alkylidene) phosphonic acids having the formula:



wherein X and Y are hydrogen or lower alkyl groups, $CH_3COH(PO_3H_2)_2$, $(H_2O_3PCH_2)_2N—CH_2CH_2—N(CH_2PO_3H_2)_2$, $CH_3(CH_2)_{11}N(CH_2PO_3H_2)_2$, $CH_3CH(PO_3H_2)_2$, $CH_2OH(PO_3H_2)_2$, and their water-soluble salts builder, with a suitable detergent system.

8 Claims, No Drawings

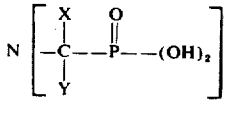
CARBONATE BUILT DETERGENTS

The present invention relates to an improved carbonate builder system. More particularly, this invention relates to an improved carbonate builder system including a phosphonic acid or salt.

Conventional laundry detergent compositions for household use (e.g., for automatic clothes washing machines) contain relatively large amounts of phosphates. Typically, such high performance compositions will contain about 35% of sodium tripolyphosphate or its equivalent, together with a detergent system. However, because of the widespread views that the use of phosphates may be ecologically undesirable, there have been introduced many detergent compositions substantially free of phosphates. It has been found, however, that these phosphatefree compositions are of a lower quality than the analogous compositions containing polyphosphates, particularly with respect to building, peptizing, soil suspending and cleaning action.

In the attempts to develop an effective detergent composition free from polyphosphates which will inhibit the precipitation of calcium carbonate and other hard ions found in most cleaning waters, and to aid in the removal of particulate matter and other foreign materials, it has been necessary to provide sequestering agents and deflocculants having equivalent effectiveness to the polyphosphates, such as pentasodium tripolyphosphate and tetrasodium pyrophosphate and analogous polyphosphoric acid salts. Among such builder salts which have been suggested and used in commercial products, are sodium nitrilotriacetate, sodium citrate, sodium silicates, sodium perborate, and various polyphosphonic acids.

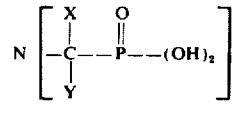
Of the previously mentioned builder compounds, the polyphosphonic acids and particularly the aminotri(lower alkylidene phosphonic acids) or their water-soluble salts of the following formula:



wherein X and Y are selected from hydrogen or a lower alkyl group; $CH_3C(OH)(PO_3H_2)_2$; $(H_2O_3PCH_2)_2N-CH_2CH_2-N(CH_2PO_3H_2)_2$; $CH_3CH(PO_3H_2)_2$; $CH_2OH\ PO_3H_2$; or $CH_3C\ OH\ (PO_3H_2)_2$, and their sodium salts have been found to be effective as sequestering agents and deflocculants.

In particular, U.S. Pat. No. 3,234,124 teaches the use of the aminotri(lower alkylidene phosphonic acids) or their salts as effective sequestering agents in liquid soaps and shampoos for sequestering iron ions; U.S. Pat. No. 3,278,446 discloses washing compositions using aminotri(lower alkylidene phosphonic acids) or their water-soluble salts in highly alkaline washing compositions; U.S. Pat. No. 3,298,956 teaches the use of organoaminopolymethylphosphonic acids and their water-soluble salts as effective lime soap dispersants in aqueous mediums containing soap and additionally other synthetic detergents and detergent additives; U.S. Pat. No. 3,394,083 discloses an effervescent detergent composition comprising water-soluble polyphosphonic acid compounds including the aminotri(lower alkylidene phosphonic acids) carbonate compounds, tripolyphosphate builders and anionic, non-ionic or amphoteric detergents; U.S. Pat. No. 3,574,524 teaches the use of the amino lower alkylidene phosphonic acids with a synthetic detergent and a polyester fibrous swelling agent for use in a cleaning composition for polyester and cellulose fiber articles; U.S. Pat. No. 3,586,633 discloses alkaline cleansing agents containing a synergistic mixture of aminopolyphosphonic acids and hydroxyalkane-1, 1-diphosphonic acids for the prevention of hydrolysis and the deposition of calcium compounds; and U.S. Pat. No. 3,269,124 discloses the use of the aminophosphonic acids in conjunction with chlorine releasing compositions, such as used for bleaching, sterilizing, disinfecting, and detergent compositions.

It is within the above environment and background that the detergent-builder composition of the present invention has been developed. Briefly, the composition of the present invention consists essentially of from 6 to 25% of detergent system, from about 15 to 50% by weight of a filler selected from alkali metal sulfates and silicates and mixtures thereof, about 35 to 60% by weight of sodium carbonate and about 2 to 10% of a phosphoric acid builder selected from phosphonic acids having the formula



wherein X and Y are selected from hydrogen or a lower alkyl group; $CH_3C(OH)(PO_3H_2)_2$; $(H_2O_3PCH_2)_2N-CH_2CH_2-N(CH_2PO_3H_2)_2$; $CH_3CH(PO_3H_2)_2$; $CH_2OH-PO_3H_2$; or $CH_3C(OH)(PO_3H_2)_2$, and the watersoluble salts thereof.

It is therefore the primary object of the present invention to provide an improved carbonate built detergent composition.

It is a still further object of the present invention to provide a detergent composition including a builder composition comprising sodium carbonate and a polyphosphonic acid, an aminotri(lower alkylidene phosphonic acid) or salt thereof.

It is a still further object of the present invention to provide an anionic-ionic soap detergent composition including an improved sodium carbonate builder system.

It is a still further object of the present invention to provide a low phosphate detergent composition with cleaning power at least equal to conventional phosphate detergents.

Still further objects and advantages of the composition of the present invention will become more apparent from the following more detailed description thereof.

In accordance with the composition of the present invention, it is found that outstanding performance can be obtained with a detergent composition substantially free of phosphate comprising from 6 to 25% by weight of a detergent system, about 15 to 50% of sodium sulfate or other filler material, about 35 to 60% sodium carbonate and about 2 to 10% of polyphosphonic acid or amino lower alkylidene phosphonic acid or the salts thereof.

In accordance with the composition of the present invention, it has been found that the incorporation of about 2 to 10% of the polyphosphonic acid or amino-tri(lower alkylidene phosphonic acid) and the salts thereof in sodium carbonate built detergents produces results approximately equivalent to polyphosphate built detergents. Further, the novel compositions of the present invention have been found to retard the usually expected calcium carbonate precipitation which occurs during the washing cycle when carbonate builders are used. The compositions do not produce fabric boardiness which results from repeated washing with carbonate built detergents and are also particularly effective in soil removal and the overall cleaning performance, while at the same time, also reduce the phosphorus content in the detergent.

The compositions of the present invention are essentially phosphate-free laundry detergent compositions having a cleaning power equal or greater than conventional high performance, high phosphate detergents. These compositions have been found to be highly effective against a wide variety of soils, including clay and carbon soils, skin soil, natural and artificial sebum soils, particulate soils, etc., as well as clean load yellowing tests, for a wide variety of fabrics, including cotton, nylon, polyester, (e.g., polyethylene terephthalate), etc. Thus, unlike the essentially phosphate-free compositions of the prior art, it provides a true replacement for the high performance, high phosphate detergents.

The novel compositions of the present invention do not produce high pH levels and are effective in hard water, without yielding significant residue or scum. Further tests with a calcium ion electrode and turbidity measurements indicate that compositions of this invention, unlike conventional phosphatecontaining compositions, do not combine with substantial quantities of calcium ions and in fact, prevent calcium ion precipitation.

The builder system of the present invention may be used in conjunction with any suitable detergent composition including non-ionic detergents, anionic detergents, soaps, non-ionic-anionic detergents, non-ionic-soap systems, anionic-soap systems and non-ionic-anionic-soap systems. The preferred detergent system for use with the builder compositions is the non-ionic-anionic-soap system and in particular an alkanol polyethenoxy-linear alkyl aryl sulfonate-sodium soap system.

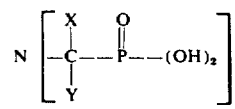
Suitable non-ionic detergents for use in the detergent system in the composition of the present invention either alone or as part of the non-ionic-anionic-soap system include polyoxyalkylene glycols wherein the alkyl groups are either ethyl or propyl groups or mixtures thereof wherein there are from 5 to 25 oxyalkylene groups and mono ethers of these glycols with long chain alkanols wherein the alkanol has about 10 to 22 carbon atoms. The mono ethers of polyethylene glycol are generally made by reacting the alkanol with alkylene oxide. Preferably, the proportion of alkylene oxide is in the range of about 60 to 65%. A particularly suitable product is made by reacting 11 moles of ethylene oxide and 1 mole of a mixture of C_{14} and C_{15} straight chain normal primary alkanols, such mixture having an average of 14 to 15 (e.g., about 14.5) carbon atoms, which product is sold under the name Neodol 45-11. Another non-ionic detergent is an ether of polyethylene glycol and a blend of C_{16} to C_{18} alcohols, containing about 60% ethylene oxide (Alphonic 16-18). Still another non-ionic detergent is a condensation product of long chain alkanol, propylene oxide and ethylene oxide known as Plurafac B26. In the present invention, the non-ionic detergent is desirable to produce high all-round detergency performance, similar to, and superior to, that of high performance, high phosphate detergents.

Although any anionic detergent may be utilized with the builder system of the present invention, the alkyl aryl sulfonate anionics are preferred and the linear alkyl aryl sulfonates are most preferred, especially sodium salts of linear alkyl benzene sulfonates. The sodium linear alkyl aryl sulfonate detergent (LAS) used in the detergent system in the composition of the present invention has an alkyl radical having average length of about 11–13 carbon atoms. Preferably, the alkyl benzene sulfonate has a high content of 3-(or higher) phenyl isomers and a correspondingly low content (well below 50%) of 2-(or lower) phenyl isomers; in other terminology, the benzene ring is preferably attached in a large part, at the 3 or higher (e.g., 4, 5, 6 or 7) position of the alkyl group and the content of isomers in which the benzene ring is attached at the 2 or 1 position is correspondingly low. One suitable type of such detergent is described in the U.S. Pat. to Rubinfeld No. 3,320,174.

The soaps are included in the composition of the present invention as anti-foaming agents and as supplemental detergents. Generally, a water-soluble soap of a higher fatty acid or a mixture of soaps will be used. Of the soaps, the alkali metal, ammonium, alkanolamine, and other water-soluble soaps are well known and are usually derived from mixtures of animal and vegetable fats and oils which are generally derivatives of higher fatty acids having about 10 to 20 carbon atoms, preferably, 12 to 18 carbon atoms. Such fatty acids are obtained from oils, such as coconut oil, palm oil, palm kernel oil, corn oil, cottonseed oil and olive oil, and animal fats, greases and oils, such as beef tallow, mutton tallow, hog greases and fish oils. The preferred soaps for use in the present composition are the alkali metal soaps, such as the sodium soaps of mixed coconut oil and tallow (or tallow-grease mixture), preferably wherein the mixtures contain a major proportion of tallow (or tallow-grease) and a minor proportion, less than 40%, of coconut oil. The best proportions of coconut oil and tallow are from 10 to 30% of coconut oil and 90 to 70% of beef tallow or a mixture of such tallow and grease. The soaps may be added as kettle soap in the crutcher or may be post-added in granular form.

The composition of the present invention contains from 35 to 60% by weight of sodium carbonate which functions as a builder salt and increases the detersive properties of the primary detergents. Although the sodium carbonate may be in any form, it is preferable to use soda ash in either dense or light form for economic reasons. Further, it is preferable to use from 45 to 55% sodium carbonate in the detergent composition.

The composition of the present invention includes from 2 to 10% and preferably 4 to 7% of phosphonic acid or the amino tri(lower alkylidene phosphonic acids) or salts thereof, which compounds are known sequestering agents and lime soap dispersants. Suitable compounds include phosphonic acids with the following formula



3

wherein X and Y are hydrogen or a lower alkyl group; $(H_2O_3PCH_2)_2$ $N—CH_2CH_2—N—(CH_2PO_3H_2)_2$; $CH_3(CH_2)_{11}—N(CH_2PO_3H_2)_2$; $CH_3CH(PO_3H)_2$; $CH_2(OH)PO_3H_2$; $CH_3C(OH)—(PO_3H_2)_2$; and their alkali metal (e.g., sodium or potassium) salts. Of these, the preferred compound is the amino tri(methylphosphonic acid) sold under the Trademark Dequest 2001.

While the prior art references discussed above seem to indicate that the phosphonic acids and the amino tri-lower alkylidene phosphonic acids and their salts are effective dispersants for calcium ions and other hard ions found in water which create curds and films on the clothes and other items being laundered, these references have also suggested that when these builder compounds are used with sodium carbonate and other alkali metal carbonates in synthetic detergents, a significant amount of a polyphosphate compound must be used to produce satisfactory results. In fact, these prior art references seem to suggest that a synergistic effect is achieved using sodium tripolyphosphate builder with the phosphonic acid builder in order to achieve useful results. Furthermore, U.S. Pat. No. 3,586,633 indicates that the amino tri-(methylphosphonic acid) above is unacceptable in water of high hardness becuase it only has a very slight effect in the prevention of the precipitate formed from the hard water cations, and must be used in combination with a hydroxy alkane-1, 1-diphosphonic acid to achieve a synergistic effect in preventing precipitation of calcium carbonate and other insoluble calcium compounds. The composition of the present invention, however, does not require these added compounds to potentiate the effectiveness of the phosphonic acid compounds.

In addition to the builders, detergents and anti-foaming compounds, the composition of the present invention includes various filler salts which do not improve detergency, but add bulk and absorption capacity for liquid constituents. These filler salts are utilized in an amount of from 15 to 50% by weight and include alkali metal sulfates and alkali metal silicates, with sodium sulfate and sodium silicate being preferred. The silicate may be present in any suitable form and has a Na_2O:SiO ratio within the range of from 2:1 to 1:3.4 Further, the filler salts, which are hydratable, having a capacity for absorbing any excess water which may be present, thereby improving the free flowing nature of the product are also preferred.

Also, water, although not required in particulate or solid compositions, is usually present therein to a minor extent. It may be a part of the soap or may be present as water of hydration with a builder or filler salt. There may also be present a small amount of solvent, emollient, or humectant materials, such as lower alkanols, diols or polyols, including ethanol, isopropanol, propylene glycol, glycerol, and sorbitol, which improves solubilization of the various other ingredients and have additional desirable effects on the final products.

Various adjuvants may be present in the detergent to give it additional desired properties, either of functional or aesthetic nature. Thus, there may be included in the formulation: soil suspending or anti-redeposition agents, e.g., polyvinyl alcohol, sodium carboxymethyl cellulose, hydroxymethyl cellulose; optical brighteners, e.g., cotton, amide and polyester brighteners (which will be described in more detail subsequently); supplemental synthetic organic detergents, e.g., sodium lauryl sulfate; myristyl polyoxyethylene ethanol, wherein the polyoxyethylene chain is 10 units long; linear tridecyl benzene sulfonate; pH adjusting agents, e.g., sodium hydroxide, triethanolamine, sulfuric acid; buffering agents, e.g., sodium borate, sodium bisulfate; other inorganic builders, e.g., borax, enzymes, e.g., protease, amylose; thickeners, e.g., gums, alginates, agar-agar; foam destroyers, e.g., silicones; bactericides, e.g., tetrachlorosalicylanilide; fungicides; dyes; pigments (water-dispersible); preservatives; ultra-violet absorbers; fabric softeners; pearlescing agents; opacifying agents, e.g., behenic acid, polystyrene suspensions, caster wax; and perfumes. In the selection of adjuvants, they will be chosen to be compatible with the main constituents of the detergent.

Of the adjuvants mentioned, perhaps the most important for functional effect are the optical brighteners, because the modern housewife has come to expect that washed clothing will no longer be merely clean and white, but will also be bright in appearance. Among these are various cotton brighteners, polyamide brighteners, polyester brighteners and bleach-stable brighteners. These may be reaction products of cyanuric chloride and the disodium salt of diaminostilbene disulfonic acid, benzidine sulfone, disulfonic acid, aminocoumarins, diphenyl pyrazoline derivatives or naphthotriazolylstilbenes. Such materials are described in the article *Optical Brighteners and Their Evaluation*, by Per S. Stensby, a reprint of articles published in *Soap and Chemical Specialties* in April, May, July, August and September, 1967, especially at pages 3–5 thereof. The fluorescent dyes or optically active brightener compounds also serve to improve the appearance of particulate detergent compositions containing them, making such compositions appear whiter or brighter.

Generally, the proportion of such adjuvants will be maintained as low as feasible, almost always being less than 20% of the composition, frequently less than 10% thereof, and preferably, less than 5% thereof in total. Normally, there will be present no more than 5% of any such composition and preferably, in most cases, the amount of adjuvant will be less than 2%.

As noted above the detergent compositions may use any number of detergent systems including a non-ionic detergent, a mixed non-ionic-anionic system, a mixed non-ionic-anionicsoap system, etc., with the preferred systems being the nonionic and non-ionic-anionic-soap systems.

The non-ionic detergent system may comprise from 6 to 25% by weight of the composition and preferably from 10 to 20%.

The anionic-non-ionic-soap system comprises from 6 to 25% by weight of the composition and includes the various components in the following ratio 7–3:1:0.5–2 anionic-non-ionicsoap with the preferred composition comprising 10 to 20% of the detergent system with the preferred system ratio being 6–4:1:0.66–1.5.

In the following examples, which are for the purposes of illustration only, the turbidity is measured with a standard colorimeter (Model 401 of Photovolt Corp. of New York), using incandescent light with a green filter; wherein after 10 minutes the hard water shows a turbidity of zero, hard water containing 0.045% Na_2CO_3 shows a turbidity of 66 and hard water containing 0.03% of linear alkyl benzene sulfonate shows a turbidity of about 90.

The calcium electrode used for the millivolt measurements in the following examples is a calcium activity electrode Model 92-20 sold by Orion Research, Inc. of

Cambridge, Mass., and is described in detail in the published instruction manual (Copyright 1966) for this instrument. This electrode develops an electrical potential across a thin layer of water immiscible ion exchanger. This liquid is held mechanically rigid by a thin, porous inert membrane disc. The liquid ion exchanger, a calcium salt of an organo-phosphoric acid, exhibits very high specificity for calcium ions. An internal filling solution of calcium chloride contacts the inside surface of the membrane disc. The calcium ion in this solution provides a stable potential between the inside of the membrane and the filling solution, while the chloride ions provide a stable potential between the Ag-AgCl reference electrode and the filling solution. Thus, changes in potential are due only to changes in sample calcium ion activity. The electrode responds only to the ionized or unbound calcium in the sample. The electrode does not respond to that portion of the calcium which is bound to complexing agents such as citrates, polyphosphates, and the Dequest compounds. According to the manufacturer, this electrode exhibits Nernst potential behavior down to 10^{-4} moles/liter of calcium ion in accordance with the following equations:

$$E = E_x + \frac{RT}{2F} \text{LOG}_{10} [A_{Ca}{}^{++}]$$

where

E = the electrode potential

E_x = approximately 90 mv. with a saturated KCl calomel reference electrode

RT/2F = Nernst potential factor for a divalent sensing electrode (29.58 mv at 25°C.)

$A_{Ca^{++}}$ = Activity of calcium ion

In making the measurements of calcium electrode potential given in the tables, the relative scale is first adjusted so that the potential for 150 ppm hard water is minus 5 millivolts with readings taken subsequent to stirring for 10 minutes. For comparative purposes, it is noted that the same instrument, with the same adjustments, gives the following readings when tested on 0.045% solutions (adjusted to pH 10.0 with NaOH) of the following compounds in hard water having 150 ppm hardness: trisodium salt of nitrilotriacetic acid (NTA), −75 millivolts; pentasodium tripolyphosphate, −55 millivolts; sodium citrate, −42 millivolts; sodium acetamidonitrilodiacetate, −36 millivolts; iminodiacetic acid, −12 millivolts; sodium oxalate, −38.4 millivolts.

As a further comparison, tests of water itself (with the hardness changed by changing the total quantity of $CaCl_2$ and MgCl, but not the relative proportions) gives the following readings: 50 ppm hardness (as $CaCo_3$), −20 millivolts; 25 ppm hardness, −27.5 millivolts; 300 ppm hardness, +5 millivolts; zero hardness, −80 millivolts.

EXAMPLE 1 AND COMPARATIVE EXAMPLES 1 TO 3

A detergent system of Neodol 45-11 (higher alkanol, polyoxyethylene, non-ionic detergent having an average alkanol carbon length of between 14 and 15 and having 11 ethylene oxide groups)/sodium carbonate/-sodium silicate as shown in Table 1 are tested for calcium ion and hard water sensitivity with various dispersants including sodium carboxymethyl cellulose, Gantrez HY-M (sold by GAF Inc.) and amino trimethylphosphonic acid. These systems were tested both with regard to eletron potential, turbidity and precipitation rate with the results tabulated in Table 1.

TABLE I

Example No.	Silicate (wt %)	Neodol (wt %)	Na_2CO_3 (wt %)	Dispersant (wt %)	E.P. (Ca) (−MV)	Turbidity (%)	Precipitation Rate
1	20	12	55	2.5(Dequest 2001)	26	3.5	0
Comp. Ex. 1	20	12	55	0	39.5	76.0	1.60
Comp. Ex. 2	20	12	55	2.5(Na CMC)	36.0	93.5	1.20
Comp. Ex. 3	20	12	55	2.5(Gantrez HY-M)	33.0	79.5	0.96

As can be readily seen with reference to Table 1, the detergent systems including the aminotrimethylphosphonic acid, Dequest 2001, bind less calcium ion and produce a system with zero precipitation rate and virtually no turbidity when compared both to the absolute scale and to the detergent system containing no dispersant and detergent systems containing sodium carboxymethylcellulose and the Gantrez dispersant.

EXAMPLE 2 AND COMPARATIVE EXAMPLES 4 TO 7

Similar precipitation, turbidity and electron potential tests are conducted on a detergent system containing a Neodol 45-11, sodium carbonate and sodium silicate system at 50°C. using water having a hardness of 50 parts per million. In each of these tests the proportion of non-ionic to carbonate to silicate is 9.2/55/21 while 10 parts of various builder salts are added with the exception of Comparative Example 7 wherein 35 parts of sodium tripolyphosphate are added.

Each of these systems are tested for electrode potential, turbidity, pH and are also tested for reflectance subsequent to washing a mixed load.

TABLE 2

	Builder	Ca Activity (MV.)	Turbidity (%)	Soil Removed (Rd)	pH
Comp.Ex. 4	0	46	87.9	75.9	10.2
Comp.Ex. 5	10 parts STP	35	86.0	79.9	10.2
Comp.Ex. 6	10 parts Na Citrate	31	85.5	76.1	10.2

TABLE 2-continued

	Builder	Ca Activity (MV.)	Turbidity (%)	Soil Removed (Rd)	pH
Example 2	Dequest 2001	35	84.8	84.0	9.9
Comp.Ex. 7	35 parts STP	50	85.9	84.4	9.0

The washing system in accordance with the composition of the present invention produces the solution with the lowest turbidity and a substantially equivalent reflectance with regard to the 35% sodium tripolyphosphate standard detergent system. Furthermore, as shown by the electrode potential the calcium ions are less tightly bound utilizing the compositions of the present invention.

EXAMPLES 3 THROUGH 8 AND COMPARATIVE EXAMPLES 8 AND 9

Various laundry detergent compositions having individual compositions as shown in Table 3 are compounded in dry form and tested regarding cleaning ability and carbonate redeposition or boardiness. A mixed load of laundry items is washed in a Tergotometer laboratory washing machine in water having 150 parts per million hardness at a temperature of 120°F.

TABLE 3

Example	Detergent Total	Las[1]	Non-ionic[2]	Soap[3]	Filler Na_2SO_4	NaSiO NaO:SiO=1:2	Na_2CO_3	Builder Dequest[4]	STP_5
3	14	10	2	2	25	—	55	6	—
4	20	14	3	3	—	25	50	5	—
5	17.5	14	2	1.5	—	29.5	50	3	—
6	6	4	1	1	24	—	60	10	—
7	25	18	4	3	20	—	50	5	—
8	21	15	3	3	42	—	35	2	—
Comp.Ex. 8	21	15	3	3	44	—	—	—	35
Comp.Ex. 9	21	15	3	3	44	—	35	—	—

[1] = C_{11-13} linear alkyl Benzene Sulfonate
[2] = Neodol 45-11(C_{14-15}alkanol + 11EO)
[3] = Mixed Sodium Soap (80% Tallow, 20% Coco)
[4] = Amino tri(methyl phosphonic acid)
[5] = Sodium Tripolyphosphate

When each of the laundry formulations of Examples 3 through 8 are compared with the laundry formulation in Comparative Example 8 which represents a conventional polyphosphate built detergent system, the cleaning and whitening ability and anti-redeposition properties are roughly equivalent. When compared, however, with the detergent composition of Comparative Example 9 which does not contain the phosphonate compound of the builder system of the present invention, the cleaning and whitening ability of the detergent composition is somewhat less than either the conventional phosphate built detergent or the detergents in accordance with the present invention. Furthermore, the fabrics have a somewhat boardy, stiff feeling representing a deposition of calcium carbonate in the fabric fibers. This last Comparative Example 9 detergent is utilized to wash the same fabric load for five times in order to determine whether or not the boardy feel is accentuated upon repeated washing. Upon such repeated washing, this boardy fabric feel relating to calcium carbonate deposition on the fabrics appears to increase with each successive washing.

EXAMPLES 9 THROUGH 15 AND COMPARATIVE EXAMPLES 10 TO 13

A detergent composition having the following composition:

Linear C_{11-13} alkyl benzene sulfonate 10%
Neodol 45-11 2%
Sodium soap (80% Tallow, 20% Coco) 2%
Sodium soap varies from 35 to 44%
Sodium carbonate 50%
Supplemental material varies from 0 to 10%

In the above formulation, the supplemental material is varied utilizing the following materials in the amounts as indicated with a concomitant increase or decrease in the sodium sulfate filler percentage.

Example 9 - 4% aminotrimethylphosphonic acid
Example 10 - 4% $CH_3COH(PO_3H_2)$
Example 11 - 4% $(H_2O_3PCH_2)_2N—CH_2CH_2—N(CH_2PO_3H_2)_2$
Example 12 - 4% $CH_3(CH_2)_{11}N(CH_2PO_3H_2)_2$
Example 13 - 4% $CH_3CH(PO_3H_2)_2$
Example 14 - 4% $CH_2OHPO_3H_2$
Example 15 - 10% aminotriethylphosphonic acid
Comparative Example 10 - 4% sodium carboxymethyl cellulose
Comparative Example 11 - 4% Gantrez HY-M
Comparative Example 12 - 4% sodium tripolyphosphate
Comparative Example 13 - 0.5% aminotrimethyl phosphonic acid.

Each of the above formulations is tested in accordance with the procedures outlined in Example 3. The detergent compositions of Examples 9 through 15 produce results wherein the laundry items have acceptable levels of whiteness and have a minimum amount of boardiness from carbonate redeposition. However, each of the Comparative Examples produces significant amounts of boardiness caused by calcium carbonate redeposition upon the fabrics. This boardiness is especially prevalent in
Comparative Example 13 wherein less than the minimum amount of phosphonic acid is utilized. In fact, when compared with similar washings wherein no phos-

phonic acid at all is utilized, the results utilizing 9.5% by weight of the phosphonic acid actually produce worse results.

EXAMPLE 15

The non-ionic anionic soap detergent system of Example 3 is replaced by the following detergent systems with a concomitant increase or decrease in the sodium sulfate filler composition:

A. 15% C_{11-14}alkanol + 7EO

B. 14% C_{11-14}alkanol + 7EO + 2% sodium soap (80% Tallow and 20% Coco)

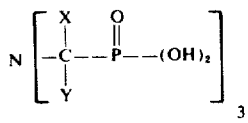
C. 12% linear C_{11-13}alkyl benzene sulfonate + 3% sodium soap (80% Tallow, 20% Coco)

Each of the above-noted detergent formulations performs adequately with regard both to cleaning ability and whiteness and with regard to calcium carbonate redeposition.

While the detergent composition and builder system of the present invention has been described by way of the foregoing specification and Examples, the same are for purposes of illustration only, and are in no way to be taken as limiting the composition of the present invention which is properly defined by the following appended claims.

What is claimed is:

1. A laundry detergent composition consisting essentially of from 6 to 25% by weight of a detergent system consisting essentially of a mixed non-ionic, synthetic anionic surfactant, soap system wherein the non-ionic is an alkanol-poly (lower alkanoxy), said alkanol having from 10 to 22 carbon atoms and said lower alkanoxy having from 2 to 3 carbon atoms and being formed by the reaction of 1 mole of the alkanol with from 5 to 25 moles of the lower alkylene oxide, the anionic is a linear alkyl benzene sulfonate wherein the alkyl group has from 11 to 13 carbon atoms and the soap is a sodium soap, the ratio of anionic-nonionic-soap, respectively, being 7–3:1:0.5–2, from about 15 to 50% by weight of a filler selected from alkali metal sulfates and alkali metal silicates, from about 35 to 60% by weight of an alkali metal carbonate and from about 2 to 10% by weight of a builder compound selected from the group consisting of amino tri(lower alkylidene)phosphonic acids having the formula:



wherein X and Y are hydrogen or lower alkyl groups, $CH_3COH(PO_3H_2)_2$, $(H_2O_3PCH_2)_2N\text{-}CH_2CH_2\text{-}N(CH_2PO_3H_2)_2$, $CH_3(CH_2)_{11}N(CH_2PO_3H_2)_2$, $CH_3CH(PO_3H_2)_2$, $CH_2OH(PO_3H_2)$, and their water-soluble salts.

2. The composition of claim **1** wherein said builder compound is aminotrimethylphosphonic acid or the water soluble salts thereof.

3. The composition of claim **1** wherein said detergent system comprises from 10 to 20% by weight, said builder compound comprises from 4 to 7% by weight and said carbonate comprises from 45 to 55% by weight.

4. The composition of claim **3** wherein said builder compound is aminotrimethylphosphonic acid or the water soluble salts thereof.

5. The composition of claim **2** wherein said filler is sodium sulfate and said carbonate is sodium carbonate.

6. The composition of claim **3** wherein said filler is sodium sulfate and said carbonate is sodium carbonate.

7. The composition of claim **2** wherein said filler is sodium silicate and said carbonate is sodium carbonate.

8. The composition of claim **3** wherein said filler is sodium silicate and said carbonate is sodium carbonate.

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