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Szymanski et al.

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[54] **BUILDERS FOR DETERGENT COMPOSITIONS BASED ON CARBOXYLATED BICYCLIC COMPOUNDS**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 343,837, March 22, 1973, abandoned, which is a continuation-in-part of Ser. No. 120,719, March 3, 1971, abandoned.

[52] **U.S. Cl.** **8/137;** 210/58; 252/89; 252/132; 252/135; 252/180; 252/DIG. 11; 260/347.3

[51] **Int. Cl.**[2] **C11D 3/20;** D06L 1/12

[58] **Field of Search** ..... 252/89, 132, 135, 180, 252/181, DIG. 11; 210/58, 64; 260/347.3, 347.5, 346.6; 424/285; 8/137

[56] **References Cited**

UNITED STATES PATENTS

2,264,103	11/1941	Tucker	210/23
2,311,008	2/1943	Tucker	210/23
2,576,080	11/1951	Tischler et al.	71/2.5
2,637,641	5/1953	Tischler	71/2.4
2,637,642	5/1953	Tischler	71/2.5
3,246,015	4/1966	Lindaberry	260/347.3
3,368,978	2/1968	Irani	252/527
3,459,670	8/1969	Carter	252/99
3,580,852	5/1971	Yang	252/135

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[57] **ABSTRACT**

Carboxylated bicyclic compounds and salts thereof are described for use as builders in detergent compositions.

9 Claims, No Drawings

BUILDERS FOR DETERGENT COMPOSITIONS BASED ON CARBOXYLATED BICYCLIC COMPOUNDS

This application is a continuation-in-part of our application Ser. No. 343,837 filed Mar. 22, 1973, now abandoned, which was a continuation-in-part of application Ser. No. 120,719 filed Mar. 3, 1971, now abandoned.

This invention relates to detergent compositions containing a member of a selected class of carboxylated bicyclic compounds as a detergent builder, said compositions being useful in aqueous washing media. In a further aspect, this invention describes an improved process for washing fabrics in an aqueous medium containing said detergent composition.

Detergent builders, as is well known to those skilled in the art, are used to improve the detergency effectiveness of detergent compositions and thereby improve their whitening powers. Polyphosphate compounds such, for example, as sodium tripolyphosphate have long been in use as builders, particularly because of their relatively low cost and their utility in increasing the whitening powers of detergent compositions with which they are used. It is also well known, however, that the presence of these polyphosphates tends to enhance the growth of algae in lakes and rivers to a significant degree sufficient to undesirably upset the natural ecology of these waters. With the recent emphasis on pollution control, phosphate pollution of water, as caused by the dumping of phosphate containing wash waters, is being closely watched and studied. There is increasing pressure to lower or discontinue their usage completely in detergent compositions in favor of non-phosphate builders.

The manner in which detergent builders improve the whitening powers of detergent compositions is related to a combination of factors. Thus, builders are believed to take part in the detergency system by such factors as emulsification of soil particles, solubilization of water-insoluble materials, promoting soil suspension in the wash water so as to retard soil redeposition, sequestering of metallic ions, and the like.

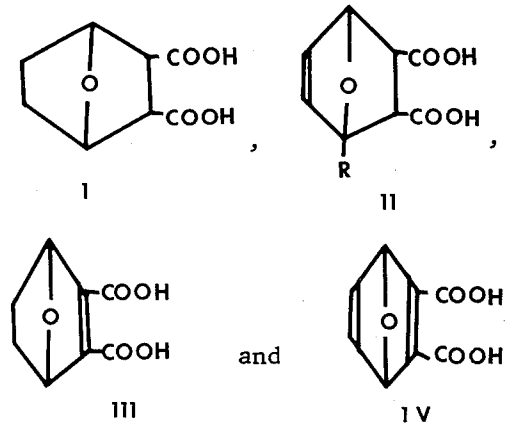
Among the important properties that must be exhibited by compounds employed as builders are: the ability to increase the whitening power of the detergent composition, non-toxicity, compatibility with the various components and additives of conventional detergent compositions, and stability with respect to hot, alkaline aqueous mediums and bleaching agents.

It is the prime object of this invention to provide a non-phosphate builder which is particularly effective in increasing the whitening power of detergent compositions. It is a further object of this invention to provide a method for washing fabrics in a medium containing detergent comprising a non-phosphate builder. Various other objects and advantages of this invention will be apparent from the following description thereof.

We have found that compounds of the class of carboxylated bicyclic compounds and salts thereof are useful as detergent builders and impart marked improvements in the whitening power of detergent compositions. Thus, the use of detergent compositions containing a described carboxylated bicyclic compound or its salt in aqueous media results in washed fabrics having a whiteness substantially equal to fabrics washed with a comparable detergent composition containing a

conventional polyphosphate detergent in equal amount.

The detergent builders of the present invention are the carboxylated bicyclic compounds corresponding to the following structural formulas:



I II

III IV

wherein R is selected from the group consisting of —H, $-CH_3$, $-CH_2OH$, $-CH_2OCOCH_3$, $-CH(OCOCH_3)_2$, and $-CH(OCH_2CH_3)_2$.

The compound represented by structure I is 7-oxabicyclo [2.2.1] heptane-2,3-dicarboxylic acid. A compound of structure II, wherein R is hydrogen, is 7-oxabicyclo [2.2.1] hept-5-ene-2,3-dicarboxylic acid. The compound represented by structure III is 7-oxabicyclo [2.2.1] hept-2-ene-2,3-dicarboxylic acid, while the compound represented by structure IV is 7-oxabicyclo [2.2.1] hepta-2,5-diene-2,3-dicarboxylic acid.

Also useful herein as the builders of our invention are the water-soluble, alkali metal salts (sodium and potassium, mono- and dicarboxylic) of the described carboxylated bicyclic compounds. In general practice, use of the disodium salt is preferred. The water solubility of these salts should be such that at least about 0.1 grams of the salt dissolves in 100 grams of water at 25°C. It is also preferred to formulate the detergent composition so that the pH of the washing media, i.e. the washing solutions containing the detergent composition, ranges from about 8 to 13. It is noted, however, that it is feasible to employ the novel detergent builders of the present invention in their acid or partially neutralized acid form. The free acid group(s) of the builder will be converted into the salt form as soon as the builder is put to use in an alkaline medium. Typical ingredients used for achieving an alkaline washing medium include phosphates, carbonates, borax, as well as other alkaline reagents such as sodium or potassium hydroxide.

Also useful herein and within the scope of our invention are precursors of the described carboxylated bicyclic compounds which give rise to the described compounds either during storage or during their use in the washing media. Examples of such precursors include the dicarboxylic anhydrides of the described bicyclic compounds. It can be appreciated by those skilled in the art that such anhydrides will readily hydrolyze in the hot, alkaline aqueous wash media to yeild ions of the subject compounds. While the use of these anhydrides in detergent compositions may not be as efficient as the use of the ultimate compounds themselves, such use does result in enhancing the whitening powers of detergent compositions.

All of the described compounds useful as builders herein may be readily prepared according to procedures described in the literature as, for example, in U.S. Pat. Nos. 2,406,657, 3,426,044 and 2,697,102 as well as in British Pat. No. 796,133. Intermediates which may be employed in preparing the described compounds are available commercially. A convenient method of preparing 7-oxabicyclo [2.2.1] hept-5-ene-2,3-dicarboxylic acid, for example, comprises the reaction of furan with maleic anhydride in equimolar concentrations, preferably at room temperature for periods of from about 8 to 168 hours. The resultant anhydride product may thereafter be converted into its sodium salt form by dissolving it in water and adding sufficient aqueous sodium hydroxide to adjust the pH of the mixture to within a range of about 8 to 13. Excess water may then be removed by distillation to yield the desired product in crystalline salt form.

It is an advantage of the present builders that in addition to enhancing the whitening power of detergents in a degree comparable to sodium tripolyphosphate, the present builders are fully compatible with and stable towards bleaching agents commonly used in conventional clothes washing. Thus, the detergent builders of the present invention neither lose their whitening power in the presence of bleaches, such as chlorine bleaches, nor do they interfere with or impair the function of the bleaches themselves.

A further advantage of the present builders is their excellent stability in aqueous detergent formulations over extended periods of time. The present builders may, therefore, be utilized in aqueous detergent formulations as well as in dry formulations. Sodium tripolyphosphate, in contrast, is unstable in aqueous formulations and can only be used in dry detergent formulations.

In utilizing these detergent builders, they are most conveniently admixed with a selected detergent composition in place of (either partially or entirely) the conventional builder as, for example, the sodium tripolyphosphate previously used therein. Ordinarily, the amount of builder utilized in these compositions will depend on the particular builder and the detergent surfactant and the intended end-use. Normally, the weight ratio of the detergent surfactant to the builder of this invention will fall within the range of about 10:1 to 1:10 and preferably about 4:1 to 1:4. Concentrations (proportions) of builder within the range of 20 to 60%, based on the weight of the total detergent composition solids, are preferred since builder concentrations of less than about 20% will usually result in insufficient whitening power.

Where the novel builders are employed in conjunction with a supplementary builder, the concentration of the supplementary builder should not exceed about 55% by weight of the total detergent composition solids.

In utilizing the novel builders herein it is to be understood that the detergent composition incorporating the builder can be prepared for use in any of several physical forms, as, for example, granular, flake, bar, tablet and liquid forms. If desired, the selected builder of our invention can be added to the wash media separately from the detergent itself without loss of effect.

The detergent composition, in addition to the detergent (i.e. detergent surfactant) and builder ingredients, may also contain a number of other optional ingredients. Thus the detergent composition may contain any of the usual types of fillers, such as sodium sulfate, sodium carbonate, and the like. Compositions employing a filler are preferred. When a filler is included in the detergent composition, the concentration of filler will ordinarily range up to 45%, preferably from 10–40%, by weight of the total detergent composition solids. Anticorrosion agents, for example, water-soluble alkali metal silicates such as sodium silicate and sodium metasilicate may be included in the detergent composition, preferably in concentrations from about 2 to 12% by weight of the detergent composition solids. Other optional ingredients, such as optical brighteners and enzymes may also be included, if desired, in concentrations known to practitioners in the art.

Supplementary detergent builders which may be used in conjunction with the novel builders of the present invention include known detergent builders of the groups alkali metal polyphosphates (e.g. sodium tripolyphosphate) and aminopolycarboxylic acids and salts (e.g. sodium salt of nitrilotriacetic acid) and mixtures thereof.

The builder described herein may be utilized in a detergent composition comprising any of the organic detergents which are commonly used for aqueous washing purposes. The detergent, i.e. the surface active compound, may be of the anionic, non-ionic, cationic or amphoteric type or character. Further description of detergents such as are useful in the detergent compositions comprehended herein are readily found in the literature, as for example, in U.S. Pat. No. 2,755,252 entitled "Partially Acetylated Polyvinyl Alcohol as a Soil-Suspending Agent" issued July 17, 1956 and U.S. Pat. No. 3,459,670 entitled "Builders for Synthetic Detergents" issued Aug. 5, 1969 which are incorporated herein by reference. It is clear that the particular detergent used in the detergent compositions of the present invention is not critical except that it should be generally useful in emulsifying and detergent applications.

The actual use of the detergent builders of this invention comprises the use of the resultant detergent composition (detergent, builder and optional additives) in concentrations from about 0.05 to 0.25%, based on the weight of the wash water, in a conventional washing procedure, ordinarily making use of agitation and temperatures ranging up to about 180°F. Use of the detergent composition in this manner has been found to enhance the whitening power of the wash medium, and the fabrics washed therewith have been found to be significantly brighter.

The invention is further illustrated in connection with the following examples in which all parts given are by weight unless otherwise noted. The water employed in the wash media as well as the rinses in all of the following examples was adjusted to have a hardness of about 150 ppm measured as calcium carbonate.

EXAMPLE I

This example illustrates the preparation of the disodium salt of 7-oxabicyclo [2.2.1] hept-5-ene-2,3-dicarboxylic acid.

98 grams of maleic anhydride was dissolved in 500 milliliters of ether with stirring. When solution of the anhydride was completed, 68 grams of furan was added and the mixture was allowed to stand one week at room temperature. The resultant precipitate was separated from the solvent by filtration, dried, and slurried in dis-

tilled water. The pH of the aqueous solution was adjusted to 7.6 with dilute sodium hydroxide. Water was removed by evaporation, yielding the dry, crystalline disodium salt of 7-oxabicyclo [2.2.1] hept-5-ene-2,3-dicarboxylic acid.

The disodium salt of 1-hydroxymethyl-7-oxabicyclo [2.2.1] hept-5-ene-2,3-dicarboxylic acid was prepared in a repetition of the above procedure, replacing the furan used therein with 98 grams of furfuryl alcohol.

EXAMPLE II

This example illustrates the preparation and evaluation of a typical detergent composition of this invention containing 7-oxabicyclo [2.2.1] hept-5-ene-2,3-dicarboxylic acid.

The detergent composition was prepared by blending togethr the following ingredients:

Sodium dodecylbenzene sulfonate (detergent)	25 parts
7-Oxabicyclo [2.2.1] hept-5-ene-2,3-1 dicarboxylic acid (builder)	40 parts
Sodium sulfate (filler)	24.5 parts
Sodium silicate (corrosion inhibitor)	10 parts
sodium carboxymethyl cellulose (soil anti-redeposition agent	0.5 parts

Two additional detergent compositions were prepared for comparison purposes which were identical to the composition described above except that one composition contained 40 parts of sodium tripolyphosphate in place of the novel bicyclic builder while the remaining composition contained no builder ingredient but the concentration of filler was proportionately increased.

A series of aqueous wash media were prepared by admixing 1.5 grams of each of the three above-described detergent compositions respectively, to 1000 milliliters of water. Swatches (3 inches by 7 inches) of undyed cotton were soiled in a small test area measuring about 1¼ inches in diameter by wiping the skin of the brow and neck of each member of a test panel of 10 male individuals, respectively, in an effort to approximate the soiling of fabrics which takes place in day-to-day situations. Each wash load contained a swatch from each panel member. The washes were conducted in a washing apparatus sold by U.S. Testing Company and called a Terg-o-Tometer with the temperature of the wash media at 120°F. The washed swatches were rinsed and ironed between two pieces of white fabric so as to eliminate any dirt transfer from the iron. Reflectance readings indicating the degree of whiteness of the test area were then made with a Photovolt Corporation Photoelectric Reflectance Meter, Model 610. Thereafter, the test procedure including the soiling of the identical test areas of each swatch, respectively, was repeated four times. Reflectance readings of the test swatches with and without soiling before washing were obtained and the readings were appropriately inserted into the following calculation in order to obtain the % Detergency of the test composition.

$$\% \text{ Detergency} = \frac{(R_1 - R_2)\,(100)}{(R_3 - R_2)}$$

wherein:

R_1 = reading of washed, soiled swatch,

R_2 = reading of unwashed, soiled swatch, and

R_3 = reading of unsoiled swatch.

Table I summarizes the results obtained with the various indicated wash media. Each of the % Detergency values given in the table is the mean reading of 10 swatches.

Table I

Test Composition	Detergency after wash No. 1	2	3	4	5
Using 7-oxabicyclo [2.2.1] hept-5-ene-2,3-dicarboxylic acid	86.6	76.0	72.6	73.9	72.6
Using sodium tripolyphosphate	84.0	83.1	72.3	74.5	68.8
Using no builder	68.8	64.9	50.8	47.0	36.2

It is seen from the above data that the test composition containing the 7-oxabicyclo compound exhibits a "% Detergency" comparable to that achieved with a composition containing a conventional commercially used builder, namely sodium tripolyphosphate. As expected, the composition containing no builder shows a poor soil removal even after one wash cycle and a strong tendency to build-up soil. A desirable detergent composition will ordinarily maintain the soil build-up to a minimum as is the case with the phosphate builder as well as the 7-oxabicyclo compound.

EXAMPLE III

This example illustrates a detergent composition wherein the builder ingredient of the composition is comprised of a combination of sodium tripolyphosphate and a novel builder of this invention.

A series of three detergent compositions were prepared containing the following ingredients:

	Composition (parts) A	B	C
Sodium dodecylbenzene sulfonate	25	25	25
Sodium tripolyphosphate	40	—	20
7-Oxabicyclo [2.2.1] hept-5-ene-2,3-dicarboxylic acid	—	40	20
Sodium sulfate	24.5	24.5	24.5
Sodium silicate	10	10	10
Sodium carboxymethyl cellulose	0.5	0.5	0.5

Table II, below, summarizes the % Detergency of the various above-described compositions when subjected to the test procedure described in Example II.

Table II

Composition	% Detergency after wash No. 1	2	3	4
A	95.7	86.3	88.7	89.5
B	93.0	90.2	81.2	85.3
C	97.7	93.5	84.8	91.3

The above data clearly illustrate the excellent compatibility of a representative builder of this invention with a known, conventional builder, i.e., sodium tripolyphosphate.

EXAMPLE IV

This example illustrates a typical detergent composition of this invention being used in a wash media containing a chlorine-releasing bleach.

Two detergent compositions each, respectively, identical to Composition A and Composition B as described in Example III were prepared. The compositions were evaluated for % Detergency as described in Example II, with the sole exception that the wash media had added thereto a chlorine-releasing bleach in a concentration equivalent to about 0.03%, by weight, of active chlorine, as recommended by the manufacturer.

Composition	% Detergency after wash No. 1	2	3	4	5
Using sodium tripolyphosphate, Composition A	100.7	100.9	100.8	103.1	101.1
Using 7-oxabicyclo [2.2.1]hept-5-ene-2,3-dicarboxylic acid, Composition B	101.0	106.4	98.5	103.7	103.4

It is seen that the builder of this invention yields results fully comparable to the results obtained with sodium tripolyphosphate when each are employed in a chlorine-containing wash medium. There is no breakdown of the novel builder in the presence of the bleach and furthermore there is no impairment of the bleaching function.

EXAMPLE V

This example illustrates additional detergent compositions utilizing other representative builders of this invention.

Two detergent compositions were prepared by blending the following ingredients:

	Composition (parts) A	B
Sodium dodecylbenzene sulfonate	25	25
Sodium tripolyphosphate	20	—
7-Oxabicyclo [2.2.1] heptane-2,3-dicarboxylic acid	—	20
Sodium sulfate	44.5	44.5
Sodium silicate	10	10
Sodium carboxymethyl cellulose	0.5	0.5

The compositions were evaluated for % Detergency as described in Example II, with the results summarized as follows:

Composition	% Detergency after wash No. 1	2	3	4	5
A	81.6	88.1	83.9	72.7	68.6
B	87.8	83.6	72.4	60.3	68.7

Thus, the detergent composition containing a novel builder of this invention, Composition B, shows % Detergency values comparable to those obtained with a detergent composition containing an equal concentration of sodium tripolyphosphate.

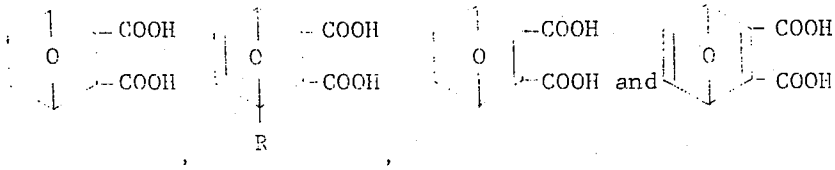
Two additional detergent compositions were prepared, as described above, to contain 1-hydroxymethyl-7-oxabicyclo [2.2.1] hept-5-ene-2.3-dicarboxylic acid, disodium salt in concentrations of 10 and 50%, respectively, based on the weight of detergent composition solids. The concentration of sodium sulfate was adjusted in each composition to compensate for the change in the concentration of builder. An evaluation of these compositions by means of the % Detergency test showed that improved % Detergency values were obtained with each composition over the composition containing no builder, with the detergent composition containing 50% of the novel builder showing substantial improvements.

Summarizing, it is seen that this invention provides a novel, effective class of non-phosphate builders for use in preparing detergent compositions.

It is to be noted that although emphasis has been placed in describing this invention in connection with the washing of fabrics, the detergent compositions comprehended within the scope of this invention are likewise useful for all washing purposes including, for example, dishwashing, floorwashing, carwashing, and the like. Variations in materials, proportions, and procedures may be made without departing from the scope and spirit of this invention as defined by the following claims.

We claim:

1. A detergent composition in substantially dry form consisting essentially of an organic detergent selected from the group consisting of anionic, cationic, nonionic and amphoteric surface active compounds, a filler selected from the group consisting of sodium sulfate and sodium carbonate and, in combination therewith as a builder, a compound selected from the group consisting of



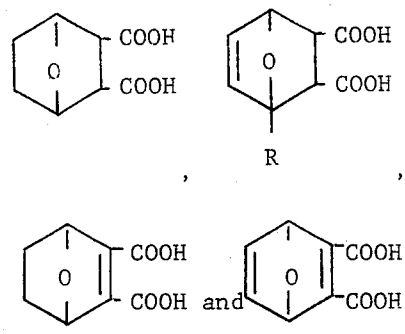
wherein R is selected from the group consisting of —H, $-CH_3$, $-CH_2OH$, $-CH_2OCOCH_3$, $-CH(OCOCH_3)_2$ and $-CH(OCH_2CH_3)_2$; and anhydrides and water-soluble alkali metal salts thereof; said detergent and said builder being present in a weight ratio of 10:1 to 1:10, and said filler present in a proportion of from about 10 to 45% based on the weight of total detergent composition solids, and the composition providing in aqueous solution a pH of from about 8 to 13.

2. The detergent composition of claim **1**, wherein the proportion of builder ranges from 20 to 60% based on the weight of total detergent composition solids.

3. The detergent composition of claim **1** wherein there is also present, in a proportion up to 55% based on the weight of total detergent composition solids, a supplemental builder selected from the group consisting of alkali metal polyphosphates and aminopolycarboxylic acids and salts, and mixtures thereof.

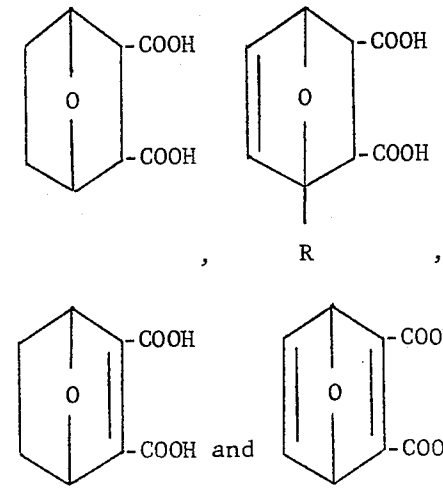
4. The detergent composition of claim 1, wherein said builder is the sodium salt of 7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid.

5. A detergent composition in a substantially dry form consisting essentially of an organic detergent selected from the group consisting of anionic, cationic, non-ionic and amphoteric surface active compounds, a water-soluble alkali metal silicate and, in combination therewith as a builder, a compound selected from the group consisting of



wherein R is selected from the group consisting of —H, $-CH_3$, $-CH_2OH$, $-CH_2OCOCH_3$, $-CH(OCOCH_3)_2$ and $-CH(OCH_2CH_3)_2$; and anhydrides and water-soluble alkali metal salts thereof; said detergent and said builder being present in a weight ratio of 10:1 to 1:10, and said water-soluble alkali metal silicate present in a proportion of from about 2 to 12% based on the weight of total detergent composition solids, and the composition providing in aqueous solution a pH of from about 8 to 13.

6. A process for removing soil from a fabric which comprises washing said fabric in an aqueous medium having a pH of about 8 to 13 containing from about 0.05 to 0.25%, based on the weight of wash water, of a detergent composition consisting essentially of a synthetic organic detergent selected from the group consisting of anionic, cationic, non-ionic and amphoteric surface active compounds and, in solution therewith as a builder, a compound selected from the group consisting of



wherein R is selected from the group consisting of —H, $-CH_3$, $-CH_2OH$, $-CH_2OCOCH_3$, $-CH(OCOCH_3)_2$ and $-CH(OCH_2CH_3)_2$, and water-soluble alkali metal salts thereof; said detergent and said builder being present in a weight ratio of 4:1 and 1:4.

7. The process of claim 6, wherein the proportion of builder ranges from 20 to 60% based on the weight of total detergent composition solids.

8. The process of claim 7, wherein there is present, in a proportion up to 55% based on the weight of total detergent composition solids, a supplemental builder selected from the group consisting of alkali metal polyphosphates and aminopolycarboxylic acids and salts, and mixtures thereof.

9. The process of claim 7, wherein there is also present, in a proportion of from 2 to 12%, a water-soluble alkali metal silicate and, in a proportion up to about 45%, a filler selected from sodium sulfate and sodium carbonate, each proportion being based on the weight of total detergent composition solids.

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