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POLYCARBOXYLIC THIOETHER DETERGENT BUILDERS

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U.S. Cl. 252—89 5 Claims

ABSTRACT OF THE DISCLOSURE

Novel builders for use in synthetic detergent compositions, said builders comprising polycarboxylic thioethers and their alkali metal salts.

This invention relates to synthetic detergent compositions containing a polycarboxylic thioether as a detergent builder, said compositions being useful in aqueous washing solutions. In a further aspect, the invention relates to 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 synthetic detergent compositions and thereby improve their whitening powers. Polyphosphate compounds such, for example, as sodium tripolyphosphate (STPP), have been in long use as builders particularly because of their relatively low cost and their utility in increasing the whitening powers of detergent compositions containing them. 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 which is sufficient to undesirably upset the natural ecology of these waters. With the recent governmental emphasis on environmental 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.

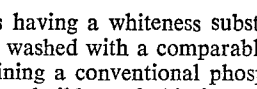
Among the important properties that must be exhibited by compounds employed as builders are included: the ability to increase the whitening power of the detergent composition, non-toxicity, compatibility with the various components and additives of conventional detergent compositions, and stability with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

It is the prime object of this invention to provide a non-phosphate builders which is particularly effective in increasing the whitening power of synthetic 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.

I have now found that compounds of the class of polycarboxylic thioethers, described below, and salts thereof are useful as detergent builders and impart marked improvements in the whitening power of synthetic detergent compositions. I have also found that the use of synthetic detergent compositions containing a polycarboxylic thioether or its salt in aqueous washing solutions results in

washed fabrics having a whiteness substantially equal to that of fabrics washed with a comparable detergent composition containing a conventional phosphate builder.

The detergent builders of this invention are polycarboxylic thioethers of the general formula



wherein

R is a saturated hydrocarbon group of 1–4 carbon atoms,
R′ may be —H, —CH_2COOH, or —CH_2CH_2COOH attached to any carbon atom of R, and
R″ may be —H or an alkyl group of 1–18 carbon atoms attached to the carbon atom of R which is bound to sulfur.

Also useful as detergent builders are the water-soluble salts of these polycarboxylic thioethers, especially the sodium salts thereof.

The polycarboxylic thioethers used as detergent builders according to this invention are not in themselves new compounds and may be prepared by methods well known to those skilled in the art. For example, a preferred compound, thiodisuccinic acid, is prepared by reacting maleic anhydride with hydrogen sulfide (F. B. Zienty, B. O. Vinyard, A. A. Schlepnik, J. Org. Chem., 27, 3140 (1962)) or by reacting thiomalic acid with maleic or fumaric acid. Similarly other polycarboxylic thioethers may be prepared by reacting mercapto acids with olefinic acids, esters, or nitriles (J. F. Mulvaney, J. G. Murphy, R. L. Evans, J. Am. Chem. Soc. 70, 2428 (1948)).

The acids made by these processes are then converted to salt form, for example, by neutralization with sodium hydroxide.

Most of these acids and their salts, when they are prepared, are characterized by an objectionable odor and are therefore not acceptable as detergent builders. Some of them produce dark solutions and off-color, non-white salts when they are neutralized which can also be undesirable in a detergent builder.

It has been found, and is according to this invention, that both objectionable odor and dark color can be essentially eliminated by treating the solutions of the salts of the acids with hydrogen peroxide. The treatment is generally performed by neutralizing the acid with sodium hydroxide to a pH of about 9. The temperature of the mixture is maintained below about 30° C. during the neutralization and during the course of the subsequent treatment with hydrogen peroxide. The hydrogen peroxide is added slowly as an aqueous solution, preferably about 30% concentration, until the odor is eliminated and the color is sufficiently improved. The amounts of hydrogen peroxide required to attain the desired effect range from 0.01 to 2 moles per mole of polycarboxylic thioether. In some few cases, the polycarboxylic thioethers are odor- and color-free and require no hydrogen peroxide treatment. The hydrogen peroxide treatment has no effect on the ability of the salt of the polycarboxylic thioether to act as an effective detergent builder.

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, sodium tripolyphosphate previously used therein. Ordinarily conventional, commercially available detergent compositions will contain from less than about 1% up to about 60% or more of builder, based on the weight of the total detergent composition solids, and it is comprehended that the present novel builders may be utilized in the same concentrations. Concentrations of builder within the range of from about 20 to 60%,

based on the weight of the total detergent composition solids, are preferred, however, since builder concentrations of less than about 20% will usually result in insufficient whitening power. In utilizing the novel builders 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, however, the selected builder of our invention can be added to the wash media separately with equal effect. The deteregnt composition, in addition to the detergent and builder, may also contain a number of other ingredients. Thus, the detergent composition may contain any of the usual types of fillers, such as sodium sulphate, sodium carbonate and the like. Anticorrosion agents such as sodium silicate and sodium metasilicate as well as optical brighteners and enzymes may also be included, if desired.

The builder described herein may be utilized in a detergent composition comprising any of the synthetic organic detergents which are commonly used for aqueous washing purposes. The detergent 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 the U.S. Pat. 2,755,252 entitled "Partially Acetylated Polyvinyl Alcohol as a Soil-Suspending Agent" issued July 17, 1956 and U.S. Pat. 3,459,670 entitled "Builders for Synthetic Detergents" issued Aug. 5, 1969. 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.

It is an advantage of the present builders that in addition to enhancing the whitening power of detergents in a degree of 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 no do they interfere with nor impair the function of the bleaches themselves.

The actual use of the detergent builders of this invention comprises the use of the resultant detergent composition (detergent, builder and optional additives) in conventional concentrations, i.e. from about 0.1 to 0.2%, 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 washed fabrics 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 p.p.m. measured as calcium carbonate.

EXAMPLE I

This example shows the decolorization and deodorization procedure of the invention and the builder properties of the products.

One mole of thiodisuccinic acid was dissolved in 250 ml. of water and neutralized to pH 9 by adding about four moles of sodium hydroxide as a 50% aqueous solution. The temperature of the mixture was kept below 30° C. during the course of the neutralization and also during the subsequent reaction with hydrogen peroxide. A 30% aqueous solution of hydrogen peroxide was added slowly in a quantity sufficient to give the solution a satisfactory color and eliminate objectionable odor.

Detergent compositions were prepared according to the following composition:

Sodium dodecylbenzene sulfonate (detergent)	25 parts.
Builder	According to Table I.
Sodium sulfate (filler)	To make 64.5 parts of builder+filler.
Sodium silicate (corrosion inhibitor)	10 parts.
Sodium carboxymethyl cellulose (soil anti-redeposition agent)	0.5 part.

A series of aqueous wash media was prepared by mixing 1.5 grams of the above detergent compositions with 1000 ml. of water. Swatches (3" x 7") of undyed cotton were soiled in a small test area measuring about 1¼" 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 also obtained and the readings were appropriately inserted into the following calculation in order to obtain the "Percent Detergency" of the test composition

$$\text{Percent detergency} = \frac{R_1 - R_2}{R_3 - R_4}(100)$$

where:

R_1=reading of washed, soiled swatch
R_2=reading of unwashed, soiled swatch
R_3=reading of unsoiled swatch
R_4=reading of unwashed, soiled swatch.

Table I summarizes the results obtained with the various indicated wash media. Each of the percent detergency values given in the table is the mean of ten swatches.

TABLE I

Composition	Builder	H_2O_2 moles	Parts	Percent detergency
1	Sodium thiodisuccinate		40	82
2	do	1.0	40	86
3	do	0.1	40	85
4	STPP		40	86
5	Sodium thiodisuccinate		20	86
6	do	1.0	20	87
7	do	0.1	20	85
8	STPP		20	86
9	Sodium thiodisuccinate		10	79
10	STPP		10	79

EXAMPLE II

This example shows the effectiveness of thiodisuccinic acid in combination with sodium tripolyphosphate or sodium hypochlorite.

Detergent compositions were prepared according to the formula of Example I using the amounts of builder indicated in Table II. A series of aqueous wash media was prepared as in Example I using in some of the compositions aqueous sodium hypochlorite solution (bleach) in the amount of about 0.03 by weight of active chlorine.

The effectiveness of the wash media was evaluated by the test procedure of Example I. Results are summarized in Table II. It may be seen that the compositions con-

taining the sodium thiodisuccinate are equivalent to those containing sodium tripolyphosphate.

TABLE II

Composition	Builder and bleach	Parts	Percent detergency
1	STPP	40	88
2	Sodium thiodisuccinate (treated with 1 mole of hydrogen peroxide) plus STPP.	20+20	86
3	STPP plus sodium hypochlorite	40	104
4	Sodium thiodisuccinate (treated with 0.1 mole of hydrogen peroxide) plus sodium hypochlorite.	40	102

EXAMPLE III

This example shows the performance of some other polycarboxylic thioethers.

Detergent compositions were prepared according to the formula of Example I using the builders and amounts listed in Table III. A series of aqueous wash media was prepared as in Example I and an effectiveness test was run according to the procedure of that example. Results are summarized in Table III. It can be seen that the performance of these builders approaches that of sodium tripolyphosphate.

TABLE III

Composition	Builder	Parts	Percent detergency
1	Sodium thiodipropionate	40	79
2	Trisodium carboxymethylthiosuccinate (treated with 0.1 mole of hydrogen peroxide).	40	78
3	Sodium nonenylthiodisuccinate (treated with 0.1 mole of hydrogen peroxide).	40	78
4	do	20	78
5	STPP	40	87
6	STPP	20	84

EXAMPLE IV

This example shows the effectiveness of another salt of a polycarboxylic thioether.

Detergent compositions were prepared according to the formula of Example I using the builders and amounts listed in Table IV. A series of aqueous wash media was prepared as in Example I and an effectiveness test was run as in that example. Results are summarized in Table IV. It can be seen that this builder approaches the effectiveness of sodium tripolyphosphate.

TABLE IV

Composition	Builder	Parts	Percent detergency
1	Trisodium carboxyethylthiosuccinate	40	71
2	do	20	81
3	STPP	40	82
4	STPP	20	84

EXAMPLE V

This example shows the effectiveness of some salts of dicarboxy-(thiosuccinic acid)butanes as detergent builders.

Detergent compositions were prepared according to the formula of Example I using the builders and amounts listed in Table V. A series of aqueous wash media was prepared as in Example I and an effectiveness test was run as in that example. Results are summarized in Table V. It can be seen that these compounds have some builder activity but appear to be somewhat inferior to sodium tripolyphosphate.

TABLE V

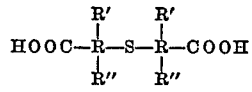
Composition	Builder	Parts	Percent detergency
1	Sodium salt of 2,4-dicarboxy-(3-thiosuccinic acid) butane.	40	68
2	do	20	74
3	Sodium salt of 1,4-dicarboxy-(3-thiosuccinic acid) butane.	40	70
6	do	20	74
4	STPP	40	84
5	STPP	20	80

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.

I claim:

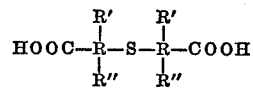
1. A detergent composition consisting essentially of a synthetic organic detergent, and in combination therewith as a builder, from about 1 percent to about 60 percent, based on the weight of the total detergent composition solids, of a salt of a polycarboxylic thioether of the formula



wherein R is a saturated hydrocarbon group of 1–4 carbon atoms, R′ is a radical selected from the group consisting of —H, —CH_2—COH, and —CH_2—CH_2—COOH, and R″ is a radical selected from the group consisting of hydrogen and alkyl groups of 1–18 carbon atoms and attached to the carbon atom of R which is bound to sulfur.

2. The composition of claim **1**, wherein there is also present a conventional, known builder in a concentration of up to about 60%, based on the total weight of the detergent weight solids.

3. A process for removing soil from a fabric which comprises washing said fabric in an aqueous medium containing a detergent composition consisting essentially of a synthetic organic detergent, and in combination therewith as a builder from about one percent to about 60 percent, based on the weight of the total detergent composition solids, of a salt of a polycarboxylic thioether of the formula



wherein R is a saturated hydrocarbon group of 1–4 carbon atoms, R′ is a radical selected from the group consisting of —H, —CH_2—COOH, and

—CH_2—CH_2—COOH,

and R″ is a radical selected from the group consisting of hydrogen and alkyl groups of 1–18 carbon atoms and attached to the carbon atom of R which is bound to sulfur.

4. The process of claim **3**, wherein said detergent composition also contains a conventional builder in a concentration of up to about 60%, based on the total weight of the detergent weight solids.

5. The composition of claim **1** in which the polycarboxylic thioether salt has been treated in aqueous solution with 0.01 to 2 moles of aqueous hydrogen peroxide per mole of thioether.

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WILLIAM E. SCHULZ, Primary Examiner

U.S. Cl. X.R.

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