

1

3,689,436

PHOSPHONATE DETERGENT BUILDERS

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No Drawing. Filed Oct. 19, 1970, Ser. No. 82,092
Int. Cl. C11d 3/36

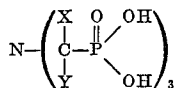
U.S. Cl. 252-545

4 Claims

ABSTRACT OF THE DISCLOSURE

The invention disclosed is directed to detergent builder compositions including:

(A) Amino tri(lower alkylidene phosphonic acids), having the formula:

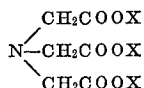


wherein X, Y or both represent hydrogen or a lower alkyl group (1-4 carbon atoms)

or a water-soluble salt or ester thereof and

(B) a member of the group consisting of:

- (1) a water soluble acrylic or methacrylic acid polymer which is polyacrylic acid, polymethylacrylic acid, acrylic acid-methacrylic acid copolymers, hydrolyzed polyacrylamide, hydrolyzed polymethacrylamide, hydrolyzed acrylamide-methacrylamide copolymers, hydrolyzed polyacrylonitrile, hydrolyzed polymethacrylonitrile, hydrolyzed acrylonitrile-methacrylonitrile copolymers, or mixtures of any two or more of the said acrylic polymers; or water-soluble salts of these acrylic polymers, or polymer mixtures; or
- (2) a water-soluble organic complexing polymer builder ingredient having a weight average molecular weight of from about 1,000,000 to about 12,000,000 and comprising a linear aliphatic backbone having N-carboxymethyl amine or N-carboxymethyl amide side chains imparting complexing properties to the polymer; or a water soluble salt of such complexing polymer; or
- (3) nitrilotriacetic acid or a water soluble salt thereof having the formula



wherein each X is independently hydrogen or a suitable cation such as alkali metal or ammonium

and to detergent compositions containing said builders.

Also disclosed are methods for enhancing the building activity of said amino phosphonic acid compounds in hard water cleaning solutions prepared from water having a hardness of up to 20 grains per gallon or more; and for enhancing the building activity of said complexing polymer in cleaning solutions prepared from water having a hardness of up to 10 grains per gallon.

The present invention relates to water-soluble laundry detergent builder compositions comprising blends of an aminophosphonic acid compound with a water-soluble acrylic polymer or salt such as sodium polyacrylate, or with a water-soluble complexing polymer having N-carboxymethyl amine or N-carboxymethyl amide ligands or a water-soluble salt of such complexing polymer, or with nitrilotriacetic acid (NTA) or its water-soluble salts.

2

The invention further relates to detergent compositions comprising an organic detergent surfactant combined with the said builders to augment the cleaning and laundry brightening power of the detergent surfactant.

Materials useful for enhancing the cleansing power of detergents are known. These materials, commonly referred to as "builders," include inorganic and organic compounds. Examples of known builder materials are water-soluble inorganic alkaline salts which can be used alone or in combination, including alkali metal carbonates, borates, phosphates, polyphosphates, bicarbonates and silicates.

Known organic builder materials include alkali metal, ammonium, or substituted ammonium salts of ethylenediamine tetraacetic acid and nitrilotriacetic acid. Alkali metal salts of phytic acid are also suitable as organic builders.

Despite the ever expanding list of builders, certain disadvantages are recognized in known builder compounds. Perhaps the most widely acknowledged limitation regards a series of more commonly used condensed inorganic polyphosphate compounds such as alkali metal triphosphate, and higher condensed phosphates such as tetra-alkali metal pyrophosphate. When used in aqueous detergent compositions these compounds have a tendency to hydrolyze into orthophosphates or other less condensed phosphorous compounds which are relatively inferior builders and which have recently been subjected to criticism because of asserted water pollution tendencies.

U.S. Pat. No. 3,308,067 issued Mar. 7, 1967 to Diehl teaches the use of complex polyelectrolytes such as poly (itaconic acid) as detergent builders. These polyelectrolytes are polymers having complex monomeric units consisting of a polymerizable ethylenic moiety having not less than two carboxylic radicals pendant thereto.

The use of aminophosphonic acid compounds as detergent builders is disclosed in U.S. Patent 3,383,323 issued May 14, 1968 to Irani. Detergent compositions containing nitrilotriacetates have been disclosed in U.S. Patent 3,392,121 issued July 9, 1968 to Gedge. The Gedge patent also suggests the use of combinations of nitrilotriacetates with ethane-1-hydroxy-1,1-diphosphonic acid and/or an inorganic polyphosphate as detergent builders. Carter et al., U.S. Patent 3,463,734 issued Aug. 26, 1969 discloses builder compositions comprising poly (itaconic acid) blended with a polyphosphate, a polyphosphonate or a nitrilotriacetate. Kessler et al., U.S. Patent 3,332,880 issued July 25, 1967 discloses detergent compositions prepared from a special blend of sulfonate surface active materials which may include inorganic or organic builders such as polyphosphates or nitrilotri- or diacetates, polymaleates, polyitaconates, polyacrylates, phytates or polyphosphonates. U.S. Patent 3,509,059 issued Apr. 28, 1970 to Renold discloses in situ polymerized carboxylic monomers as dispersing agents for polyphosphate built liquid detergent compositions. U.S. Patent 3,518,200 issued June 30, 1970 to Fitch et al. discloses detergent compositions based on higher molecular weight phosphonates and which may include builders such as amino polycarboxylic acids, amino phosphonic acids, alkylene phosphonic acids or inorganic phosphates, carbonates, etc.

Generally stated, the detergent builder compositions of this invention comprise, in weight percent, based on total weight:

(I)

(a) From about 40 to about 80 percent of a water-soluble acrylic or methacrylic acid polymer or water-soluble salt thereof together with

(b) From about 60 to about 20 percent of a water-soluble amino tri (lower alkylidene phosphonic acid) compound; or

3
(II)

(a) From about 40 to about 80 percent of a water-soluble amino tri (lower alkylidene phosphonic acid) complexing polymer having N-carboxymethyl amine or N-carboxymethyl amide ligands or a water-soluble salt thereof together with

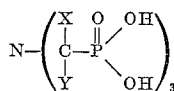
(b) From about 60 to about 20 percent of a water-soluble amino tri (lower alkylidene phosphonic acid) compound; or

(III)

(a) From about 40 to about 80 percent of nitrilotriacetic acid or a water-soluble salt thereof together with

(b) From about 60 to about 20 percent of a water-soluble amino tri (lower alkylidene phosphonic acid) compound.

The organo phosphonic acid compound used in the builder compositions of this invention is an amino tri (lower alkylidene phosphonic acid) having the following formula:



wherein X, Y or both represent hydrogen or a lower alkyl group (1-4 carbon atoms) or a water soluble salt or ester of said acids.

Illustrative acids are amino tri(methylphosphonic acid), amino tri(ethylidenephosphonic acid) and amino tri(isopropylidene phosphonic acid), amino mono(methylphosphonic acid), di(ethylidene phosphonic acid) and amino tri(butylidenephosphonic acid). Although the sodium salts of amino tri-lower alkylidenephosphonic acids are preferred, and in particular pentasodium amino tri(methylphosphonic acid), hereinafter ATMPNa₅ for the sake of brevity, other alkali metal salts, such as potassium, lithium and the like, as well as mixtures of the alkali metal salts, may be substituted therefor. In addition, any water-soluble salt, such as the ammonium salt and the amino salt, which exhibit the characteristics of the alkali metal salt may be used to practice the invention. In particular, amine salts prepared from low molecular weight amines, i.e., having a molecular weight below about 300, and more particularly the alkyl amines, alkylene amines and alkanol amines containing not more than 2 amine groups, such as ethylamine, diethylamine, propylamine, propylenediamine, hexylamine, 2-ethyl hexylamine, N-butylethanolamine, triethanolamine and the like, are the preferred amine salts. Furthermore, water-soluble esters of these acids with lower alkanols having from 1 to 4 carbon atoms may be suitably used. The amino phosphonic acid compounds, and methods for preparing them are known to the art.

The acrylic or methacrylic acid polymers which may be used in practicing the invention are water-soluble polyacrylic acid, polymethacrylic acid, acrylic acid-methacrylic acid copolymers, hydrolyzed polyacrylamide, hydrolyzed polymethacrylamide, hydrolyzed acrylamide-methacrylamide copolymers, hydrolyzed polyacrylonitrile, hydrolyzed polymethacrylonitrile hydrolyzed acrylonitrile-methacrylonitrile copolymers, mixtures of any two or more of the said polymers or the water-soluble salts of these polymers, or polymer mixtures; such as the respective alkali metal (e.g., sodium, potassium), ammonium or amine salts. The acrylic polymer builder component has a weight average molecular weight of from about 1,000 to about 15,000,000 and is preferably within the range of from 1,000 to 120,000. The preferred polymer is polyacrylic acid or sodium polyacrylate having a weight average molecular weight within the range of about 80,000 to 120,000. These polymers are commercially available, and methods for their preparation are well known in the art.

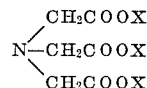
The water-soluble complexing polymer builders used in the builder compositions in accordance with one embodiment

4

ment of this invention are known, per se, to the art. A number of suitable polymeric builders for the purposes of this invention are disclosed in each of Gunderson et al. United States Patents 3,285,886 and 3,331,773 issued Nov. 15, 1966 and July 18, 1967 respectively. The entire disclosure of each of these patents is incorporated herein by reference. Of the polymers disclosed in the Gunderson et al. patents, the polymer presently preferred for the purposes of the present invention is poly (N,N-dicarboxymethylacrylamide) having molecular weight of from about 1,000,000 to about 12,000,000; especially about 2,000,000 to about 5,000,000, e.g., 3,000,000. An additional example of a suitable polymeric complexing builder is poly(N,N-dicarboxymethyl vinyl amine) and its water-soluble salts such as the disodium salt. Water-soluble salts of other like complexing polymers may also be used. Examples of suitable water soluble polymer salts are the alkali metal, ammonium or amine salts.

In accordance with the present invention the N-carboxymethyl amine and/or N-carboxymethyl amide groups in the complexing polymer builder ingredient must constitute at least about 10, preferably at least about 50, and most preferably from about 80 to 100 (for example 95) percent (on a numerical basis) of the reactive side chains in the complexing polymer used.

Nitrilotriacetic acid and water-soluble salts thereof used in the practice of this invention have the formula



wherein each X is independently selected from the group consisting of hydrogen or a monovalent alkali metal, ammonium or substituted ammonium cation. The preferred nitrilotriacetic acid and compound is the trisodium salt N(CH₂COONa)₃, hereinafter referred to as NTANa₃ for the sake of brevity.

The builder compositions of the present invention may be used in combination with most any water-soluble detergent surfactant. Representative classes of suitable detergent surfactants include alkali metal soaps, anionic synthetic detergents, nonionic synthetic detergents, zwitterionic synthetic detergents and ampholytic synthetic detergents. All of these detergent surfactants are known in the art. For the sake of brevity, reference is made to the disclosure of Chaffee et al., United States Patent 3,324,038 issued June 6, 1967, especially at column 2, line 40 through column 5, line 7. The entire disclosure of the said Chaffee, U.S. Patent 3,324,038 is also hereby incorporated herein by reference. The detergent surfactant may be present in amounts ranging from about 5 to about 100 parts by weight and preferably from about 10 to about 50 parts by weight, per 100 parts by weight of the detergent builder composition. The detergent compositions of this invention may include any of the known fillers or diluents such as sodium chloride, sodium sulfate and the like, soil suspending agents such as carboxymethyl cellulose, and other known detergent additives known in the art such as sodium hydroxide, potassium hydroxide, bactericides, optical brighteners, chelating agents, dyes, sequestering agents, and corrosion inhibitors, such as alkali metal silicates.

A typical water-soluble detergent base composition with which the present builder may be usefully combined includes about 32 weight percent of linear alkyl, aryl or alkaryl sulfonate, about 2 weight percent of sodium carboxymethyl cellulose, about 14 weight percent of sodium metasilicate pentahydrate, and about 52 weight percent of sodium chloride diluent.

The detergent compositions of this invention may be prepared and stored or used as a dry powder or granular mixture, as tablets or like agglomerates, or in aqueous solutions containing up to 90 or 95 percent by weight, based on total solution weight, of water or water-cosolvent (e.g., alcohol) mixtures.

5

The present invention will be further illustrated by the following specific but non-limiting examples.

In the examples all parts are parts by weight unless otherwise specifically stated. Where "hard water" is used in various solutions throughout the following examples X grains of hardness means X grains of CaCO_3 plus MgCO_3 are in solution per gallon of water. The ratio of CaCO_3 to MgCO_3 is 2:1 by weight, and X is a specified number such as 10. "Hard water" solutions were prepared from a stock solution of artificially prepared 200 grain per gallon hard water. Zero hardness solutions were prepared with de-ionized water.

The laundry detergent base composition (containing no builder) used in each of the examples was formulated as follows:

TABLE I.—DETERGENT BASE COMPOSITION

Component:	Parts by weight
Linear dodecyl benzene sulfonate	32
Sodium carboxymethyl cellulose	2
Sodium metasilicate pentahydrate	14
Sodium chloride	52

Detergent compositions containing equal parts by weight of the aforesaid base composition and of various builder compositions were prepared and tested for laundering ability at various builder concentrations in aqueous solutions made up from deionized water (zero hardness) and water having hardness of 5 to 20 grains per gallon. The laundering ability of the detergent solutions was determined by laundering duplicate test specimens prepared as hereinafter described to simulate white laundry goods soiled by human body oil and grime. Test specimens were prepared by initially saturating 6" by 6" white cotton swatches with an agitated solution having the following composition:

TABLE II.—SIMULATED SOIL SOLUTION

Component:	Parts by weight
Carbon black	0.125
Virgin olive oil	5.000
Carbon tetrachloride	94.875

The saturated cotton swatches were removed from the soil solution, dried, and manually rubbed to effect a uniform black oil coating on the swatches. Duplicate soiled specimens were thereafter laundered in a Tergotometer using the various detergent solutions at a temperature of 140° Fahrenheit and a speed of 150 revolutions per minute. After a 15 minute wash cycle, the specimens were removed from the Tergotometer, water rinsed and dried to substantial dryness.

The substantially dry laundered test swatches were then tested for brightness using a Photovolt Reflectometer equipped with a 15° head and no filter. The reflectometer was set at 0 percent brightness using an unlaundered swatch soiled with carbon black and olive oil, and was set at 100 percent brightness using an unsoiled cotton swatch placed over white paper. Ten brightness observations, including 5 for each of the two duplicate laundered swatches, were made and averaged in each test.

6

The following detergent formulae were tested in accordance with the foregoing procedure:

COMPARATIVE FORMULA A (NO BUILDER)

Component:	Parts by weight
Base composition of Table I	50.0
Sodium chloride	50.0

COMPARATIVE FORMULA B (AMINO PHOSPHONATE BUILDER)

Base composition of Table I	50.0
ATMPNa ₅	50.0

COMPARATIVE FORMULA C (SODIUM POLYACRYLATE BUILDER)

Base composition of Table I	50.0
Sodium polyacrylate weight average molecular weight of 100,000	50.0

COMPARATIVE FORMULA D (COMPLEXING POLYMER BUILDER)

Base composition of Table I	50.0
Poly (N,N-dicarboxymethyl acrylamide) weight average molecular weight of 3,000,000	50.0

COMPARATIVE FORMULA E (NITRILOTRI-ACETATE BUILDER)

Base composition of Table I	50.0
NTANa ₃	50.0

EXAMPLE 1

Base composition of Table I	50.0
Polyacrylate of Formula C	40.0
ATMPNa ₅	10.0

EXAMPLE 2

Base composition of Table I	50.0
Polyacrylate of Formula C	20.0
ATMPNa ₅	30.0

EXAMPLE 3

Base composition of Table I	50.0
Complexing polymer of Formula D	40.0
ATMPNa ₅	10.0

EXAMPLE 4

Base composition of Table I	50.0
Complexing polymer of Formula D	20.0
ATMPNa ₅	30.0

EXAMPLE 5

Base composition of Table I	50.0
NTANa ₃	40.0
ATMPNa ₅	10.0

EXAMPLE 6

Base composition of Table I	50.0
NTANa ₃	20.0
ATMPNa ₅	30.0

Results of the laundering tests are shown in the following Table III.

TABLE III.—PERCENT BRIGHTNESS AT VARYING BUILDER CONCENTRATIONS AND WITH VARYING WATER HARDNESS

Builder concentration (weight percent)	.10					.06				
	0	5	10	15	20	0	5	10	15	20
Solution water hardness (grains per gallon)										
Test Formula:										
A	55	47.5	40.5	40	39.5	53	44.5	36	33.5	31
B	68	67.5	54	41	27.5	56	50	44	38	32
C	66	65	64.5	64	63.5	61.5	61	60.5	60.5	60
D	49	48	47.5	46.5	45.5	48	47.5	47	46.5	46
E	76.5	68	64.5	63.5	62.5	76.5	64	57.5	50.5	33
Examples:										
1	70	69	68.5	67.5	67	67	60.5	54	47.5	41
2	71	69.5	64.5	59.5	54.5	69	64	54	43.5	33
3	30	35	41.5	48	54.5	17.5	18.5	28.5	38	48
4	61.5	56	50	44	38	30	33	40	47	54
5	77.5	75.5	73	70.5	68	70	62	41.5	21.5	1.5
6	85	82.5	66	50	34	72.5	68	46	24	2.5

The following conclusions were drawn from the results of the evaluations as reflected in the data shown in Table III:

(1) At a builder concentration of 0.10% the combination of 80% sodium polyacrylate and 20% ATMPNa₅ as the builder (Example 1) gave better results than the use of 100% of either builder alone (Comparative Formulae C and B, respectively) at all levels of water hardness from 0 to 20 grains per gallon. The combination of 40% polyacrylate and 60% ATMPNa₅ (Example 2) gave similar synergistic performance at water hardness levels up to about 10 grains per gallon, at which point this combination was about equivalent to the use of polyacrylate alone. At all water hardness levels up to 20 grains per gallon, the addition of about 0.67 part of polyacrylate for each part of ATMPNa₅ (Example 2) greatly enhanced the builder activity of the latter, which, by itself, is worse or not much better than no builder at all (Comparative Formula A) at the higher hardness levels of 15 and 20 grains per gallon.

(2) At a builder concentration of 0.06% the combination of 40% polyacrylate and 60% ATMPNa₅ (Example 2) again provides synergistic results at a water hardness level of 5 grains per gallon. The results also show that addition of about 0.67 to about 4.0 parts of polyacrylate for each part by weight of ATMPNa₅ (Example 2 and Example 1 respectively) enhances the builder activity of the latter at all water hardness levels.

(3) The combination of 80% high molecular weight complexing polymer and 20% ATMPNa₅ (Example 3) gives synergistic builder activity better than either material alone (Comparative Formulae D and B, respectively) at water hardness levels above about 15 grains per gallon and builder concentration of 0.10%. At these same concentrations the addition of about 1.5 parts of ATMPNa₅ for each part of the complexing polymer (Example 4) enhances the builder activity of the latter at water hardness levels of up to about 10 grains per gallon or more. When the builder concentration is 0.06% the combination of 80% high molecular weight complexing polymer and 20% ATMPNa₅ again gives synergistic results at a water hardness of 20 grains per gallon and the combination of 40% complexing polymer and 60% ATMPNa₅ (Example 4) gives synergistic results at hardness levels of 15 and 20 grains per gallon.

(4) At a builder concentration of 0.10% the combination of 80% NTANa₃ and 20% ATMPNa₅ (Example 5) gives synergistic results, better than either ingredient alone (Formulae E and B, respectively), at all water hardness levels. The combination of 40% NTANa₃ and 60% ATMPNa₅ (Example 6) also gives synergistic results at water hardness levels of up to about 10 grains per gallon and shows enhancement of the builder activity of ATMPNa₅ at water hardness levels up to about 15 grains per gallon or more. At builder concentrations of 0.06% the combination of Example 6 shows synergistic results at

a hardness level of 5 grains per gallon and enhancement of the activity of ATMPNa₅ at hardness levels up to about 10 grains per gallon, whereas the combination of Example 5 shows only enhancement of the activity of ATMPNa₅ at hardness levels up to just less than 10 grains per gallon.

It is understood that the foregoing detailed description is given merely by way of illustration and that various modifications may be made thereto without departing from the spirit or scope of the present invention.

What is claimed is:

1. A water-soluble detergent builder composition consisting essentially of, by weight, from about 20 to about 60 percent of pentasodium amino tri(methylphosphonic acid) and from about 40 to about 80 percent of poly (N,N - dicarboxymethyl acrylamide) having a molecular weight of about 3,000,000.

2. A water-soluble detergent builder composition consisting essentially of, by weight, from about 20 to about 60 percent of pentasodium amino tri(methylphosphonic acid) and from about 40 to about 80 percent of the trisodium salt of nitrilotriacetic acid.

3. A detergent composition consisting essentially of a blend of about 5 to about 100 parts by weight of an organic detergent surfactant selected from the group consisting of alkyl, aryl, and alkaryl sulfonates; and about 100 parts by weight of the detergent builder composition of claim 1.

4. A detergent composition consisting essentially of a blend of about 5 to about 100 parts by weight of an organic detergent surfactant selected from the group consisting of alkyl, aryl, and alkaryl sulfonates; and about 100 parts by weight of the detergent builder composition of claim 2.

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U.S. Cl. X.R.
252—526, 527, 546