

1

3,586,633
ALKALINE CLEANSING AGENT
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 No Drawing. Continuation of application Ser. No. 510,961, Dec. 1, 1965. This application Apr. 3, 1969, Ser. No. 816,154
 Claims priority, application Germany, Apr. 1, 1965, H 55,665
 Int. Cl. C11d 3/06
 U.S. Cl. 252-137 **5 Claims**

ABSTRACT OF THE DISCLOSURE

Alkaline cleansing agents containing additives which prevent hydrolysis and the deposit of calcium compounds due to the use of hard water. The additives are present in quantities ranging from 0.5 to 20 weight percent and are a mixture of a hydroxyalkane-1,1-diphosphonic acid with an aminopolyphosphonic acid in mutual weight proportions of 3:1 to 1:3. The water-soluble salts of both these compounds may be used in lieu of the acids themselves.

This is a continuation of Ser. No. 510,961, Dec. 1, 1965, now abandoned.

The invention relates to alkaline cleansing agents and, more particularly, to cleansing agents containing additives which are stable against hydrolysis and which effectively prevent the deposit of calcium compounds due to the use of hard water.

When hard water is used in the manufacture of alkaline cleansing agents and also for the ensuing rinsing step, the hardness-formers precipitate and form films or coatings upon the surfaces of the articles to be cleansed and in the cleansing devices themselves. It is a known fact that such deposits are quite undesirable from both an operational and esthetic point of view.

For this reason, alkaline cleansing agents frequently contain not only the customary components, i.e., caustic alkalis, alkali carbonates, -silicates, -phosphates and/or -borates, detergents and foam suppressants, but also materials which are to serve to prevent the formation of calcium deposits from the hardness-formers in the water.

Polymeric phosphates often are incorporated in alkaline cleansing agents to prevent the precipitation of the hardness-formers in the water. However, polyphosphates are not resistant to hydrolysis in the cleansing solutions and decompose into ortho- and pyrophosphates within a comparatively short period of time. Losses of polymeric phosphates by hydrolysis frequently even occur during storage, especially when the cleansing agents are highly alkaline.

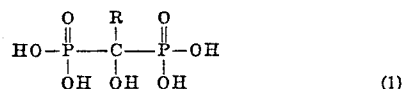
It also had previously been attempted to avoid the precipitation by the addition of organic complex-formers. These experiments have not led to satisfactory results in each and every instance. In part, the complex-formers are effective only at comparatively high concentrations, or else they do not perform satisfactorily. This is true, for instance, for ethylenediaminetetraacetic acid (EDTA) and for gluconates. Other complex-formers yield good results solely within very limited concentrations, as in the case of hydroxyethanediphosphonic acid. When the limits of concentration are exceeded by adding more than re-

2

quired or due to concentration upon replenishment of the agents in solution, an increase in the calcification and precipitation occurs. Other complex-formers, such as aminotri-(methylphosphonic acid), merely have a very slight effect which in practice is unacceptable when water of high hardness is employed, with which particularly great and undesirable precipitation occurs.

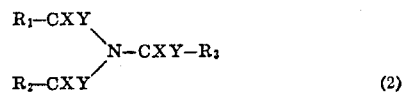
It now has been found unexpectedly and surprisingly that these drawbacks are averted by the use of the alkaline cleansing agents according to the invention. These agents have as their salient feature a content of water-soluble salts of

(a) A hydroxyalkane-1,1-diphosphonic acid having the Formula 1:

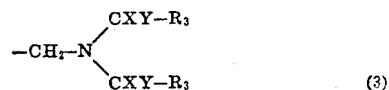


wherein R is a straight-chain or branched alkyl having 1 to 5 carbon atoms; plus

(b) An aminopolyphosphonic acid of Formula 2



wherein X and Y individually represent either hydrogen or an alkyl having 1 to 4 carbon atoms; R₁ and R₂ individually may be a -PO₃H₂ group or a group or radical of Formula 3:

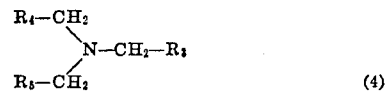


X and Y having the same connotation as in Formula 2; and R₃ denoting a -PO₃H₂ group.

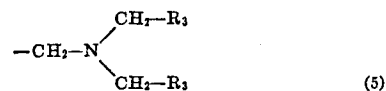
The weight proportions of (a) to (b) vary from 3:1 to 1:3.

Examples for group (a) are hydroxyethane-, hydroxypropane-, hydroxybutane-, hydroxypentane- and hydroxyhexane-1,1-diphosphonic acids.

As representatives of group (b), aminotri-(1-ethylphosphonic acid), ethylenediaminetetra-(1-ethylphosphonic acid), ethylenediaminetetra-(1-ethylphosphonic acid), aminotri-(1-propylphosphonic acid), and aminotri-(isopropylphosphonic acid) may be named, and preferably aminopolyphosphonic acids of Formula 4:



wherein R₃ (as in the preceding formulae) is a -PO₃H₂ group, R₄ and R₅ may individually be a -PO₃H₂ group or a radical having Formula 5:



R₃ again having the same connotation as before; such as aminotri-(methylphosphonic acid), ethylenediaminetetra-(methylphosphonic acid) and diethylenetriaminopentamethylphosphonic acid).

In lieu of individual hydroxyalkane-1,1-diphosphonic acid and individual aminopolyphosphonic acid, mixtures of each of these can be employed. However, it is the

salient feature that in all instances at least one member of group (a) and at least one of group (b) be present in mixture with each other.

The production of all these acids is accomplished according to known processes.

Very good results are obtained especially with cleansing agents which contain a mixture of readily available hydroxyethane-1,1-diphosphonic acid with aminotri-(methylphosphonic acid). The mixture, as stated, should be in weight proportions of 3:1 to 1:3. These proportions are actual limits whose extremes already exhibit a certain decrease in effectiveness. Therefore, as preferred embodiments the proportions of (a) to (b) between 3:2 and 2:3 are to be named, within which limits the most favorable results are obtained.

The concentrations in which the mixtures of hydroxyalkane-1,1-diphosphonic acid with aminopolyphosphonic acid are introduced in to the cleansing agents can vary within a wide range and lay between 0.5 and 20% by weight, calculated on the content of alkali. The addition to the alkaline cleansing agent should be calculated in such a manner that the concentration of the mixture of (a) and (b) in the aqueous solution of said alkaline cleansing is substantially 0.05-1 g./l. These values relate to the pure free acids. Both the component acids can be added to the alkaline cleansing agent as free acid or in the form of their water-soluble salts, preferably their alkali metal-, ammonium- or alkanolamine salts. Preferred are the sodium and potassium salts.

The hydroxyalkane-1,1-diphosphonic acid and the aminopolyphosphonic acid or their salts, respectively, may be incorporated in liquid or solid cleansing agents. The manner of incorporation is not critical. Solids can be added to solid cleansing agents during the mixing step; they may be sprayed thereon in concentrated solutions; or they may be slurried and added to liquid material prior to spray-drying. The phosphonic acids named and their mixtures are readily soluble and completely resistant to hydrolysis and therefore are especially suited for addition to highly alkaline cleansers and to alkaline concentrates, but also to acid concentrates to which alkali later is added to produce an alkaline cleansing agent.

The alkaline cleansing agents contain, aside from the mixture of hydroxyalkane-1,1-diphosphonic acid and aminopolyphosphonic, the commonly used alkali carriers in a concentration of 5-95 weight percent, such as caustic alkali, preferably NaOH, or KOH, alkali carbonates, preferably soda, alkali silicates, alkali phosphates, alkali borates, singly or in mixture, and, if desired or required, detergents, antifoams, bleaching agents, and disinfectants, in concentrations of 0.05 to 30 weight percent. The amount of alkali in the alkaline cleansing agents should be calculated in such a manner that the concentration of the alkaline carriers in the aqueous solution of said alkaline cleansing agents is substantially 1-50 g./l.

The cleansing agents according to the invention can be used in all cleansing and washing processes wherein a coating or calcium deposit and precipitation (stone formation) is apt to occur due to the hardness of the water employed, for instance in all kinds of washing and rinsing machines.

The cleansers according to the invention containing a mixture of hydroxyalkane-1,1-diphosphonic acid with aminopolyphosphonic acid faultlessly prevent a formation of coating or stone even with the use of very hard water, e.g., of a hardness above 30°. The effect is far better than with cleansers which contain the components (a) or (b) singly and also is superior to a purely additive effect of the single substances. Moreover, upon excessive addition of the mixture or upon concentration due to the replenishment of the cleansing solution to restore a desired alkalinity, the stone formation of coating deposit does not increase.

Because of the complete stability of the additives

against hydrolysis, no loss of effectiveness occurs upon storage, regardless whether in solid or liquid state, including highly alkaline cleansing agents, and at all temperatures of the cleansing solutions.

The hardness degrees in this specification are so-called "d.H.", i.e., degrees of German hardness, a German industrial standard, wherein 1°d.H. equals 10 mg. CaO per liter.

The invention now will be further explained by the following examples. However, it should be understood that these are given merely by way of illustration, and not of limitation, and that numerous changes may be made in the details thereof without departing from the spirit and the scope of the invention as hereinafter claimed.

Temperatures are in degrees centigrade; percentages are percent by weight; solutions are aqueous; unless otherwise specified.

EXAMPLE 1

Stainless steel sheets were immersed for 2 minutes in 1% NaOH solution at 50°, then rinsed for 2 minutes in water at room temperature, and dried for 2-3 minutes in a current of hot air. This cycle was repeated 500 times. Thereafter, the deposit (or coating) formed on the surfaces of the sheets was determined by weighing. The NaOH solution was prepared with water of 36° hardness, and increasing amounts of hydroxyethane-1,1-diphosphonic acid, aminotri-(methylphosphonic acid) and mixtures of these two acids in weight proportions of 3:1, 1:1, and 1:3, added. The rinse water also had a 36° hardness. The coating weights are listed as g./m.² in Table 1.

TABLE 1
(Deposit in g./m.²)

Additive, mg./l.	0	200	300	450	750
Hydroxyethane-1,1-diphosphonic acid (a)	55	3.3	4.1	13.1	19.7
Aminotri-(methylphosphonic acid) (b)	55	7.7	10.0	12.5	24.1
(a)+(b) 3:1	55	1.3	0.3	23.1	
(a)+(b) 1:1	55	2.0	2.0	0.8	0.6
(a)+(b) 1:3	55	5.4	4.0	1.0	

EXAMPLE 2

The test was identical to the one described in Example 1, with the sole exception that for both the NaOH solution and as rinse water, the water had a hardness of 17°. The results are found in Table 2.

TABLE 2
(Deposit in g./m.²)

Additive, mg./l.	0	75	200	300	600
Hydroxyethane-1,1-diphosphonic acid (a)	21.8	6.0	0.4	7.1	
Aminotri-(methylphosphonic acid) (b)	21.8	6.2	4.4	3.7	
(a)+(b) 1:1	21.8	3.2	0.2	0.2	0.2

EXAMPLE 3

The following cleansing agent was produced:

	Percent
NaOH	-----
Sodium silicate (Na ₂ O:SiO ₂ =3.35)	4.5
Antifoam (additive of propylene oxide on triethanolamine with 27.5 propylene oxide groups per molecule)	1.75
Tetrasodium salt of hydroxyethane-1,1-diphosphonic acid.3H ₂ O	2.5
Hexasodium salt of aminotri-(methylphosphonic acid) (4% H ₂ O)	2.25
Sodium sulfate, anhydrous	Balance

5

This cleanser was applied in commercial bottle washing machines having 2 solution zones and an hourly throughput of 10,000 units, for the cleaning of beer bottles. The concentration of the solid cleanser was 1 to 2%. The temperature of the solution was 70°. The water used had a temporary hardness of 32°.

The bottles were faultlessly clean. No calcium deposit appeared in the warm water zone even after several months.

EXAMPLE 4

The cleansing compound had the following composition:

	Percent
NaOH	30
Nonionic detergent (additive of 9 mols ethylene oxide and 10 mols propylene oxide on nonyl phenol)	0.35
70% hydroxyethane - 1,1 - diphosphonic acid solution	0.4
70% ethylene diaminotetra-(methylphosphonic acid) solution	0.6
Water and solution promoter	Balance

Mineral water bottles were cleaned in a commercial bottle washing machine. The concentration of the cleansing compound was 5 percent. The water used had a temporary hardness of 24°, and the temperature was 70-75°. The cleansing effect was excellent, and no deposit or precipitation occurred.

EXAMPLE 5

12,000 milk bottles per hour were washed in a dairy using a commercial bottle washing machine having 2 solution zones. The cleansing solution for both zones was 1.2% NaOH which had been prepared by dilution of 50% NaOH. To this NaOH solution an active concentrate, was added in a concentration of 0.1%, of the following composition:

	Percent
Hydroxyethane-1,1-diphosphonic acid	20
Aminotri-(methylphosphonic acid)	20
Nonionic antifoam (additive of ethylene oxide on polypropyleneglycol)	25
Water	Balance

The solution was brought up to strength, as required, by adding the needed quantities of NaOH and active concentrate. The water employed had a temporary hardness of 30°; the temperature of the cleansing solution was 65°. The cleaning effect was excellent, and even after a period of 10 months no deposit was noticeable.

EXAMPLE 6

Soft drink bottles were washed in a commercial bottle washing machine equipped with 3 immersion zones. For each of these zones, a 2% KOH was used, prepared by diluting a highly concentrated KOH solution. To the dilute solution an active concentrate was added in a concentration of 0.07%, composed of the following:

	Percent
Tetrapotassium salt of hydroxypropane-1,1-diphosphonic acid (5% H ₂ O)	25
Pentapotassium salt of aminotri - (isopropylphosphonic acid)	22.5
Nonionic antifoam (additive of ethylene oxide on a reaction product of propylene oxide and ethylenediamine)	15
Sodium sulfate, anhydrous	Balance

The solution was replenished with KOH and concentrate, as required. The water used had a temporary hardness of 16°; the solution temperature was 80°. The cleaning action was very satisfactory, and no stone deposit could be found in the warm water zone or in other parts of the machine after prolonged use.

6

EXAMPLE 7

A solid compound was produced having the following composition:

	Percent
NaOH	60
Trisodium phosphate, anhydrous	20
Sodium silicate (Na ₂ O:SiO ₂ =3.30)	5
Nonionic antifoam (reaction product of propylene oxide and polyglycerol with 6.6 propylene oxide groups per OH group)	2.5
Tetrasodium salt of ethylenediaminetetra-(1-ethylphosphonic acid)	1.25
Tetrasodium salt of hydroxyhexane - 1,1 - diphosphonic acid.3H ₂ O	1.25
Sodium sulfate	10

Beer-, mineral water- and soft drink bottles were washed in a commercial bottle washing machine using the above compound in a concentration of 1.5 percent at a solution temperature of 70-75°. The water used had a temporary hardness of 17°. Even after a long operational time no coating or stone deposit could be found in the machine.

EXAMPLE 8

A solid cleansing compound was prepared by jet-spraying a 70% solution each of hydroxyethane-1,1-diphosphonic acid and aminotri-(methylphosphonic acid), respectively, on the mixture of the other components of the compound. The latter had the following composition:

	Percent
Sodium pyrophosphate	35
Sodium silicate (Na ₂ O:SiO ₂ =3.35)	30
Detergent (fatty alcohol ether sulfate)	1
Hydroxyethane-1,1-diphosphonic acid	0.75
Aminotri-(methylphosphonic acid)	0.75
Soda, anhydrous	Balance

This cleanser was successfully used in commercial cleansing and washing machines without incurring coating deposits or stone formation. The application concentration depended upon the machine type and the materials to be cleaned, and generally was approximately 0.5-1%.

EXAMPLE 9

With a cleanser of the composition:

	Percent
Na ₂ B ₄ O ₇	44.5
Sodium metasilicate	50
Nonionic detergent (additive of 2 mols ethylene oxide on oleyl alcohol)	1.5
Triammonium salt of hydroxyethane-1,1-diphosphonic acid.2.5H ₂ O	2
Pentasodium salt of aminotri-(1-ethyl-phosphonic acid)	2

dissolved in a concentration of 5 g./l. in water of 16° hardness, metal parts were cleaned. The cleansing device was used for more than 6 months with weekly replenishment of the solution, without deposit or stone formation.

EXAMPLE 10

Washing agent was prepared having the following concentration:

	Percent
Sodium pyrophosphate	42
Sodium silicate	5
Sodium perborate	15
Dodecylbenzenesulfonate	8
Sodium soap (coconut fatty acids)	4
Hydroxyethane-1,1-diphosphonic acid	2.5
Aminotri-(methylphosphonic acid)	2.5
Sodium sulfate	Balance

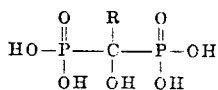
The compound was produced in the customary manner by spray-drying and adding to the slurry, prior to atomization, both phosphonic acid solutions after their neutralization with NaOH. The concentration of the solid agent upon

7

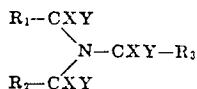
dilution for application was 5 g./l. The washing machine wherein this was used exhibited no deposit or stone formation after prolonged use. The water employed had a hardness of 19°.

I claim:

1. In the process of cleansing solid materials resistant to strongly alkaline solutions which consists essentially of contacting said solid materials with an aqueous solution containing an alkaline cleansing agent for use in hard water, said alkaline cleansing agent containing from 5% to 95% by weight of strongly alkaline alkali metal compounds selected from the group consisting of caustic alkalis, alkali metal carbonates, alkali metal silicates, alkali metal ortho phosphates, alkali metal pyrophosphates, alkali metal borates and mixtures thereof, the concentration of said strongly alkaline alkali metal compounds in said aqueous solution being from 1 to 50 g./l. and an additive to prevent calcium precipitation and thereafter rinsing said solid materials, the improvement which consists of utilizing from 0.05 to 1 g./l. of a mixture selected from the group consisting of at least one first acid with at least one second acid, and of their alkali- and ammonium-salts; said first acid having the formula



wherein R is selected from the group consisting of straight-chain and branched alkyls having 1 to 5 carbon atoms; said second acid is selected from the group consisting of ethylenediaminetetra-(1-ethylphosphonic acid), ethylenediamino-tetra-(1-methylphosphonic acid) and compounds having the formula



8

wherein X and Y individually are selected from the group consisting of hydrogen and an alkyl group having 1 to 4 carbon atoms, and R₁, R₂, and R₃ are —PO₃H₂; the first acid (a) and the second acid (b) being present in the said mixture of these said acids in weight proportions of (a) to (b) between 3:1 and 1:3, as said additive.

2. The process of claim 1, wherein said first acid and said second acid are present in the said mixture of these acids in weight proportions of (a) to (b) between 3:2 and 2:3.

3. The process of claim 1, wherein said first acid is selected from the group consisting of hydroxyethane-, hydroxypropane-, and hydroxyhexane-1, 1-diphosphonic acid.

4. The process of claim 1, wherein said second acid is selected from the group consisting of aminotri-(methylene-phosphonic acid), ethylenediaminetetra-(methylphosphonic acid), aminotri-(1-ethylphosphonic acid), ethylenediaminetetra-(1-ethylphosphonic acid), and aminotri-(isopropylphosphonic acid).

5. The process of claim 1 wherein, in said mixture of said first acid with said second acid, said first acid is hydroxyethane-1,1-diphosphonic acid and said second acid is aminotri-(methylphosphonic acid), said first acid and said second acid being present in said mixture in weight proportions of 3:2 to 2:3.

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MAYER WEINBLATT, Primary Examiner

U.S. Cl. X.R.

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