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[54] **DESCALING DETERGENT COMPOSITION**
4 Claims, No Drawings

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252/99

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[56]

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ABSTRACT: A descaling detergent composition is disclosed which includes in combination, a tetra-alkali metal pyrophosphate, an alkali metal tripolyphosphate, and a water-soluble alkali metal polyelectrolyte polymer. Articles may be effectively descaled by an aqueous solution of the present descaling detergent with greater scale removal and better hard water control than related compositions known to the art.

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DESCALING DETERGENT COMPOSITION

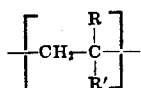
This invention relates to a descaling detergent composition which effectively removes scale composed of calcium and magnesium ions. More particularly, the present invention provides a new descaling detergent composition which includes in combination, a tetra-alkali metal pyrophosphate, an alkali metal tripolyphosphate, and a water-soluble alkali metal polyelectrolyte polymer.

It is commonly known that a solution of sequestering agents in amounts which exceed that necessary to sequester the hardness in the solvent water will not exhibit a hard water scale precipitate which adheres to vessels and articles. Articles coated with hard water scale, when placed in solutions containing such sequestering agents may be descaled to some degree. It has now been found that descaling and prevention of scale deposition takes place when the present formulations are used at concentrations which provide sequestering levels below the level at which ordinary compositions prevent hard water salt precipitates or cause only slight removal of hard water scale from articles.

Use of various polyelectrolytes in conjunction with organic detergents has been disclosed in British Pat. Nos. 451,342 and 1,073,947, and in U.S. Pat. No. 3,308,067. However, in these systems polyelectrolytes have been used in conjunction with organic soaps and detergents in substantially neutral systems where effective descaling is not required.

By the practice of the present invention, there is provided a superior descaling detergent composition which more effectively removes scale composed of calcium and magnesium ions.

Generally stated, the descaling detergent composition of this invention comprises, in combination, from about 2 to about 40 parts by weight of a tetra-alkali metal pyrophosphate; from about 5 to about 50 parts by weight of an alkali metal tripolyphosphate; and from about 0.1 to about 20 parts by weight of a water-soluble alkali metal polyelectrolyte polymer having a molecular weight of from 1,000 to 15,000,000 and having repeated groups with the formula:



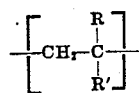
wherein R is either hydrogen or a methyl radical, and R' is selected from the group consisting of amide radical, carboxyl radical and salts thereof. The present polymer composition may be combined with up to about 99 parts by weight for water use as a liquid although it is desirably prepared as a dry solid.

The tetra-alkali metal pyrophosphate component of the present invention may include an alkali metal such as sodium or potassium. The preferred condensed phosphate, however, is tetra sodium pyrophosphate. The tetra-alkali metal pyrophosphate is added in an amount from about 2 to about 40 parts by weight, and preferably in an amount from about 5 to about 30 parts by weight.

The alkali metal tripolyphosphate component of the present invention may include most any alkali metal with sodium tripolyphosphate being preferred. The alkali metal tripolyphosphate is generally added in an amount from about 5 to about 50 parts by weight and preferably in an amount from about 10 to about 40 parts by weight. The alkali metal tripolyphosphate may be replaced, in part by up to about 10 percent by weight, with alkali metal phosphates such as sodium hexametaphosphate, sodium trimetaphosphate, or the like. Materials such as nitrilotriacetic acid trisodium salt, and the like may also be included as replacement ingredients if desired.

The water soluble organic polymer of the present invention is generally a polyacrylate component having a molecular weight in the range from about 1,000 to about 15,000,000 and having repeated groups with the formula

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wherein R is either hydrogen or a methyl radical, and R' is either an amide or carboxyl radical and salts thereof. The water soluble organic polymer is included in an amount from about 0.1 to about 20 parts by weight, and preferably in an amount from about 1 to about 10 parts by weight on an anhydrous basis.

Particularly suitable water soluble alkali metal polyelectrolyte polymers for use in this invention are those derived from acrylic or methacrylic acid. These materials include, for example, acrylic acid and the alkali metal and ammonium salts thereof; methacrylic acid and the alkali metal and ammonium salts thereof; acrylamide, methacrylamide, the N-alkyl substituted amides; the N-aminoalkylamides, and the corresponding N-alkyl-aminoalkyl substituted amides; the aminoalkyl acrylates; the aminoalkyl methacrylamides; and the N-alkyl substituted aminoalkyl esters of either acrylic or methacrylic acids. These polymeric compositions may be homopolymers or they may be copolymers with other copolymerizing monomers, such as ethylene, propylene, isobutylene, styrene, *a*-methylstyrene, vinyl acetate, vinyl formate, alkyl ether, acrylonitrile, methacrylonitrile, vinyl chloride, vinylidene chloride, the alkyl acrylates, the alkyl methacrylates, the alkyl maleates, and the alkyl fumarites, and other olefinic monomers copolymerizable therewith. The copolymers of this type, having at least 50 mole percent of the acrylic or methacrylic acid derivatives, are preferred, and especially when the comonomer is hydrophobic or has no ionizable groups. Polymers of this type may be prepared directly by the polymerization of suitable monomers, or by the after-chemical reaction of other polymers such as for example by the hydrolysis of acrylonitrile or methacrylonitrile polymers.

The hydrophilic polymer of polyelectrolyte polymers suitable for the practice of this invention may be prepared directly by the polymerization of one or more of the various available organic monomers with aliphatic unsaturation, if the said compounds contain a hydrophilic group, for example, carboxyl groups. Generally, more types of polyelectrolyte polymers may be prepared by subsequent reactions of polymers and copolymers. For example, polymers containing nitrile groups may be hydrolyzed to form water-soluble amide and carboxy containing polymers or hydrogenated to form amine-containing polymers. Similarly, copolymers of maleic anhydride and vinyl acetate may be hydrolyzed to form polymers containing hydrophilic lactone rings. Other hydrophilic polymers may be prepared by hydrolysis of the copolymers of vinyl acetate wherein the acetyl groups are removed leaving hydroxy groups which promote the solubilization effect of polyelectrolyte groups present. By other reactions non-hydrophilic polymers may be converted into lactam or amide containing polymers which are more hydrophilic. Polyvinyl alcohol, not in itself a polyelectrolyte, may be converted into polyelectrolyte by esterification with dibasic acids, one of said carboxylic acid groups reacting with the alcohol radical and the other providing the hydrophilic characteristics by a carboxy group on the side chain. Still other types of polymers may be prepared by reacting halogen containing polymers, for example, the polymers or copolymers of vinyl chloroacetate or vinyl chloroethyl ether, with amines to form amine salt radicals and quaternary ammonium radicals whereby hydrophilic characteristics are introduced into what otherwise would be an insoluble polymer. Other soluble polymers may be prepared by ammonolysis of ketone containing polymers, for example, polyvinyl methyl ketone. Similarly active halogen atoms may be reacted with bisulfite to substitute sulfonic acid groups for the reactive halogens.

Thus, the various polyelectrolytes of the types described above are ethylenic polymers having numerous side chains distributed along a substantially linear continuous carbon

atom molecule. The side chains may be hydrocarbon groups, carboxylic acid groups or derivatives thereof, sulfonic acid groups or derivatives thereof, phosphoric acid or derivatives thereof, heterocyclic nitrogen groups, aminoalkyl groups, alkoxy radicals and other organic groups, the number of which groups and the relative proportions of hydrophilic and hydrophobic groups being such as to provide a water-soluble polymeric compound having a substantially large number of ionizable radicals. The length of the said continuous carbon chain must be such as to provide compounds having a weight average molecular weight of at least 1,000.

Among the various polymers as described above and water-soluble salts thereof useful in the practice of the present invention, there may be mentioned hydrolyzed polyacrylonitrile and polyacrylamide, sulfonated polystyrene, acrylamide-acrylic acid copolymers, polyacrylic acid, one-half calcium salt of hydrolyzed 1:1 copolymer of vinyl acetate-maleic anhydride, hydrolyzed styrene-maleic anhydride copolymer, ammonium polyacrylate, sodium polyacrylate, ammonium polymethacrylate, sodium polymethacrylate, diethanolammonium polyacrylate, guanidinium polyacrylate, dimethylaminoethyl polymethacrylate, acrylamideacrylonitrile copolymer, methacrylic acid-dimethylaminoethyl methacrylate copolymer, sodium polyacrylate-vinyl alcohol copolymer, hydrolyzed methacrylic acid-acrylonitrile copolymer, vinyl acetate-maleic anhydride copolymer, vinyl formate-maleic anhydride copolymer, vinyl methyl ether-maleic anhydride copolymer, isobutylene-maleic anhydride copolymer, styrene-maleic anhydride copolymer, ethyl acrylate-maleic anhydride copolymer, vinyl chloride-maleic anhydride copolymer, hydrolyzed acrylonitrile vinyl acetate copolymer, hydrolyzed acrylonitrile-methacrylonitrile copolymer, hydrolyzed acrylonitrile-methacrylonitrile-vinyl acetate terpolymer, hydrolyzed acrylonitrile-methacrylic acid copolymer, vinyl pyridine-acrylonitrile copolymer, etc. Polymers containing cation-active groups also are useful. Suitable compounds are, for example, ethyl acrylate and acrylamidopropyl-benzyl-dimethyl-ammonium chloride, copolymers of methyloacrylamide and acrylamidopropylbenzyl-dimethylammonium chloride, copolymers of butadiene and 2-vinyl pyridine, and certain quaternary compounds such as polydimethylamino-styrene quaternized with benzyl chloride, allyl chloride, etc. and quaternized copolymers of vinyl alcohol and morpholinylethylvinylether and the like.

The preferred polymers are polyacrylic acid, polymethacrylic acid, polyacrylamide, polymethacrylamide, hydrolysis products of the polyamides, or water-soluble salts thereof having a molecular weight of from 1,000 to 200,000 calculated as polyacrylic acid.

Desirably, the present descaling detergent composition further includes an alkali metal metasilicate such as sodium anhydrous metasilicate. This material may, however, be replaced in part with sodium metasilicate $5H_2O$. Stronger alkaline materials such as sodium or potassium hydroxide, or sodium or potassium orthophosphates may be substituted to a limited extent for some of the metasilicate if desired. These alkaline materials individually or in combination may be used to replace from about 1 to about 50 weight percent of the alkali metal metasilicate.

The alkali metal metasilicate component of the present invention may include most any alkali metal although sodium metasilicate is preferred. The alkali metal metasilicate is generally added in an amount from about 2 to about 40 parts by weight although an amount of about 5 to about 30 parts by weight is preferred.

An alkali metal salt is desirably included in the present composition to serve as a filler. Examples of useful alkali metal salt fillers include sodium chloride, sodium sulfate, and the like. These fillers may be added to the present composition in an amount from about 10 to about 70 parts by weight, and desirably from about 20 to about 60 parts by weight.

Alkali metal chlorine release agents may also be included in the present composition if desired. Examples of such release

agents include potassium dichloroisocyanurate, sodium dichloroisocyanurate, and the like. These agents may be added in an amount up to about 5 parts by weight, and desirably in an amount of about 1 to about 4 parts by weight.

The composition of this invention may be stored and used as either a dry mixture of the above ingredients or a concentrated solution with from about 20 to about 80 percent water. Preferably, liquid concentrates of this composition may contain from about 40 to about 60 percent water.

A preferred descaling detergent composition of this invention is as follows:

Ingredient	Preferred Parts by Weight
Sodium chloride	20-60
Tetra-sodium pyrophosphate	5-30
Sodium tripolyphosphate	10-40
Polyacrylate (25% Solution)	1-10
Sodium anhydrous metasilicate	5-30
Potassium dichloroisocyanurate	1-4

Although any technique may be used for applying the aqueous solution of the present composition to fouled surfaces, it is highly effective when used with spray washing equipment. Highly effective descaling is obtained with this composition. After the step of the cleaning, the articles are rinsed with water, and dried.

This invention is further illustrated by the following specific but nonlimiting examples. Example I-IV

In order to show the improved results obtained with the descaling detergent composition of the present invention, the following compositions were prepared and tested as subsequently indicated:

Ingredients	Examples (Parts by Weight)			
	I	II	III	IV
Sodium chloride	40.9	22.2	45.9	23.2
Sodium tripolyphosphate	31.6	20.3	31.6	20.3
Tetrasodium pyrophosphate	20.0	30.0	20.0	30.0
Sodium anhydrous metasilicate	20.0	20.0	20.0	20.0
Potassium dichloroisocyanurate	2.5	2.5	2.5	2.5
Sodium polyacrylate (Avr. M.W. 90,000)	5.0	5.0		
Calculated water hardness tolerance at 0.3% concentration ± 5 mg. $CaCO_3$	223 mg/g	223 mg/g	223 mg/g	223 mg/g
Hardness of water in test solution as $CaCO_3$	$CaCO_3$	$CaCO_3$	$CaCO_3$	$CaCO_3$
	257 mg	257 mg	257 mg	257 mg

To test the various formulas the following procedure was used:

A. FORMATION OF HARD WATER SCALE

Scale from Cincinnati Tap Water

To produce a scale on water glasses, 10 oz. heat-treated water tumblers were filled two-thirds full with Cincinnati tap water and placed in an oven at a temperature of 105° C. until the water was evaporated. A heavy, tenacious scale resulted which consists of the total dissolved solids of 175 ml. of water having a hardness of 140 p.p.m. as calcium carbonate, and a total dissolved solids of 270 p.p.m. The ratio of calcium to magnesium ion was 6.4 calcium to 1 magnesium.

All Calcium Scale

It is common practice in the trade to formulate products with contain some quantity of tetrasodium or potassium pyrophosphate expressly for the purpose of sequestering magnesium cations due to the fact that it is more efficient for this purpose than other types of sequestering agents. Conversely, pyrophosphate is not as efficient a calcium chelating agent as others commonly used. Thus, in order to prove the synergism between pyrophosphate and polyelectrolyte, scale was produced on glasses consisting of all calcium and no magnesium.

The scale was produced by adding to each liter of distilled water 250 milligrams of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 170mg. of sodium bicarbonate. During the evaporation process described above the calcium bicarbonate breaks down to form the scale of calcium carbonate on the glass and is left when the water evaporates.

B. TEST PROCEDURE

To test the scale removal properties of the various compositions under conditions close to actual operating conditions, a closely controlled device was built which employs a 4 liter reservoir held at a temperature of $150^\circ \pm 2^\circ \text{F}$. From this reservoir the test solution is pumped through a single spray nozzle which is directed into the interior of the test glass which is clamped in an inverted position directly over the spray. The solution is collected and recirculated. The duration of the test is 15 minutes of spray followed by a 15 second rinse.

The test compositions all have a water hardness tolerance of 223 milligrams of calcium carbonate when used at a concentration of 0.3 percent. The compositions were tested first by making solutions in tap water having a hardness of 15 grains per gallon (256.5 mg. CaCO_3) and testing for descaling properties on glasses having the combined scale of calcium and magnesium from the evaporated tap water.

The same compositions were tested for descaling properties on the glasses having an all calcium scale by making the cleaning solution in 15 grain synthetic hard water by adding calcium acetate to distilled water.

The following results were noted:

Event	Examples			
	I	II	III	IV
*% scale removed in the tap water system on glasses scaled with tap water	80%	90%	70%	60%
*% scale removed in the all calcium hard water on glasses having all calcium scale	40%	55%	50%	45%
Appearance of solution	Clear	Clear	Turbid	Turbid

*Evaluation of % scale removed is a visual comparison against an untested scaled glass.

It is apparent from the above results, that the composition containing the combination of sodium tripolyphosphate, tetrasodium pyrophosphate and polyelectrolyte gives superior

scale removal properties and obviously better hard water control than the other compositions tested in the tap water system. Superior results are normally expected from the composition having the all higher percentage of sodium tripolyphosphate in the calcium system. This is the case in sample III versus sample IV where no polyelectrolyte is present. However, in the case of sample II as compared to sample IV, the presence of polyelectrolyte effects a greater scale removal. This presence causes results superior to those obtained by sample III which ordinarily should out perform it in all calcium system due to its higher tripolyphosphate content. This effect is attributed to a synergism between the tetrasodium pyrophosphate, the polyelectrolyte, and the sodium tripolyphosphate.

The compositions of the present invention have application to descaling and water conditioning and may be extended to form laundry detergents, machine dish washing detergents, soaker tank detergents, spray waster detergents, cleaning in-place detergents, or the like including other areas of detergentcy where water conditioning and the prevention of scale deposits and their removal are a consideration.

It is understood that the foregoing detailed description is given merely by way of illustration and that many variations may be made therein without departing from the spirit of this invention.

What is claimed is:

1. A descaling detergent composition which comprises in combination:
 - a. from about 5 to about 30 parts by weight of a tetra-alkali metal pyrophosphate, said alkali metal selected from the group consisting of sodium and potassium;
 - b. from about 10 to about 40 parts by weight of sodium tripolyphosphate;
 - c. from about 1 to about 10 parts by weight of a water-soluble polymer having a molecular weight of from 1,000 to 200,000 and selected from the group consisting of polyacrylic acid, polymethacrylic acid, polyacrylamide, polymethacrylamide, hydrolyzed polyacrylamide, hydrolyzed polymethacrylamide, and water-soluble salts thereof;
 - d. from about 20 to about 60 parts by weight of a member of the group consisting of sodium chloride and sodium sulfate;
 - e. from about 5 to about 30 parts by weight of sodium metasilicate; and
 - f. from about 1 to about 4 parts by weight of a chlorine release agent selected from the group consisting of sodium dichloroisocyanurate and potassium dichloroisocyanurate.
2. The composition of claim 1 combined with from about 20 to about 80 percent by weight water.
3. The composition of claim 1 combined with from about 40 to about 60 percent by weight water.
4. A descaling detergent composition which comprises about 20 to 60 parts by weight sodium chloride, about 5 to 30 parts by weight tetra-sodium pyrophosphate, about 10 to 40 parts by weight sodium tripolyphosphate, about 1 to 10 parts by weight sodium polyacrylate, about 5 to 30 parts by weight sodium anhydrous metasilicate, and about 1 to 4 parts by weight potassium dichloroisocyanurate.

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