

**United States Patent**[11] **3,627,686**

- [72] Inventors **Philip M. Sabatelli**  
Cincinnati, Ohio;  
**Charles A. Brungs**, Ft. Wright, Ky.; **Edwin**  
**R. Loder**, Cincinnati, Ohio; **Carmen R.**  
**Sarge**, Ft. Thomas, Ky.
- [21] Appl. No. **763,917**  
[22] Filed **Sept. 30, 1968**  
[45] Patented **Dec. 14, 1971**  
[73] Assignee **Chemed Corporation**

- [54] **MACHINE DISHWASHING COMPOSITIONS**  
**CONTAINING SODIUM POLYACRYLATE AND**  
**NTA**  
**3 Claims, No Drawings**

- [52] U.S. Cl. .... 252/527,  
252/89, 252/99, 252/135  
[51] Int. Cl. .... C11d 7/16,  
C11d 7/26, C11d 7/32  
[50] Field of Search ..... 252/89, 99,  
137, 135, 110

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*Primary Examiner*—Leon D. Rosdol

*Assistant Examiner*—Dennis L. Albrecht

*Attorneys*—Eugene M. Bond and Kenneth E. Prince

**ABSTRACT:** A machine dishwashing composition is disclosed which includes the combination of a chelating agent and a water-soluble polymer as detergent builders and specifically the combination of a water-soluble organic alkaline salt of nitrilotriacetic acid, and a water-soluble polyacrylate. Cooking and eating utensils may be cleaned by a low-foaming aqueous solution of the present machine dishwashing composition with less spotting and greater clarity. The present composition is particularly useful for sequestering hard water salts and for extending the normal water-softening capacity of machine dishwashing compositions.

# MACHINE DISHWASHING COMPOSITIONS CONTAINING SODIUM POLYACRYLATE AND NTA

This invention relates to a dishwashing composition and a method for using same which effectively removes food soils from glassware, dishes and the like with less spotting and greater clarity. More particularly, the present invention provides a new dishwashing composition which includes a chelating agent and a water-soluble polymer desirably in combination as detergent builders and specifically the use of a water-soluble organic alkaline salt of nitrilotriacetic acid, and a water-soluble polyacrylate desirably in combination. The invention is based on the discovery of unexpected and remarkable synergistic builder action obtained with the present novel builder compositions.

The general concept of built detergent compositions has been known for sometime. This concept envisages the capability possessed by certain substances for substantially improving the effectiveness of detergent compounds. The improved or enhanced result, as evidenced by the washed articles appearing generally cleaner, is characterized as the builder effect and compounds which perform in this manner are generally referred to as builders.

The effect of any given detergent composition when used in solution to perform a washing operation will vary with such factors as concentration, temperature, the nature of the soil, the nature of the active detergent ingredient, the amount of active ingredient in the solution, the ratio of builder to active ingredient, the hardness of the water and the like. It is sometimes observed that a detergent compound which itself has a low-detergency value may appear to be helped more by a given quantity of a given builder than a detergent which has superior detergent detergentive properties.

The nature of the building action, while quite widely recognized in the prior art is not fully understood. There does appear to be some connection between the ability of a builder to soften the water which is used to make up the washing solution, and the improved results in detergency obtained when the builder is used. However, not all materials which act to sequester hardness-imparting calcium and magnesium ions perform satisfactorily as builders. Further, useful building actions with the most effective builders can be noted both above and below the point at which the builder is present in the washing solution in stoichiometric proportions to the hardness in water.

Building effects have been noted in connection with various inorganic alkaline salts such as alkali metal carbonates, bicarbonates, phosphates, polyphosphates and silicate. Similar building properties have also hitherto been noted in connection with certain organic salts such as alkali metal, ammonium or substituted ammonium aminopolycarboxylates, e.g., sodium and potassium ethyl enediaminetetraacetate, sodium and potassium N-(2-hydroxyethyl)-ethylene-diamine-triacetate, sodium and potassium nitrilotriacetate and sodium, potassium and triethanolammonium-N-(2-hydroxyethyl)-nitrilotriacetate. Alkali metal salts of phytic acid have also been used as organic builders.

Sodium tripolyphosphate is commonly used as a low-priced builder in cleaning compounds to assist the detergency action and to inactivate the hardness of the water in which the cleaner is used.

Heretofore, alkaline solutions have been used in institutional and household dishwashing machines for washing dishware, glasses, and other cooking and eating utensils. Ordinary tapwater is customarily used with the cleaning composition to form a cleaning solution and for rinsing purposes subsequent to the cleaning operation. As is well-known, spotting on dishes and glassware by inorganic salt residues and precipitates may be a major problem. Deposit formation may also interfere with the operation of the washing equipment by requiring frequent maintenance.

Detergent compositions containing nitrilotriacetates have been disclosed in U.S. Pat. No. 3,324,038 and Canadian Pat. No. 755,588. However, these compositions contain

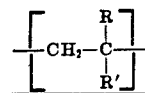
nitriloacetates as cleaning promoters for soaps and organic detergents in substantially neutral systems where foaming is desirable. Prior to this invention, the utility of nitrilotriacetates in alkaline, low-foaming dishwashing compositions was not known.

Use of various polyelectrolytes in conjunction with organic detergents has been disclosed in British specification 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 foaming is desirable. Thus, these patents do not provide alkaline, low-foaming detergent systems.

According to the present invention, an unexpected and synergistic building action is displayed, by builder mix-containing a water-soluble organic alkaline salt of nitrilotriacetic acid in combination with a water-soluble polyacrylate.

By the practice of the present invention, there is provided a superior machine dishwashing composition which more effectively removes food soils and residues from eating and cooking utensils such as dishes, glassware and the like with decreased spotting and greater clarity of the glassware and dishes.

Generally stated, the machine dishwashing composition of this invention comprises from about 20 to about 60 parts by weight of an alkali metal carbonate; from about 2 to about 20 parts by weight of a tetra-alkali metal pyrophosphate; from about 1 to about 20 parts by weight of an alkali metal nitrilotriacetate; from about 0.1 to about 10 parts by weight, dry basis, of a water-soluble 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; and from about 20 to about 60 parts by weight alkali metal metasilicate. The composition may be combined with up to about 99 parts by weight of water for use as a liquid although it is desirably prepared as a dry solid. The composition may also be made into any of the several commercially desirable composition forms, for example, granules, flake and tablet forms.

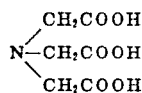
The process of the present invention for washing dishes and other eating and cooking utensils involves the steps of, applying an aqueous solution of about 0.02 to about 1 weight percent based on the weight of dry solid components of the dishwashing composition of the present invention while at a solution temperature of about 140° F. to about 200° F., and preferably about 140° F. to about 160° F. to the surface of an article to be cleaned, subsequently rinsing the articles free of cleaning solution with water, and allowing the rinsed article to dry.

The alkali metal carbonate forming an alkaline component of the present dishwashing composition may be sodium carbonate, potassium carbonate, or mixtures thereof in an amount from about 20 to about 60 parts by weight, and preferably in an amount from about 30 to about 50 parts by weight. Stronger alkaline materials such as sodium or potassium orthophosphates may be substituted to a limited extent for some of the carbonate if desired. Sodium tripolyphosphate may also be included 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 carbonate. Preferably, however, sodium carbonate is used as the alkaline component.

The tetra-alkali metal pyrophosphate component of the present invention may include any 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 20 parts by weight, and preferably in an amount from about 2 to about 10 parts by weight.

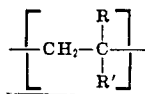
Water-soluble alkaline salts of nitrilotraicetic acid useful herein have the formula



wherein a suitable cation is substituted for the acidic hydrogens in the above formula, the cation being sodium. The trisodium salt of nitrilotriacetic acid is used, referred to in the following description of Na<sub>3</sub>NTA or more broadly as NTA.

The addition of a combination of NTA and partially hydrolyzed polyacrylate acts like a polyphosphate in cleaning compounds. The combination shows both chelating and threshold effects, resulting in prevention of scum deposition due to hardness in the water at economic threshold levels. The alkali metal nitrilotriacetic acid component is generally added in an amount from about 5 to about 25 parts by weight and preferably in an amount from about 5 to about 15 parts by weight.

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



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 10 parts by weight, and preferably in an amount from about 1 to about 8 parts by weight on an anhydrous basis.

Particularly suitable water-soluble organic polymers for use in this invention are polyelectrolyte polymers such as 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-alkylaminoalkyl 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, α-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 afterchemical reaction of other polymers, for example by the hydrolysis of acrylonitrile or methacrylonitrile polymers.

In connection with the various types of polyelectrolyte polymers suitable for the practice of this invention, the hydrophilic polymer 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 can 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 can be prepared by the hydrolysis of 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 nonhydrophilic 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 can be prepared by the amonoanalysis 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, diethylaminoethyl polymethacrylate, acrylamideacrylonitrile copolymer, methacrylic acid-dimethylaminoethyl methacrylate copolymer, sodium polyacrylate-vinyl alcohol copolymer, hydrolyzed methacrylic acid-acrylonitrile copolymer, vinyl acetate-maleic anhydride copolymer, vinyl formatemaleic 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 methyoacrylamide and acrylamidopropylbenzyl-dimethylammonium chloride, copolymers of butadiene and 2-vinyl pyridine, and certain quaternary compounds such as

polydimethylaminostyrene 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 the polyamides, or water-soluble salts thereof having a molecular weight of from 1,000 to 200,000 calculated as polyacrylic acid.

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 20 to about 60 parts by weight although an amount of about 40 to about 50 parts by weight is preferred.

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 dishwashing composition may contain from about 30 to about 60 percent water.

A preferred machine dishwashing composition of this invention is shown below:

	Parts by Weight
Sodium carbonate	44
Tetra-sodium pyrophosphate	4
Nitrilotriacetate trisodium salt	13
Polyacrylate (25% solution)	5
Sodium metasilicate	34

In the process of this invention, an aqueous solution containing from about 0.05 to about 1 and preferably from about 0.05 to about 0.5 weight percent of the above dishwashing composition is prepared having a temperature of from about 140° F. to about 200° F., and preferably from about 140° F. to about 160° F. This cleaning solution is applied to the surfaces of articles to be cleaned. Although any technique can be used for applying the aqueous solution of the dishwashing composition to the fouled surfaces, it is specifically designed for and is highly effective when used with spray washing equipment of the type conventionally used in cleaning cooking and eating utensils. Highly effective cleaning with low foaming is obtained in institutional dishwashing machines with this composition. After the step of the cleaning, the articles are rinsed with water, and allowed to dry.

The unique alkaline dishwashing composition of this invention is highly effective in removing food soils and residues from dishes, glassware, and other cooking and eating utensils in conventional dishwashing machines. Not only are the food residues more effectively removed with the present composition, but also the cleaned dishes and glassware exhibit less spotting and greater clarity than with conventional cleaning compositions.

This invention is further illustrated by the following specific but nonlimiting examples.

#### EXAMPLE 1

This example shows the improved results obtained with a machine dishwashing composition containing sodium polyacrylate, compared with the same composition without the polyacrylate. The washing compositions used in this test are as follows:

Ingredients	Parts by Weight			
	Control	Samples		III
		I	II	
Sodium carbonate	44	44	44	44
Sodium metasilicate 5H <sub>2</sub> O	39	29.4	39	29.4
Sodium hexametaphosphate	13	13	—	—
Tetra-sodium pyrophosphate	4	4	4	4
Polyacrylate (ave. M.W. 93,000) (25% solution)	—	9.6	—	9.6
Nitrilotriacetate acid trisodium salt	—	—	13	13

Squares of plate glass 4 inches on each edge were soiled with 1 gram of a soil containing 50 parts peanut butter, 25 parts hydrogenated vegetable oil, and 25 parts butter. A Hobart A.M. dishwashing machine was used for the test, the machine having a 48 second wash cycle and a 12 second rinse cycle. No rinse additive was used. The wash water contained 0.3 percent of the dishwashing composition and had a temperature of 150° F. in the wash section. The rinse water had a temperature of 180° F. The water used was Cincinnati tap-water having a hardness of 161.5 p.p.m. In the test a set of 10 plates of glass were run through eight cycles in the machine with a drying period of 15 minutes allowed between cycles.

Comparing plates cleaned with the Control and Sample I-III compositions, the plates tested with the preferred composition of this invention (Sample III) were clearer and less streaked in appearance, and the unspotted areas were brighter than on the plates washed with the Control. The plates tested with Sample II were clearer and less streaked in appearance than Sample I plates while both of this series of plates proved cleaner and brighter than plates washed with the Control.

A grid 1 inch × 1 inch scored into 100 equal parts was applied to the center of each of the 10 glass plates. The percent area covered by spots, streaks, or film is determined by counting the number of squares thus effected.

The standard product exhibited a coverage of 85.6 percent of the grid surface covered by spots, streaks, or film while that of Samples I-III exhibited a coverage of 84.3, 78.4 and 65.3 percent of the grid area respectfully.

To demonstrate the ability of the compositions to condition hard water, the composition of the present invention was compared to a conventional dishwashing composition.

Each of the compositions was diluted to a 0.3 percent solution in 15 grain hard water and transferred to a 27 mm. × 275 mm. glass cylinder. The solutions were allowed to stand for 20 hours and exhibited varying degrees of hard water precipitate as exemplified by the depth of floc in the bottom of the cylinder.

Composition	mm. of floc after 20 hours
Control	21 mm.
Sample I	9 mm.
Sample II	11 mm.
Sample III	4 mm.

The tests showed that the composition of the invention has greater hard water conditioning power than conventional dishwashing compositions and also a greater cleaning power.

The tests proved improved water conditioning when using polyacrylate in conjunction with hexametaphosphate or by replacing hexametaphosphate with nitrilotriacetic acid trisodium salt or a combination of NTA and polyacrylate.

The compound with a combination of nitrilotriacetic acid trisodium salt and polyacrylate exhibits greater water softening ability and hard water salt suspension than either compound which employs them singly as aids for this purpose.

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 low-foaming machine dishwashing composition consisting essentially of:

- 44 parts by weight of sodium carbonate;
  - 29.4 parts by weight of sodium ~~average~~ *META SILICATE* 5H<sub>2</sub>O;
  - 4 parts by weight of tetra-sodium pyrophosphate;
  - 9.6 parts by weight of 25 percent aqueous solution of a sodium polyacrylate having an average molecular weight of 93,000; and
  - 13 parts by weight of trisodium nitrilotriacetate.
2. The dishwashing composition of claim 1 combined with from about 20 to about 80 percent by weight water.
3. The dishwashing composition of claim 1 combined with from about 30 to about 60 percent by weight water.

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