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[54] MACHINE DISHWASHING DETERGENT  
HAVING A REDUCED CONDENSED  
PHOSPHATE CONTENT

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252/DIG. 11, 103

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[57] ABSTRACT

Machine dishwashing detergents having a low condensed phosphate content and characterized by the presence therein of a metallic salt of citric acid (e.g. sodium citrate). An alkaline machine dishwashing detergent (e.g. pH at 1% concentration above 10.5) containing less than 30 weight percent on a dry basis of sodium tripolyphosphate and at least 5 weight percent of an alkali metal citrate.

21 Claims, No Drawings

## MACHINE DISHWASHING DETERGENT HAVING A REDUCED CONDENSED PHOSPHATE CONTENT

### CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of our application Ser. No. 70,528 filed Sept. 8, 1970, which was copending with this application and is now abandoned.

### BACKGROUND OF THE INVENTION

Machine dishwashing detergents constitute a generally recognized class of detergent compositions. Machine dishwashing detergents are mixtures of ingredients whose purpose, in combination, is to emulsify and remove food soils, to inhibit the foam caused by certain food soils, to promote the wetting of dinnerware to thereby minimize or eliminate visually observable spotting, to remove stains such as those caused by coffee and tea, to prevent a buildup of soil films on dinnerware surfaces, to reduce or eliminate tarnishing of flatware, and to destroy bacteria. Additionally, machine dishwashing detergents must possess these characteristics without substantially etching or corroding or otherwise damaging the surfaces of dinnerware and flatware.

Machine dishwashing detergents are often highly alkaline (a pH above 10.0 and frequently above 12.5 at concentrations of 1 weight % in water). Machine dishwashing detergents are often formulated by mixing or otherwise combining alkaline detergent salts and alkaline condensed phosphate salts. Frequently, chlorine releasing agents and low-foaming or non-foaming organic surface active agents (e.g. nonionic surfactants) are optionally and preferably included in such compositions.

In recent years, increasing attention has been focused upon environmental pollution problems (e.g. water pollution). Phosphates have been identified as a contributing factor to water pollution (e.g. by promoting the growth of algae) and considerable effort has been devoted to attempts at replacing all or at least some significant part of the alkaline condensed phosphates used in machine dishwashing detergents with chemicals that are more ecologically acceptable. Of the numerous compounds that have been tested as substitutes for alkaline condensed phosphates (particularly as substitutes for sodium tripolyphosphate), very few chemicals have given promising results. Many chemicals lack the desired cleansing ability. Other chemicals lack a threshold effect, i.e. the ability to sequester hard water metal ions beyond their stoichiometric presence (contrary to sodium tripolyphosphate which has such an ability). Still others create foam problems and still others are as much or more ecologically undesirable as the alkaline condensed phosphates.

Among the many chemicals tested for use as a substitute for sodium tripolyphosphate, nitrilo triacetic acid appears to be one of the most promising candidates. However, one disadvantageous effect of nitrilo triacetic acid (often call "NTA") is its tendency to de-stabilize chlorine in use solutions of machine dishwashing detergents. Other disadvantages of NTA at the present time include cost, lack of general availability, and lack of a threshold effect.

### SUMMARY OF THE INVENTION

The present invention is based upon the discovery that metallic salts of citric acid (e.g. sodium citrate) are effective partial substitutes for alkaline condensed

phosphates in machine dishwashing detergents. The use of citrates in combination with reduced amounts of alkaline condensed phosphates (e.g. reduced amounts of sodium tripolyphosphate) produces dishwashing results that are commercially acceptable by today's industrial and home standards. By retaining some alkaline condensed phosphate in the detergent, effective sequestration and deflocculation of hard water metal ions can be obtained. Additionally, the citrates are very stable in the presence of chlorine releasing agents (e.g. potassium di-chloroisocyanurate).

### DETAILED DISCUSSION

Machine dishwashing detergents of the present invention can be formulated as a solid detergent or as single or multiple package liquid detergents.

Solid or dry detergents can be formed by blending together the various detergent-forming ingredients to form a powdered or granular product, or they can be agglomerated, pelletized or the like.

Multiple package liquid detergents are those machine dishwashing detergents which are formulated into two or more separate liquid components, each component being packaged separately. In the dishwashing operation, the separate components are dispensed from their separate containers into the dishwashing tank by suitable dispensing apparatus.

Although the present invention can be applied to or embodied in any of these various types of machine dishwashing detergents, its greatest advantage is associated with the production of solid detergent compositions and single package liquid detergent compositions. Of these, the formulation and use of solid machine dishwashing detergents is of particular significance.

The machine dishwashing detergent compositions of the present invention will normally contain at least one alkaline detergent salt other than an alkaline condensed phosphate salt, at least one alkaline condensed phosphate salt, at least one citrate, and, optionally, a chlorine releasing agent and various surfactants. If desired, other ingredients can be included in the detergent compositions of the present invention.

The pH of these machine dishwashing detergents will normally be at least 10.0 and generally not above about 12.8 at a concentration of 1 weight percent in water. The effectiveness of the present compositions at these high pH's is unexpected since alkali metal citrates are not normally used to sequester calcium, magnesium, or ferric ions in alkaline aqueous media having a pH above 9. When the present compositions are to be used for institutional machine dishwashing, they will generally be used to form an alkaline wash water with a pH which is not in excess of 12.8, and a pH of 11.0-12.7 is ordinarily adequate for such institutional use. For home machine dishwashing use, a pH range of 10.0-11.0 for the wash water, particularly 10.0-10.5 is preferable. These pH values can be obtained by calculating the negative of the logarithm of the hydroxyl ion concentration but are preferably determined by pH measuring instruments which can accurately determine the negative of the logarithm of the hydroxyl ion activity, e.g. Corning Model 12, Research pH meter, with Beckman 39099 E-3 glass electrode (0°-100°C., pH 0-14 range) and matched calomel reference electrode. Additionally, nomographs can be used for sodium ion error correction.

A sufficient amount of the dry or liquid detergents formulations of this invention should be used to provide wash water containing at least 0.1 percent by weight of detergent solids in water. It is preferred that the wash water contain these solids in stable aqueous solution. In liquid machine dishwashing detergent compositions of this invention, the condensed alkali metal phosphate content is preferably near the lower end of the ranges defined herein for greater water solubility and hydrolytic stability of the liquid composition. It is permissible and even preferred for these liquid detergent compositions to contain an aqueous diluting medium which acts as a solvating phase rather than the continuous phase of an emulsion or dispersion. In solid detergent formulations of this invention, the ingredients and/or their proportions are selected for good water solubility so as to permit at least one part by weight of the solid formulation to be totally dissolved in 99 (and preferably no more than 1,000, typically no more than 500) parts by weight of water.

In use, the amount of liquid or solid detergent composition added to the wash water will preferably be limited so that the dissolved solids of the composition do not exceed 1 percent by weight of the wash water, the preferred concentration in the wash water being 0.25–0.75 weight percent. Concentrations of less than 0.5 percent by weight are typically sufficient for good machine dishwashing.

The solid, high pH detergent compositions of this invention (e.g. for institutional use) typically contain fairly substantial amounts of sodium carbonate and caustic soda (sodium hydroxide) or other alkali metal hydroxides, e.g. KOH. However, the amount of caustic soda should preferably not exceed about 20 or 30 percent by weight so that the wash water will contain only a fraction of 1 percent by weight of caustic and will exhibit a pH measurement less than 12.8. The lower pH formulations of this invention typically contain a metasilicate as a non-sequestering builder salt, the same or smaller amounts of caustic, and a relatively small amount of sodium carbonate.

All the ingredients of either of the solid or liquid compositions of this invention should be selected so as to provide a detergent which produces little or no foam during machine dishwashing, even in interaction with foamable food soils such as egg or milk residues. Low-foaming or non-foaming ingredients can be used to help provide this freedom from excessive foaming, and, as will be pointed out in more detail subsequently, surfactants with low foaming or even de-foaming properties can be added to reduce or control foaming. A realistic test for low foaming detergent compositions containing builder salts, condensed phosphates, surfactants, etc. is the commercial dishwashing machine test described in column 2, line 59 et seq. and Table III and IV of U.S. Pat. No. 3,444,242 (Rue et al), issued May 13, 1969. Detergent formulations of this invention do not unduly reduce either the r.p.m. of the spray arm or the wash pressure in this test.

#### ALKALINE DETERGENT SALTS

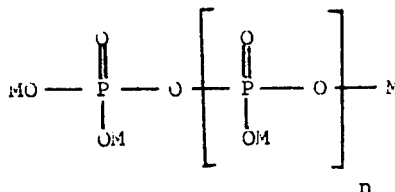
Alkaline detergent salts or detergent builder salts as they are sometimes called (other than alkaline condensed phosphate salts) are well known to those engaged in the detergent industry and include such chemicals as di and tri-sodium orthophosphates, sodium carbonate, sodium bicarbonate, sodium silicates, sodium

metasilicate, sodium borate, caustic soda, caustic potash, and the like. These salts are used primarily to adjust the pH of the wash water and/or to minimize corrosion. These salts may have a water conditioning effect, but this effect is characterized by the precipitation of hardness rather than by a sequestration or soluble complex formation or other solubilization effect. In machine dishwashing, sequestration is the preferred means for reducing hardness, since precipitated calcium carbonate or the like can form a film upon dishes or glassware. Thus, another way of characterizing these salts would be to describe them as the non-sequestering detergent builder salts, and they are included primarily for their pH-adjusting and/or buffering rather than their water conditioning properties. The sodium silicates inhibit corrosion of glass, ceramic and metal surfaces in addition to buffering and adjusting the pH.

The combined amount of these non-sequestering detergent builder salts will generally but not always be less than 80 weight percent of the total dishwashing detergent formula (on a dry basis). More usually, the total amount of such detergent salts will range from 2 to 70 weight percent on the same basis.

#### ALKALINE CONDENSED PHOSPHATE SALTS

Alkaline condensed phosphate salts are also well known to those engaged in the detergent industry. These salts are generally characterized by the structural formula:



wherein M is hydrogen or an alkali metal (at least one M being an alkali metal) and  $n$  is an integer ranging from 1 to about 60. The lower numerical values of  $n$  are preferred, e.g. 1–6. It is permissible to use condensed polyphosphates wherein  $n$  is larger than 60; however, such high molecular weight phosphates are less preferred, due to their relative lack of availability and lower water solubility. Cyclic condensed phosphates (wherein a plurality of  $-\text{PO}_3\text{M}-$  units join to form a ring) can also be used.

Typical alkaline condensed phosphates include tetrasodium pyrophosphate, tetra potassium pyrophosphate, sodium tripolyphosphate, other sodium polyphosphates and the like.

These alkaline condensed phosphate salts have a number of properties which make them particularly suitable for use in machine dishwashing detergent compositions. Other classes of compounds investigated by detergent chemists have equal or even superior sequestering capabilities but often lack the buffering, deflocculation, solubilizing or peptizing, and other desirable effects provided by these condensed phosphate salts. The so-called threshold effect (the ability to sequester hard water metal ions beyond the stoichiometric presence of the sequestering agent) has already been alluded to and is observed with sodium tripolyphosphate at the levels of about 5 to about 20 parts per million. It is also known that these condensed phos-

phate salts are active sequestering agents in aqueous alkaline media.

As used in the compositions of the present invention, the amount of alkaline condensed phosphate in the detergent compositions will be less than 35 weight percent on a dry basis, typically less than 30 weight percent on the same basis. To provide a reasonable assurance that the threshold effect will be obtained, more than 0.5 weight percent of the alkaline condensed phosphate (dry basis) is used in the composition. Normally, the amount of alkaline condensed phosphate used in these compositions will be from 2-20 percent, e.g. 2-10 percent, on the same basis.

### THE CITRATES

Any of the water soluble metal salts of citric acid can be used in the practice of the present invention. However, all salts do not serve with equal effectiveness, and the alkali metal salts, particularly the sodium and potassium citrates, are preferred. There are three COOH radicals on the citric acid molecule. Commercial "sodium citrate" is fully neutralized and is more accurately described as trisodium citrate. Trisodium citrate is available as white crystals or granular powder. It is odorless, stable in air, and has a pleasant saline taste. Each molecule of trisodium citrate dihydrate loses two molecules of water of hydration when heated to 150°C. Commercial potassium citrate also exists as white crystals or powder. It is normally available as the monohydrate (as contrasted to sodium citrate which exists as the dihydrate).

As used in the present invention, the amount of citrate employed will be above 5 percent and will generally fall within the range of 5-60 weight percent on a dry basis (expressed as trisodium citrate). Water of hydration can be considered to be part of the salt. More usually, the amount of citrate (whether hydrated or not) employed will be from 5-40 weight percent, e.g. 10-30 percent on the same basis.

If desired, mixtures of citrates can be used. Although it is not preferred, a citrate can be formed in situ from, for example, the combination of citric acid with sodium or potassium hydroxide. The use of a pre-formed alkali metal citrate or a mixture thereof is particularly preferred with dry blended solid detergents.

The combination of the citrate and the condensed phosphate salt (e.g. sodium tripolyphosphate) appears to cooperate in some fashion, and the total of the citrate and the condensed phosphate salt will be in the range of 7-90 weight percent on a dry basis and will generally not exceed 65 weight percent (dry basis) of the total composition. Excellent results can be obtained from the combination of sodium tripolyphosphate and sodium citrate when the ratio on a dry weight basis of polyphosphate to citrate is less than about 2:1 but greater than about 0.05:1, i.e., 1:2 to 20:1 citrate:polyphosphate. One preferred method for formulating a detergent composition of this invention is to modify a conventional machine dishwashing detergent formula by replacing more than one-third of the condensed phosphate salt with citrate; provided, of course, that the condensed phosphate content is reduced below 35 percent on a dry weight basis. A typical elemental analysis for phosphorus in compositions of this invention shows less than 8.7% (e.g. less than 5%) by weight phosphorus. Orthophosphates are preferably not used

as builder salts (or used in very small amounts), so that this low phosphorus level can be maintained.

Although the alkali metal citrates can be chelating agents and are known to have some water conditioning effects, these compounds are not particularly effective sequestering agents at alkaline pH levels. Nor are the citrates themselves known to be particularly outstanding in performing the variety of functions, in addition to sequestering, attributed to sodium tripolyphosphate (buffering, de-flocculation, solubilizing or peptizing, etc.)

However, one-third, one-half, or even nine-tenths or more of the polyphosphate can be replaced by citrate with little or no significant loss in overall performance characteristics of the detergent composition. Although this invention is not bound by any theory, it appears that so long as sufficient condensed alkali metal phosphate is present to preserve the threshold effect, the citrate is an effective substitute for the remainder of the polyphosphate that would normally be present in a machine dishwashing detergent. However, partial replacement of condensed alkali metal phosphate with other carboxylic acid salt water conditioning agents (e.g. gluconate salts) does not appear to provide the same performance as the partial replacement with citrates.

When citrates are formed in situ from citric acid in compositions of the present invention, either solid or dissolved citric acid can be used. Commercially available aqueous citric acid solutions at concentrations of about 25-40 percent by weight are suitable.

### CHLORINE RELEASING AGENTS

Among the various chlorine releasing agents are chlorinated trisodium phosphate, potassium and sodium dichloroisocyanurate, trichloroisocyanuric acid and "double salts" or crystalline complex salts or hydrated salts thereof (See U.S. Pat. No. 3,272,813), trichloromelamine, "Chloramine T," alkali metal and alkaline earth metal hypochlorites (e.g. sodium or potassium salt). These agents are not always required for good dishwashing, and, in any event, less than 5 or 10 percent by weight (e.g. 0.1-3%), based on the dry solids of the total composition, is ordinarily effective.

In solid machine dishwashing compositions of the invention, the preferred chlorine-releasing agents are the chlorinated cyanurates and their salts. In liquid formulas, the alkali metal hypochlorites are also particularly useful.

### LOW FOAMING, NON-FOAMING OR DE-FOAMING SURFACTANTS

Although surfactants are useful in many types of detergent compositions, those which have a tendency to produce stable foam are preferably excluded or used in minimum amounts in machine dishwashing compositions. The preferred surfactants of this composition have a cloud point of about 45°C. or less (preferably less than 35°C, e.g. 20°-30°C.) determined in distilled water at a concentration of 1 percent. These preferred surfactants, at 0.1 weight percent concentration in water, have Ross-Miles test values indicating the formation of very little stable foam after several minutes. The Ross-Miles test is performed by pipetting the 0.1 percent detergent solution into a column of water, measuring the height of foam immediately after pipetting and measuring again after 5 minutes. Water hardness is preferably specified for the test, but foam height values

for nonionic surfactants tend to be independent of the hardness of the test water. In a column of water maintained at 50°C., non-foaming or low-foaming detergents used in this invention have Ross-Miles foam height values of less than 45 mm/15 mm (initial value/ 5 minute value). Typical of these preferred surfactants are nonionic surfactants containing oxyethylene and, if desired, some oxypropylene units. See for example U.S. Pat. No. 3,048,548, issued Aug. 7, 1962, and U.S. Pat. No. 3,444,242, issued May 13, 1969. Another useful low foaming surfactant system is a blend of low foaming oxyethylene-oxypropylene adduct and alkyl ( $C_{12}$ - $C_{18}$ ) phosphate ester as described in U.S. Pat. Nos. 3,314,891 (Schmolka et al) and 3,595,968 (Groves).

The aforementioned commercial machine dishwashing test of the Rue et al U.S. Pat. No. 3,444,242 provides a criterion for the low foaming characteristics of completely formulated compositions of this invention. The compositions of this invention control foam to the extent that when used at 0.25 to 0.75 percent by weight (dry basis) in 6.5 liters of 140°F. wash water, the r.p.m. of the wash arm with detergent alone, or with detergent plus 0.1 percent by weight of mixed whole raw egg soil is greater than 80 percent of the r.p.m. measured with water alone.

The aforementioned surfactants are used in limited amounts, e.g. 0-5 percent by weight of the total formulation.

#### OTHER ADDITIVES

Depending upon the end use and desired performance characteristics of compositions of the invention, bases such as sodium and potassium hydroxide, filler, corrosion inhibitors, anti-caking agents, coloring agents and the like can be included in machine dishwashing detergents of this invention. If desired, neutral salts such as sodium sulfate and sodium chloride can be used as fillers.

Generally speaking, all ingredients of compositions of this invention, other than the aforementioned surfactants, anti-caking agents and chlorine release agents, are water soluble. By "water soluble" is meant the ability to form at least a 10 weight percent solution in deionized water.

The present invention is further illustrated by the following specific examples. Unless otherwise indicated, all parts and percentages are by weight.

#### EXAMPLE I

This example illustrates the preparation of a solid or dry detergent according to this invention.

The following dry ingredients are mixed together in the proportions indicated. pH of the resulting composition is above 10.0.

Ingredient	Amount (%)
sodium citrate dihydrate	25.0
sodium tripolyphosphate (anhydrous)	5.1
caustic soda (anhydrous)	21.0
sodium metasilicate (anhydrous)	25.0
sodium carbonate	21.9
sodium dichloroisocyanurate	2.0
	100.0%

#### EXAMPLE II

This example illustrates the preparation of a single package liquid machine dishwashing detergent concentrate having a pH above 10.0

Ingredient	Amount (%)
citric acid	10.0
tetra potassium pyrophosphate	5.0
liquid KOH (45%)	55.0
NaOCl (added as 10-15% NaOCl solution)	1.5
water	28.5
	100.0%

The above-noted ingredients are mixed in the following manner. Citric acid is dissolved in part or all of the water. Next, the KOH is added to neutralize the citric acid (i.e., form a citrate in situ). After the solution cools, the remaining ingredients are added.

#### EXAMPLES III-V

Solid detergent compositions for machine dishwashing were prepared by blending soda ash (anhydrous sodium carbonate), caustic soda (anhydrous sodium hydroxide), the low foaming nonionic surfactant described in U.S. Pat. No. 3,048,548, various amounts of sodium tripolyphosphate (STP) and sodium citrate (i.e. trisodium citrate dihydrate), the citrate and the STP each being varied over the range of 0-33.40 parts by weight. The detergent composition containing no citrate was referred to as the "Standard;" the detergent containing no STP was referred to as the "All-Citrate" sample. The low foaming nonionic surfactant was premixed with sodium carbonate to form an 85/15 (weight/weight)  $Na_2CO_3$ /surfactant composition hereinafter referred to as the "pre-mix."

The resulting formulations were:

#### INGREDIENTS IN PARTS BY WEIGHT

Example	Soda Ash	Caustic Soda	Pre-Mix	Chlorine Dry Bleach	STP	Sodium Citrate
Standard	30.80	21.40	12.00	2.40	33.40	0.0
III	30.80	21.40	12.00	2.40	16.70	16.70
IV	30.80	21.40	12.00	2.40	5.56	27.74
V	30.80	21.40	12.00	2.40	3.04	30.36
All-Citrate	30.80	21.40	12.00	2.40	0.0	33.40

The pH of the Standard was measured with a Corning glass electrode pH meter at 1.0 percent by weight and 0.1 percent by weight concentration in aqueous solution. The results were:

Concentration	pH
1%	12.65
0.1%	11.55

The detergent formulations were tested and compared to the "Standard" as to their performance in machine dishwashing. In the test, glasses were washed in a Hobart C-44 dishwasher using well water of 13 grains hardness heated to 160°F. The glasses were cycled ten times in the dishwasher, during which time the detergent concentration was maintained at a level of 2,000 parts per million (plus or minus 5 percent). Following completion of the test, the glasses were inspected for filming and spotting. The results reported subsequently in Table I were based upon an average rating of three glasses. The detergents were ranked in order of performance from the least film (1) to the heaviest film (5). Essentially no foaming was observed in the wash tank in connection with any of the detergent formulations tested.

Table I

Performance of Examples III-V vs. Standard and All-Citrate	
Example	Glass Film Results
V	1 (Slight)
Standard	2 (Very light)
III	3 (Very light)
IV	4 (Light)
All-Citrate	5 (Light)

## EXAMPLES VI-VIII

Solid detergent compositions were prepared substantially as in Examples III-V except that no premix was included, and amounts of caustic soda were different, and sodium metasilicate was used in place of soda ash. The resulting formulations were:

Example	STP	Parts by Weight	
		Sodium Citrate	Other Ingredients*
Standard	52.60	0.0	47.40
VI	26.30	26.30	47.40
VII	8.80	43.80	47.40
VIII	4.80	47.80	47.40
All-Citrate	0.0	52.60	47.40

\*Metasilicate: 23.70 parts, chlorine dry bleach: 2.40 parts, and caustic soda: 21.30 parts.

The above Standard was also measured for pH in the same manner as the Standard of Examples III-V with the following results:

Concentration	pH
1%	12.75
0.1%	11.55

Results of the glass film test are shown in Table II. Again, essentially no foaming was observed in the wash tank when these formulations were used. The test method was the same as that of Examples III-V.

Table II

Performance of Examples VI-VIII vs. Standard and All-Citrate	
Example	Glass Film Results
Standard	1 (Extra Slight)
VIII	2 (Extra Slight)
VI	3 (Slight)
VII	4 (Slight)
All-Citrate	5 (Light)

## EXAMPLE IX

As a further comparison with Examples V and VIII, the performance of low tripolyphosphate formulations containing no citrate were investigated. In comparison Examples V-A and VIII-A, the formulations were the same as Examples V and VIII except that the citrate was simply omitted so that the total parts used were only 69.64 and 52.20, respectively. In comparison Examples V-B and VIII-B, the citrate was replaced with 30.36 parts and 47.80 parts, respectively, of soda ash. Test results were determined as in Examples III-VIII and are set forth in Table III.

Table III

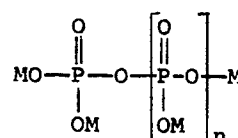
Comparison Examples	
Example	Glass Film Results
V-A	3 (Slight)
V-B	4 (Slight)
VIII-A	5 (Light)
VIII-B	6 (Light)

(Ratings 1 and 2 applied to Examples V and VIII.)

What is claimed is:

1. In the process of preparing a low-foaming or non-foaming machine dishwashing detergent composition from the components comprising:

1. an alkaline condensed phosphate salt generally characterized by the structural formula



wherein M is hydrogen or an alkali metal, at least one M being an alkali metal, and

n is an integer ranging from 1 to 60; and

2. 2 - 80% by weight, on a dry basis, of a nonsequestering, alkaline, pH-adjusting or buffering detergent builder salt;

said detergent Composition having a pH of about 10.0 to 12.8 and a Ross-Miles foam height, determined at a concentration of 0.1 percent by weight of said detergent composition in water, of less than 45 mm initially and less than 15mm after five minutes in a column of water maintained at 50°C.; the improvement which comprises:

substituting into said detergent composition at least 5 - 60 parts by weight per 100 parts by weight of said detergent composition, of a water soluble metal salt of citric acid;

whereby said salt of citric acid substitutes for part of said condensed phosphate; whereby the amount of said condensed phosphate in the resulting detergent composition is in the range of 0.5 to 35 percent by weight of the resulting detergent composition; and whereby the amount of said detergent builder salt in the resulting detergent composition is within the range of 2 - 80% by weight; all of the foregoing parts by weight and percentages by weight being on a dry basis.

2. Improved process according to claim 1, wherein said salt of citric acid substitutes for at least one-third by weight, on a dry basis, said alkaline condensed phosphate, whereby the ratio of said salt of citric acid to said condensed phosphate in said resulting detergent composition, on a dry weight basis, is in the range of from 1:3 to 20:1.

3. Improved process of claim 2 wherein said salt of citric acid is an alkali metal citrate; the amount of said citrate is 10 - 30 percent by weight and the amount of said alkaline condensed phosphate on the same basis is less than 30 percent by weight, all on a dry basis.

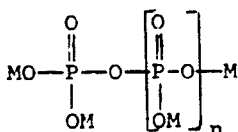
4. Improved process according to claim 1, wherein said detergent composition consists essentially of solids including a chlorine-releasing agent selected from the group consisting of chlorinated trisodium phosphate, potassium dichloroisocyanurate, sodium dichloroisocyanurate, trichloroisocyanuric acid, double salts or crystalline complex salts or hydrated salts of trichloroisocyanuric acid, trichloromelamine, and Chlo-ramine T.

5. Improved process according to claim 1, wherein said detergent composition is a liquid concentrate containing a chlorine releasing agent comprising an alkali metal hypochlorite.

6. Improved process according to claim 5 wherein said salt of citric acid is formed in situ.

7. A machine dishwashing detergent composition which, in 0.1 weight percent concentration in water, has Ross-Miles foam heights, using a water column maintained at 50°C., of less than 45mm initially and less than 15mm after five minutes, and which has a pH, determined at 1 weight percent solution in water, of about 10 to 12.8, said composition consisting essentially of:

- 2 - 70 percent by weight of at least one nonsequestering, alkaline, pH adjusting or buffering, water soluble detergent builder salt,
- 0 - 5 percent by weight of a surfactant which, in 0.1 weight percent concentration in water, has the said Ross-Miles foam heights, using a water column maintained at 50°C.,
- from 5 to 60 percent by weight of a water soluble metal salt of citric acid, and
- 0.5 to 35 percent by weight of water soluble alkaline condensed phosphate of the formula



wherein M is hydrogen or an alkali metal, at least one M being an alkali metal, and

$n$  is an integer from 1 to 6, all of the said percentages being on a dry basis.

8. Composition according to claim 7 wherein the ratio, on a dry weight basis, of said component (c) to said component (d) is in the range of 1:2 to 20:1, and total of said components (c) and (d) does not exceed 65 percent by weight of said composition on a dry basis.

9. Composition according to claim 7 wherein said component (c) is the product of the in situ reaction of citric acid and an alkali metal hydroxide.

10. Composition according to claim 7 wherein said detergent composition consists essentially of solids including a chlorine-releasing agent selected from the group consisting of chlorinated trisodium phosphate, potassium dichloroisocyanurate, sodium dichloroisocyanurate, trichloroisocyanuric acid, double salts or crystalline complex salts or hydrated salts of trichloroisocyanuric acid, trichloromelamine, and Chlo-ramine T.

11. Composition according to claim 7 wherein said detergent composition is a liquid concentrate containing a chlorine releasing agent comprising an alkali metal hypochlorite.

12. Composition according to claim 7 wherein said water soluble detergent builder salt is capable of precipitating hardness from water in the form of calcium carbonate in water having a pH of about 10 to 12.8.

13. Composition according to claim 12 wherein said water soluble detergent builder salt is sodium carbonate.

14. Composition according to claim 7 wherein said component (c) comprises an alkali metal citrate and said component (d) comprises an alkali metal tripolyphosphate.

15. Composition according to claim 14 wherein said composition comprises 10-30 percent by weight of said citrate and 2-20 percent by weight of sodium tripolyphosphate.

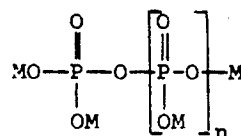
16. In the process of machine dishwashing, the improvement which comprises using as the dishwashing detergent added to the wash water the composition of claim 7.

17. The process of claim 16 wherein the wash water used in said process, after addition of said composition, comprises 0.1-1 percent by weight of said composition on a dry basis.

18. In the process of machine dishwashing, the improvement which comprises using as the dishwashing detergent the composition of claim 15.

19. Treated wash water useful for machine dishwashing having a pH in the range of about 10 - 12.8 and being substantially free of stable foam comprising:

- a machine detergent composition comprising:
  - 5 - 60 percent by weight of an alkali metal citrate,
  - 0.5 - 35 percent by weight of an alkali metal condensed phosphate of the formula



wherein M is hydrogen or an alkali metal, at least one M being an alkali metal, and

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- $n$  is an integer from 1 to 6, and
- c. 2 - 70 percent by weight of a non-sequestering, alkaline, pH-adjusting or buffering alkali metal detergent builder salt, all on a dry basis, and
2. 99 - 1,000 parts by weight of water for each part by weight of dry solids contained in component (1), said component (1) being totally dissolved in said water.
20. Treated wash water according to claim 19 wherein said machine dishwashing detergent composition further contains up to 5 percent by weight of a surfactant which, in 0.1 percent by weight concentration

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in water, has Ross-Miles foam heights, using a water column maintained at 50°C., of less than 45 mm initially and less than 15 mm after five minutes and a cloud point, determined in distilled water at a concentration of 1 percent by weight of less than 45°C.

21. Improved process according to claim 1 wherein all surfactants included in said dishwashing detergent composition, when tested individually at a concentration of 0.1% by weight in water, have said Ross-Miles foam height characteristics.

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