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**LOW-FOAMING DISHWASHING COMPOSITION**  
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No Drawing. Filed Oct. 8, 1963, Ser. No. 314,626  
8 Claims. (Cl. 252-99)

This invention relates to low-foaming detergent compositions for use in automatic dishwashers and is directed particularly to detergent compositions which do not attack overglaze colors and decorations of fine china and the aluminum of pots and pans, and do not tarnish stainless steel used in cutlery and on the surfaces of dishwashers which are exposed to them.

The dishwashing compounds used in automatic dishwashers preferably are characterized by their low-forming properties, since the washing action of such equipment relies largely on the scrubbing effect of vigorous jets or sprays of liquid which would be rendered relatively ineffective if cushioned by the action of large amounts of foam. However, the low-foaming compositions heretofore used in automatic dishwashers have sometimes been relatively strong or harsh in their action on the surface or decorations carried by the articles being washed. For example, most dishwashing compounds contain polyphosphates as soil emulsifiers and water softeners; such phosphates tend to attack aluminum articles such as pots and pans and are injurious to overglaze decorations on dinnerware. The injury to decorations on fine china is particularly objectionable and is believed to be due to weakening or destruction of the bonding material by which the decoration is secured to the glaze on the china. The bond generally consists of a glass-like lead bore-silicate flux containing about 60 to 65% lead and minor proportions of boric oxide and silica. The detergents used in the usual dishwashing compounds are believed to attack the flux constituents, weakening the bond to such an extent that the decorative material may be washed or rubbed off of the glaze.

It is known that sodium silicate serves to reduce the attack of polyphosphates on glazing and decorative material. It also has been suggested that the action of alkali-carbonates, -orthophosphates and -sulfates, also common ingredients in dishwashing compounds can be inhibited in their attack upon vitreous and ceramic surfaces by the use of water-soluble zinc, beryllium or aluminum compounds. However, when soluble silicate and aluminate compounds have both been used in dishwashing compounds heretofore, an undesirable precipitate has been formed which tends to deposit on the dishes, cutlery and exposed surfaces of the dishwasher leaving them tarnished or unclean in appearance. While such an objectionable precipitate can be emulsified or suspended if a suitable surfactant composition is employed, the surfactants heretofore considered suitable for this purpose have been employed in such large amounts as to render the compositions unacceptable for use in automatic dishwashers due to the excessive amount of foam produced.

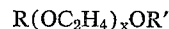
Accordingly, the principal objects of the present invention are to reduce the injury or attack upon decorated china by dishwashing compositions, to limit the formation of undesired precipitates in dishwashing solutions, and to assure the effective cleaning and protection of articles subjected to the action of low foaming detergent materials in automatic dishwashers.

These and other objects and features of the present invention will appear from the following description thereof wherein typical and preferred dishwashing compositions are shown and their use described.

These advantages are attained in accordance with the

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present invention by suitably combining and relating the character and proportions of the ingredients of the herein dishwashing compounds. In particular, it has now been found possible to provide excellent dishwashing compounds in which the formation of objectionable amounts of the undesired precipitate heretofore produced upon dissolving polyphosphate, orthophosphate, carbonate, sulfate and other alkaline and detergent agents in the presence of aluminate and silicate are prevented without resorting to the use of large, foaming amounts of surfactants. This advantage is attained by providing a dry composition containing as essential ingredients an alkali salt of an amphoteric metal, particularly an alkali aluminate, zincate or berylliate, in the amount of about 0.5 to 5%, and preferably 1 to 3%, by weight, an alkali silicate having an  $Me_2O$  to  $SiO_2$  ratio of 1:1 to 1:3 in the amount of about 10 to 30%, and preferably 15 to 20%, by weight, a dry agent which yields available chlorine in aqueous solution, preferably a chlorinated cyanuric compound from the group consisting of trichlorocyanuric, dichlorocyanuric acid or an alkali salt of dichlorocyanuric acid, in the amount of about 1 to 5%, and preferably 2 to 3%, by weight, a sodium polyphosphate in the amount of about 20 to 50%, and preferably 30 to 45%, by weight, a nonionic surfactant resistant to the action of available chlorine, particularly such a surfactant having the formula



in which R is an alkaryl group in which the alkyl group has 6 to 13 carbon atoms or an alkyl group having 8 to 18 carbon atoms, x is 10 to 18, and R' is an alkyl, aryl, alkaryl or aralkyl group having 3 to 12 carbon atoms, in the amount of about 1 to 5%, and preferably 1 to 3%, by weight, and the balance an alkali sulfate, orthophosphate, carbonate or chloride.

The conjoint presence of the amphoteric metal ions and the silicate in this composition effectively inhibits attack of aqueous solutions of the composition on overglaze decorations by alkaline agents present in the dishwashing solution. In this way, destruction of the bond by which the decorative material is secured to the underlying glaze is reduced or eliminated. The relationship or ratio of the amphoteric ion material with respect to the silicate as well as to the other ingredients in these compositions is critical, and whereas heretofore it was considered necessary to employ large amounts of surfactant materials in order to provide effective cleaning in compositions containing the amphoteric metal ions and silicate, the present compositions are extremely effective cleansing agents despite the small amount of surfactant, a nonionic available chlorine-resistant surfactant, employed in them. It is believed that the joint action of the nonionic surfactant with the polyphosphate and the chlorinated compound is responsible for the effective cleaning. In any event, the ability of the composition to clean dishware effectively without requiring excessive and foam-producing amounts of surfactant is most important in utilization of this composition.

The dishwashing compositions of this invention contain a major part, about 20 to 50%, and preferably 30 to 45%, by weight of a sodium salt of a polyphosphoric acid having from 2 to 20 phosphorus atoms, particularly sodium tripolyphosphate and tetrasodium pyrophosphate.

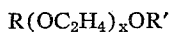
This ingredient serves as detergency builder, soil emulsifier and a water softener. Use of more than the indicated maximum amount of the polyphosphate is apt to result in attack on china, while use of less than the indicated minimum provides ineffective dishwashing.

The chlorinated compound, preferably trichlorocyanuric acid, dichlorocyanuric acid or an alkali salt of dichlorocyanuric acid, and particularly the sodium and

potassium salts, is employed in the amount of about 1 to 5%, and preferably 2 to 3%, by weight in the dishwashing composition. Other chlorinated compounds available in dry form and capable of yielding available chlorine in aqueous solution may be used. Such other compounds include chlorinated trisodium orthophosphate and dichlorodimethyl hydantoin. Likewise, other alkaline salts of dichlorocyanuric acid can be used, for example the magnesium and calcium salts.

This chlorinated compound coacts with the polyphosphate and the nonionic surfactant to provide effective cleansing of the dishware and cutlery. It not only serves to oxidize and aid in the removal and emulsification of proteinaceous soil, but at the same time acts as a bleach through its available chlorine, thereby removing coffee, tea and the like stains. Use of this ingredient in the amount of 1 to 5%, and preferably 2 to 3%, by weight makes it possible to employ amounts of the herein nonionic surfactant which are sufficiently small to avoid excessive foaming, while at the same time providing effective cleaning of dishware and cutlery.

The nonionic surfactants useful in the herein compositions are the nonionic surfactants resistant to the action of available chlorine, particularly those having the following formula:



in which R is an alkaryl group in which the alkyl group has 6 to 13 carbon atoms or an alkyl group having 8 to 18 carbon atoms, x is 10 to 18, and R' is an alkyl, aryl, alkaryl or aralkyl group having 3 to 12 carbon atoms. The preferred agents are those in which R is an alkyl phenylene group in which the alkyl group has 8 to 9 carbon atoms, x is 10 to 18 and R' is an alkyl group having 3 to 7 carbon atoms or is a benzyl group. These agents are used in the present composition in the amount of only about 1 to 5%, and preferably 1 to 3%, by weight. It is interesting to note by way of contrast that the anionic surfactants are ineffective in the compositions of this invention, serving to create excessive amounts of foam, even when they are used in small amounts. The foam binds pumps and prevents the necessary strong mechanical action which results from impingement of water on the surface of dishes in a dishwasher. Likewise, the cationic surfactants are ineffective since they are incompatible with alkaline systems. Accordingly, the kind and amount of surfactant employed in the dishwashing compositions of this invention are quite specific; the specified minimum amount is required to provide effective cleansing, while use of more is uneconomical and is not needed for effective cleaning.

The compositions of the present invention also contain both amphoteric metal compounds, such as sodium aluminate, and a sodium silicate. The amounts of these agents employed and the ratio of one to the other, as well as the form in which they are present in the dishwashing composition and solution, is important. Thus, when the polyphosphate sodium triphosphate is employed in the amount of about 20 to 50% by weight of the composition, the alkali aluminate is employed in the amount of about 0.5 to 5% of the weight of the total dishwashing composition. The sodium silicate or other alkali silicate is employed under these circumstances in the amount of about 10 to 30% by weight. Preferred compositions contain about 1 to 3% by weight of sodium aluminate or other amphoteric metal compound and about 15 to 20% by weight of sodium silicate or other alkali silicate.

The amphoteric metal compound employed preferably is sodium aluminate, although other alkali aluminates and alkali zincates and beryllates are also useful. The type of silicate employed is important; the silicates having an  $Me_2O$  to  $SiO_2$  ratio of 1:1 to 1:3 in which the Me is an alkali metal, and preferably sodium or potassium, are the useful silicates. The silicates not falling

within the above class have been found to be substantially less effective in the compositions of this invention.

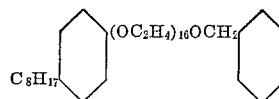
The alkali carbonates, orthophosphates, sulfates and chlorides employed in compositions of this invention are employed for their usual purpose, principally as fillers. The preferred agents from this class are sodium sulfate, sodium orthophosphate, sodium chloride and sodium carbonate, although other alkali metal salts from this group have been found useful.

The pH of dishwashing solutions containing the compositions of the present invention may vary considerably, as for example, from about 10 to 12. The preferred pH of aqueous dishwashing solutions containing 0.3% of the dishwashing composition is about 10.5, or, from about 10.0 to 11.0. The pH in any case depends primarily upon the amount and character of the alkali polyphosphate and the alkali sulfates, orthophosphates, carbonates or chlorides used in producing the composition. In general, the amount of the sodium aluminate or other alkali compound of an amphoteric metal employed may be increased as the pH of the dishwashing solution is increased; but undesired amounts of precipitate may be formed if the amount of sodium aluminate used substantially exceeds about 5% by weight of the composition.

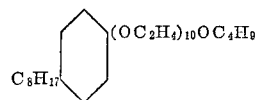
When the various ingredients used in producing dishwashing compositions in accordance with the present invention are employed in amounts and proportions substantially as indicated above, it is found that a chemical, or perhaps physical, balance is maintained which assures the continued presence of aluminate or other amphoteric metal ions in the dishwashing solution. Moreover, the formation of objectionable deposits or unsightly films on the surfaces of the articles being washed is prevented. Overglaze decorations on fine china are thereby protected and tarnishing of stainless steel, aluminum and other metallic surfaces or articles exposed to the dishwashing solution does not occur. Furthermore, undesirable foaming of the dishwashing solution is avoided even under the severe conditions encountered in automatic dishwashers.

In order to illustrate typical dishwashing compositions embodying the present invention, the following examples are cited wherein the percentages indicate percent by weight of the mixture, and the compositions were blended in a twin shell liquids-solids blender.

Nonionic Surfactant A in the examples is:



Nonionic Surfactant B is:



Example 1

	Percent
Sodium triphosphate	20
Sodium hexametaphosphate	10
Disodium phosphate	10
Sodium chloride	41
Sodium silicate ( $Na_2O:2SiO_2$ )	13
Sodium aluminate	2
Nonionic Surfactant B	1.5
Potassium dichlorocyanurate	2.5

Example 2

	Percent
Tetrasodium pyrophosphate	30
Sodium carbonate	39
Sodium metasilicate, anhydrous	25
Sodium zincate	2
Nonionic Surfactant A	1.5
Sodium dichlorocyanurate	2.5

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## Example 3

	Percent
Sodium tripolyphosphate -----	40
Sodium sulfate -----	37
Sodium silicate (Na <sub>2</sub> O:2SiO <sub>2</sub> ) -----	17
Sodium aluminate -----	2
Nonionic Surfactant B -----	1.5
Sodium dichlorocyanurate -----	2.5

The formulations of Examples 1, 2 and 3 above cleaned dishes, cutlery and glasses very efficiently without creation of foam when they were used in automatic dishwashers. Furthermore, in each example the formulations showed no attack upon overglaze decorations of china, and no tarnishing of metals due to formation of objectionable amounts of precipitates in the dishwashing liquid.

Examples A and B which follow are presented to demonstrate the importance of employing both of the silicate and the amphoteric metal salt in the herein composition.

## Example A

	Percent
Sodium tripolyphosphate -----	20
Sodium hexametaphosphate -----	10
Disodium phosphate -----	10
Sodium chloride -----	43
Sodium silicate (Na <sub>2</sub> O:2SiO <sub>2</sub> ) -----	13
Nonionic Surfactant B -----	1.5
Potassium dichlorocyanurate -----	2.5

The formulation cited above (Example A) is identical to that presented in Example 1 with the exception that the sodium aluminate has been replaced with sodium chloride.

## Example B

	Percent
Sodium tripolyphosphate -----	40
Sodium sulfate -----	39
Sodium silicate (Na <sub>2</sub> O:2SiO <sub>2</sub> ) -----	17
Nonionic Surfactant B -----	1.5
Sodium dichlorocyanurate -----	2.5

The formulation of this Example B is identical to that presented in Example 3 with the exception that the sodium aluminate has been replaced with sodium sulfate.

## Example 6.—China-attack test

Wedge shaped sections (five different patterns) of overglaze chinaware dinner plates, containing a wide variety of different colored pigments, were immersed in 0.3% solutions of the compositions of Examples 1, 2, 3, A and B for 3 hours at boiling. Upon completion of the test, the sections were removed from the solution, wiped with a dry cloth and examined for iridescence, dulling and pattern erosion. The chinaware patterns were noticeably dulled and eroded by the compositions given in Examples A and B while patterns tested with the aluminate-containing compositions given in Examples 1, 2 and 3 remained bright and unaffected.

The formulas for dishwashing compositions set forth in Examples 1 through 3 are, of course, merely illustrative and other compositions and amounts and ratios of the ingredients may be employed within the herein limits. Although the chlorinated compounds shown by way of example are dichlorocyanurates, other chlorinated compounds, e.g. trichlorocyanuric acid, chlorinated trisodium phosphate and dichlorodimethyl hydantoin serve as effective replacements for them in the formulations of the above examples. Likewise, other salts of the amphoteric metals are effective replacements for sodium aluminate and zincate.

What is claimed is:

1. A low-foaming dishwashing composition which does not attack overglaze colors and decorations of fine china consisting essentially of the following ingredients in the indicated weight percentages: 20 to 50% of a sodium polyphosphate, 1 to 5% of an alkali metal salt of dichloro-

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cyanuric acid, 10 to 30% of a sodium silicate having an Na<sub>2</sub>O:SiO<sub>2</sub> ratio of 1:1 to 1:3, 0.5 to 5% of an amphoteric metal compound from the group consisting of alkali aluminates and alkali zincates, 1 to 5% of a nonionic surfactant having the following formula:



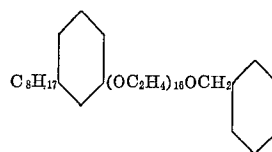
in which R is an alkylphenyl group in which the alkyl group has 6 to 13 carbon atoms or an alkyl group having 8 to 18 carbon atoms, x is 10 to 18, and R' is an alkyl, phenyl, alkylphenyl or phenylalkyl group, said R' having 3 to 12 carbon atoms, and the balance an alkali metal salt from the group consisting of sulfates, orthophosphates, carbonates and chlorides.

2. A low-foaming dishwashing composition which does not attack overglaze colors and decorations of fine china consisting essentially of the following ingredients in the indicated weight percentages: 30 to 45% of a sodium polyphosphate, 2 to 3% of an alkali metal salt of dichlorocyanuric acid, 15 to 20% of a sodium silicate having an Na<sub>2</sub>O to SiO<sub>2</sub> ratio of 1:1 to 1:3, 1 to 3% of an amphoteric metal compound from the group consisting of alkali aluminates and alkali zincates, 1 to 3% of a nonionic surfactant having the following formula:



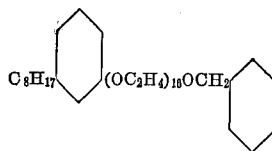
in which R is an alkylphenyl group in which the alkyl group has 6 to 13 carbon atoms or an alkyl group having 8 to 18 carbon atoms, x is 10 to 18, and R' is an alkyl, phenyl, alkylphenyl, or phenylalkyl group, said R' having 3 to 12 carbon atoms, and the balance an alkali metal salt from the group consisting of sulfates, orthophosphates, carbonates and chlorides.

3. A low-foaming dishwashing composition which does not attack overglaze colors and decorations of fine china consisting essentially of the following ingredients in the indicated weight percentages: 20 to 50% of sodium tripolyphosphate, 1 to 5% of an alkali metal dichlorocyanurate, 10 to 30% of a sodium silicate having an Na<sub>2</sub>O to SiO<sub>2</sub> ratio of 1:2, 0.5 to 5% of sodium aluminate, 1 to 5% of a nonionic surfactant having the following formula:



and the balance sodium sulfate.

4. A low-foaming dishwashing composition which does not attack overglaze colors and decorations of fine china consisting essentially of the following ingredients in the indicated weight percentages: 30 to 45% of sodium tripolyphosphate, .2 to 3% of an alkali metal dichlorocyanurate, 15 to 20% of a sodium silicate having an Na<sub>2</sub>O to SiO<sub>2</sub> ratio of 1:2, 1 to 3% of sodium aluminate, 1 to 3% of a nonionic surfactant having the following formula:



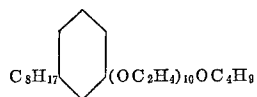
and the balance sodium sulfate.

5. The composition of claim 4 in which the alkali metal dichlorocyanurate is sodium dichlorocyanurate.

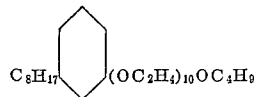
6. The composition of claim 8 in which the alkali metal dichlorocyanurate is potassium dichlorocyanurate.

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7. The composition of claim 3 in which the nonionic surfactant has the following formula:



8. The composition of claim 4 in which the nonionic surfactant has the following formula: 10



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