

1

3,544,473

ALKALINE DISHWASHER DETERGENT

Everitt A. Kitchen and Judith K. Simmons, Cincinnati, Ohio, assignors to The Procter & Gamble Company, Cincinnati, Ohio, a corporation of Ohio
No Drawing. Filed Sept. 6, 1968, Ser. No. 758,121
Int. Cl. C11d 7/56

U.S. Cl. 252—99

3 Claims

ABSTRACT OF THE DISCLOSURE

Alkaline dishwasher detergent based on an alkaline sequestrant builder, sodium silicate, a chlorine bleach, an alcohol ethoxylate nonionic surfactant and an insoluble phthalocyanine green dye.

BACKGROUND

Since the introduction of mechanical dishwashing equipment, considerable attention has been directed to the improvement of alkaline dishwasher detergents. To obtain efficient cleaning in mechanical dishwashers, the detergent used therein must be well formulated. Such detergents should contain an alkaline sequestrant builder salt, sodium silicate, a chlorine bleach and a nonionic surfactant. Most dishwasher detergents employ nonionic surfactants which are based on propylene oxide/ethylene oxide condensation products.

It has been found desirable to include a dye in dishwasher detergents in order to identify it as a dishwasher detergent and thereby avoid its confusion with other white granular products used in the kitchen. Avoidance of such confusion is desirable because dishwasher detergents necessarily are alkaline and contain a chlorine bleach. Because of these components an effort should be made to change its appearance from other white kitchen powders such as sugar, salt, cornstarch and the like. A very useful color for this purpose is green, particularly because of the traditional association of green with chlorine bleach, chlorine gas being green colored. Moreover, housewives associate green in their minds with an ability to clean well. The most suitable and readily available green dye is insoluble phthalocyanine green. It has been found, however, that when insoluble phthalocyanine green is used with the nonionic surfactants of condensed propylene oxide/ethylene oxide, severe straining problems are encountered. These problems involve the green staining of plastic tableware and plastic dishwasher parts after a few months usage. Because of this staining problem it has been necessary to use the more expensive and less available soluble phthalocyanine green dyes in conjunction with the propylene oxide/ethylene oxide nonionics.

It is, therefore, an object of this invention to provide a dishwasher detergent employing a specific type of nonionic surfactant which surprisingly permits the use of the readily available insoluble phthalocyanine green dye without encountering the expected staining problems on plastic tableware and dishwasher parts.

DESCRIPTION OF THE INVENTION

This invention is an alkaline dishwasher detergent composition comprising an alkaline sequestrant builder salt, sodium silicate, a chlorine bleach, insoluble phthalocyanine green dye and, as a nonionic surfactant, the condensation product of C_{13} - C_{21} normal fatty alcohol with from 5 to 12 moles of ethylene oxide. This dishwasher detergent is effective and has a pleasing and useful green color but does not, in use in a mechanical dishwasher, result in objectionable staining of plastic dinnerware and dishwasher parts.

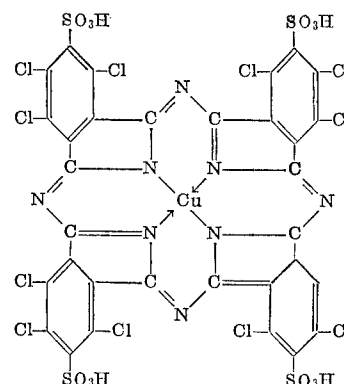
2

The alkaline sequestrant builder salt is a primary cleaning component of the dishwasher detergent and is employed in an amount ranging from 25% to 75%, preferably 35% to 60%, of the composition. It also sequesters water hardness to preclude deposition of hardness salts on the kitchenware being washed. Organic or inorganic sequestrant builder salts or mixtures thereof can be used. The preferred sequestrant builder salt classes are the alkali metal (e.g., sodium and potassium) inorganic polyphosphates, organic aminopolyacetates and organic polyphosphonates. Specific examples of these preferred builder salts are sodium tripolyphosphate, tetrasodium pyrophosphate, tri- and tetra-sodium ethylene diamine tetraacetate, trisodium nitrilotriacetate, tri- or tetra-sodium ethane 1-hydroxy-1,1-diphosphonate and tri- and tetra-sodium ethane-1-hydroxy-1,1,2-triphosphonate. Additional examples of such salts are found in Zimmerer's U.S. Pat. 3,351,558, especially from line 64, column 2 to line 38, column 3 which is incorporated herein by reference.

The sodium silicate is employed in the dishwasher detergents also as a primary cleaning ingredient, as a source of alkalinity, as an inhibitor of metallic corrosion and as a protector of glaze on china tableware. It is used in an amount ranging from 5% to 50%, preferably 10% to 25% of the composition and has a $SiO_2:Na_2O$ ratio ranging from about 3.6:1 to about 1:1, preferably from 3:1 to 1:1.

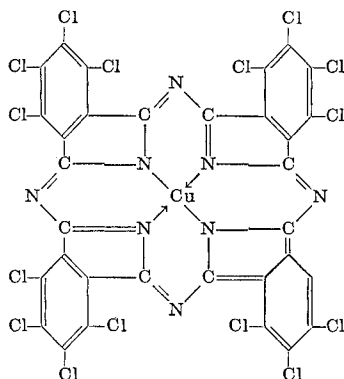
The chlorine bleach component is a compound which contains chlorine in an active form. Such compounds are often characterized as hypochlorite compounds and are well known as a class. The dishwasher detergent should contain 0.5% to 25% of an active chlorine-containing bleaching compound, preferably 1% to 15%. Examples of such compounds are: dichlorocyanuric acid; 1,3-dichloro-5,5-dimethyl hydantoin; N,N'-dichlorobenzoylene urea; paratoluene sulfondichloroamide; trichloromelamine; N-chloroammeline; N-chlorosuccinimide; N,N'-dichloroazodicarbonamide; N-chloroacetyl urea; N,N'-dichlorobiuret; chlorinated dicyandiamide; sodium hypochlorite; calcium hypochlorite; lithium hypochlorite; chlorinated trisodium phosphate. Preferred compounds are chlorinated trisodium phosphate and sodium and potassium dichlorocyanurate. The term "chlorinated trisodium phosphate" is used to designate a composition consisting of trisodium phosphate and sodium hypochlorite in intimate association in a crystalline form. The chlorinated trisodium phosphate can contain from 1% to 5% available chlorine (calculated on the basis of the hydrated material) and may be prepared by the methods of U.S. Letters Patent 1,555,474 or 1,965,304, or modifications thereof.

Phthalocyanine green dye is an organic pigment having as a structural unit four isoindole groups (C_6H_4) C_2N , linked by four nitrogen atoms so as to form a conjugated chain. The expensive, and not readily-available, soluble phthalocyanine green dye has the following structural formula:



3

The less expensive and more readily-available phthalocyanine green dye of the composition of this invention has the following formula:



It is used in the detergents of this invention in an amount ranging from 0.001% to 0.015%, preferably 0.002% to 0.01%. Lesser amounts do not provide a desired green color in the composition and greater amounts are unnecessary and would tend to cause stain problems notwithstanding the unexpected advantages provided with specific nonionic surfactant described below.

The nonionic surfactants employed in the dishwasher detergents of this invention, the use of which surprisingly overcomes the plastic tableware staining tendencies of insoluble phthalocyanine green dye, are C_{13} - C_{21} normal fatty alcohol-ethylene oxide condensates, i.e., condensation products of one mole of a fatty alcohol containing from 13 to 21 carbon atoms with from 5 to 12, preferably 6 to 11, moles of ethylene oxide. C_{16} - C_{18} alcohol such as tallow fatty alcohol is preferred in the condensates. It usually comprises a mixture of 65% octadecanol, 33% hexadecanol and 2% tetradecanol, but can vary, depending on the tallow source. Small amounts up to 10% of C_{12} and C_{22} alcohols can be tolerated but at least 90% must be C_{13} - C_{21} to obtain good cleaning without undue sudsing. Such condensates are well known in the detergent art but are not believed to have been used, prior to this invention, in dishwasher detergents containing insoluble phthalocyanine green dye. Prior attempts to use insoluble phthalocyanine green dye in dishwashing detergents, involving the use of propylene oxide containing nonionic surfactants, have resulted in objectionable plastic tableware and dishwasher parts staining problems. Why the higher alcohol/ethylene oxide condensates of the compositions of this invention solve this plastic staining problem is not known, but the solution thereto was unexpected. These alcohol/ethylene oxide condensates are employed in an amount ranging from 1/2% to 10%, preferably from 1% to 5% of the composition.

The compositions of this invention have a pH in the range of 9.7 to 12.1 (measured in 1% aqueous solution) in order to obtain satisfactory cleaning in the dishwasher. They can be prepared by dry-mixing the ingredients or by agglomeration processes such as those described in U.S. Patent 2,895,916, Milenkevich, issued July 21, 1959, incorporated herein by reference.

The instant dishwasher detergents can contain minor amounts of optional ingredients such as perfume, suds depressants such as mono- or di-stearyl acid phosphate or silicones, inert salts such as NaCl or sodium sulfate, anti-tarnish agents such as benzotriazole and aluminum salts, enzymes, alkaline agents such as caustic soda, or sodium carbonate, anticaking agents such as urea. Preferably from 0.1% to 1% mono- and/or di-stearyl and phosphates are used, desirably as the sodium salt.

The percentage figures listed above for the ingredients are on a dry basis. In practice the compositions preferably contain significant amounts of water as water of hydration. This water can be in amounts from 0% to 35% of the composition.

4

Below are working examples illustrative of the compositions of this invention which should not be considered as limiting. All parts, percentages and ratios used in the specification, examples and claims herein are by weight unless otherwise specified.

EXAMPLE I

A dishwasher detergent composition is prepared by the following procedure:

- 45 45 parts of anhydrous granular sodium tripolyphosphate, and
- 14 parts of sodium silicate having an $SiO_2:Na_2O$ ratio of 2.9:1 are placed in a mixer and thoroughly mixed,
- 27.6 parts of water are then added to this mixture and blended in to agglomerate the tripolyphosphate-silicate mixture,
- 15 9.7 parts of chlorinated trisodium phosphate (calculated on an anhydrous basis and containing 7.5% available chlorine) are then added to the mixture with agitation. The added water all hydrates into the ingredients of the mixture. The following additives are then blended into the mixture with agitation:
- 0.8 part sodium monostearyl acid phosphate,
- 0.07 part insoluble phthalocyanine green dye, and
- 2.6 parts of the condensate of one mole of tallow fatty alcohol and 9 moles of ethylene oxide. The resultant green-colored detergent has a pH of 10.6 and cleans soiled plastic tableware effectively in a mechanical dishwasher, but without staining on repeated usage.

The same composition was prepared except that the tallow alcohol/ethylene oxide condensate was replaced with the condensation product of ethylene oxide with a hydrophobic base formed by condensing propylene oxide with propylene glycol, the product having a molecular weight of 4000. This composition, as changed to represent the prior art, cleaned well, but resulted in severe plastic dinnerware staining problems in just a few months usage time.

EXAMPLE II

The following dishwasher detergent is prepared by dry mixing the listed ingredients.

- 45 45% sodium tripolyphosphate (anhydrous basis),
- 3.5% potassium dichlorocyanurate,
- 2.6% condensation product of one mole of tallow fatty alcohol and nine moles of ethylene oxide,
- 0.8% mixture of mono- and di-stearyl acid phosphate, sodium salt,
- 20% sodium meta silicate (having an $SiO_2:Na_2O$ ratio of 1:1),
- 15.5% sodium sulfate,
- 0.007% insoluble phthalocyanine green dye,
- 55 balance water, as water of hydration in the sodium tripolyphosphate which was prehydrated before admixture.

The resulting composition is an excellent alkaline dishwasher detergent having a green color and a pH of 10.6 in 1% aqueous solution. It cleans soiled dishes very well in a mechanical dishwasher, resulting in no noticeable staining of plastic dinner ware or dishwasher parts in several months time.

The following are additional examples of dishwasher detergents which have a pleasing and useful green color and which clean soiled plastic tableware in a mechanical dishwasher having plastic parts without staining either. They have a pH of about 10.5.

EXAMPLE III

- 70 50% trisodium nitrilotriacetate,
- 15% sodium silicate having an $SiO_2:Na_2O$ ratio of 2.1:1,
- 10% potassium dichlorocyanurate,
- 2% condensation product of 1 mole of octadecanol and
- 75 10 moles of ethylene oxide,

5

0.005% insoluble phthalocyanine green dye,
balance, water as moisture and water of hydration.

EXAMPLE IV

25% tetrasodium pyrophosphate,
25% tetrasodium ethylenediamine tetraacetate,
15% sodium silicate having an $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of 2:1,
10% sodium dichlorocyanurate,
2% condensation product of 1 mole of a 1:1 mixture of
pentadecanol and hexadecanol and 8 moles of ethylene
oxide,
0.005% insoluble phthalocyanine green dye,
balance, water of hydration and moisture.

EXAMPLE V

50% trisodium ethane 1-hydroxy-1,1-diphosphonate,
15% sodium silicate having an $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of 1.6:1,
10% $4(\text{Na}_3\text{PO}_4 \cdot 11\text{H}_2\text{O}) \cdot \text{NaOCl}$,
3% condensation product of 1 mole of tallow fatty alco-
hol and 6 moles of ethylene oxide,
0.01% insoluble phthalocyanine green dye,
balance, water of hydration and moisture.

EXAMPLE VI

10% tetrasodium ethane-1-hydroxy-1,1,2-triphosphonate,
20% trisodium nitrilotriacetate,
15% sodium silicate having an $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of 2.6:1,
10% calcium hypochlorite,
2% condensation product of 1 mole of nonadecanol and
9 moles of ethylene oxide,
.005% insoluble phthalocyanine green dye,
balance, water of hydration and moisture.

What is claimed is:

1. An alkaline dishwasher detergent composition con-
sisting essentially of:

6

- (a) 25% to 75% alkaline sequestrant builder salt se-
lected from the group consisting of an inorganic poly-
phosphate, an organic aminopolyacetate, or an or-
ganic polyphosphonate,
- (b) 5% to 50% sodium silicate having an $\text{SiO}_2:\text{Na}_2\text{O}$
ratio ranging from 3.6:1 to 1:1,
- (c) 0.5% to 25% active chlorine containing bleaching
compound,
- (d) $\frac{1}{2}\%$ to 10% condensation product of 1 mole of
 $\text{C}_{13}\text{--C}_{21}$ fatty alcohol with 5 to 12 moles of ethylene
oxide, and
- (e) 0.001 to 0.015% insoluble phthalocyanine green
dye percentage by weight.

2. The composition of claim 1 wherein the builder salt
is in an amount of 35% to 60%; the silicate in an amount
of 10% to 25%; the chlorine-containing bleaching com-
pound is chlorinated trisodium phosphate, or sodium or
potassium dichlorocyanurate and the amount thereof is
1% to 15%; the condensation product is of 1 mole of
 $\text{C}_{16}\text{--C}_{18}$ fatty alcohol with 6 to 11 moles of ethylene
oxide.

3. The composition of claim 2 wherein the builder salt
is sodium tripolyphosphate, the bleaching compound is
chlorinated trisodium phosphate, the alcohol in the con-
densation product is tallow fatty alcohol and the amount
of green dye is 0.002% to 0.01%.

References Cited

UNITED STATES PATENTS

2,863,835	12/1958	Goldsmith et al.	252—99
3,468,803	9/1969	Knapp et al.	252—99 X

MAYER WEINBLATT, Primary Examiner

U.S. Cl. X.R.

252—187