

1

3,122,508

HEAVY DUTY DETERGENT COMPOSITIONS

Richard A. Grifo, Easton, Pa., Raymond L. Mayhew, Phillipsburg, N.J., Andrew Stefick, Easton, Pa., and Fred E. Woodward, Plainfield, N.J., assignors to General Aniline & Film Corporation, New York, N.Y., a corporation of Delaware

No Drawing. Filed July 28, 1960, Ser. No. 45,788

14 Claims. (Cl. 252-135)

This invention relates to heavy duty detergent compositions, and more particularly to alkaline detergent compositions containing an alkali metal polyphosphate.

A great number of heavy duty detergent compositions are known in the art, such compositions generally being alkaline in nature and containing an alkali metal polyphosphate usually combined with other neutral or alkaline reacting inorganic salts such as alkali metal silicates, carbonates, bicarbonates, phosphates, sulfates, borates, and the like. In these compositions, the alkalinity is responsible for a large part of the cleaning function by virtue of the resulting ability to saponify fats, dissolve proteins, etc. The polyphosphates sequester the water hardness by forming complexes with the calcium and magnesium ions normally present in most natural waters, thereby preventing the formation of undesirable precipitates. They also function to prevent the formation of sticky soap curds and the like. They are accordingly highly desirable components of heavy duty detergent compositions, contributing a high proportion of detergency, soil removal and other similar functions.

It has also been customary to include in such heavy duty detergent compositions one or more synthetic organic detergents to provide the desired amount of detergent, foaming and wetting action necessary in a heavy duty liquid detergent suitable for household use.

A number of other auxiliary agents have also been included in such compositions to adapt them to certain specific application. Thus, optical brighteners, foam stabilizers, soil suspending agents and the like have been employed in heavy duty clothes washing compositions to improve whiteness of the washed clothes, supply a higher or smaller proportion of foam or suds as desired, prevent soil redeposition, and the like. Coloring materials which may or may not be fluorescent, perfumes, corrosion inhibitors and inhibitors to prevent tarnishing of German silver such as mercaptobenzothiazole, benzotriazole, ethylene thiourea, and the like have also been made use of in such heavy duty detergent compositions.

Such known heavy duty detergent compositions have been commonly troubled with one or a number of deficiencies and disadvantages. Thus, the presence of the polyphosphate tends to cause the usual organic synthetic detergents in the composition to separate from solution at room temperature whereby a heterogeneous or multiphase composition results. Hydrotropes or solubilizers such as sodium xylene sulfonate, sodium benzene sulfonate, sodium toluene sulfonate, and the like have been employed to promote solubility of the organic synthetic detergents in the presence of the polyphosphates, but the addition of such solubilizers involves added costs and tends to dilute or diminish the desired detergent activity of the compositions since they do not contribute any detergent function thereto. This problem of compatibility and/or solubility of the organic detergent in the presence of the polyphosphate is important in the case of liquid concentrates such as heavy duty liquid clothes washing compositions, floor and wax cleaners and other hard surface cleaners, all-purpose cleaners, and the like which should be provided in a clear, homogeneous form. Further, such liquid concentrates as have been provided often do not have the desired viscosity and/or slippery feel and

2

are too "watery." In addition, these compositions often cause corrosion, tarnishing, etc. of metal, vitreous, ceramic, and other surfaces with which they come in contact. Still further, such heavy duty detergent compositions often yield too much or too little foam or suds.

Previously available heavy duty detergent compositions in powder form have also been subject to caking, gumming, dusting, and/or decomposition of components of the composition. The use of certain types of synthetic organic detergents in such compositions has been found to result in decreased brightener efficiency. This decrease is evidenced by a lower brightness or reflectance of the washed objects, attributable to a decrease in the proportion of brightener adsorbed on the washed objects.

Still further, the problem of obtaining maximum detergency per unit of detergent composition is of course always present, which problem may be intensified by any one of the above mentioned deficiencies or disadvantages.

It is an object of this invention to provide a heavy duty detergent composition which will not be subject to one or more of the above mentioned deficiencies and disadvantages. Other objects and advantages will appear as the description proceeds.

The attainment of the above objects is made possible by this invention, which broadly comprises the provision of an alkaline cleaning composition, which in the form of an 0.3% by weight aqueous solution has a pH of about 8 to 12, comprising approximately by weight, 1 to 10 parts of an alkali metal polyphosphate, and 1 to 10 parts of the reaction product of P_2O_5 with a nonionic surface active agent having the molecular configuration of a condensation product of at least 1 mole of ethylene oxide with 1 mole of a compound containing at least 6 carbon atoms and at least 1 reactive hydrogen atom in a ratio of 1 mole of P_2O_5 for each 2 to 4.5 hydroxy groups in such nonionic agent. The invention also includes such an alkaline cleaning composition further containing about 0.025 to 3%, based on the weight of said reaction product, of an optical brightening agent soluble to the extent of less than about 0.1% in water at 25° C.

The compositions of this invention have been found to be highly effective and improved with respect to one or more of the above mentioned deficiencies and disadvantages. They may be employed for the production of homogeneous liquid concentrates containing relatively high proportions of polyphosphate and the defined surface active reaction product. Such concentrates may also be provided which have a desirable viscosity and feel. The compositions of this invention when provided in particulate form have improved resistance to dusting, caking, gumming, and/or decomposition of components of the composition. Further, these compositions have highly desirable low or controlled foaming properties, relatively high detergency properties, and reduced corrosive action on metal surfaces with which they may come in contact. Still further, an unexpectedly improved brightener efficiency is obtained as compared with heavy duty detergent compositions containing alkali metal polyphosphates in combination with other synthetic organic detergents, particularly with respect to optical brightening agents of relatively low solubility.

The alkali metal polyphosphates employed in the compositions of this invention are well known in the art and may also be referred to as condensed phosphates or molecularly dehydrated phosphates. In general, these polyphosphates have an analytical ratio of alkali metal oxide to P_2O_5 of less than 3:1, such ratio usually falling within the range of about 1:2 to 5:3. These polyphosphates are available as alkali metal pyrophosphates, metaphosphates, and polyphosphates in monomeric or polymeric form as the pyrophosphates, triphosphates, tetraphosphates, decaphosphates and the like. As representa-

tive of commonly employed alkali metal polyphosphates, useful in the compositions of this invention, there may be mentioned the tetrasodium and tetrapotassium pyrophosphates, sodium and potassium tripolyphosphates, tetraphosphates, pentaphosphates, hexametaphosphates, and mixtures of two or more thereof and the like. It will be understood that the ammonium and amine salts of polyphosphoric acids are to be regarded as substantial equivalents of the above-described alkali metal polyphosphates.

The above defined reaction product of P_2O_5 with a non-ionic surface active agent may be prepared by the process described and claimed in the copending applications of Nunn and Hesse, Serial No. 852,188, filed November 12, 1959, and of Nunn, Serial No. 856,367, filed December 1, 1959, now respectively U.S. Patents 3,004,056 and 3,004,057. As described in the said Nunn and Hesse application, the reaction between the P_2O_5 and the non-ionic surface active agent is conducted under substantially anhydrous conditions and at a temperature below about 110° C. In its preferred form, the reaction is carried out by adding the P_2O_5 gradually, with vigorous agitation to the nonionic surface active agent in liquid form. The reaction is exothermic and cooling is in some cases necessary to keep the temperature below 110° C., since discolored and darkened products tend to be produced above this temperature. The reaction proceeds continuously during the addition of the P_2O_5 and is preferably followed by maintenance of the reaction mixture at ambient temperatures up to 110° C. for an additional period of time after completion of such addition to allow for complete solution of the P_2O_5 and reaction with the non-ionic surface active agent.

The exact chemical constitution of the products produced by the above described reaction is not definitely known in view of the recognized tendency of the P_2O_5 to form complex products and polymers in such reactions with hydroxylic compounds. In general, the product will usually contain about 20 to 45% of the secondary phosphate ester of the nonionic agent, 30 to 80% of the primary phosphate ester, 0 to 40% of unreacted nonionic agent, and small amounts of unidentified by-products.

By carrying out the reaction in the presence of a small amount of a phosphorus-containing compound selected from the group consisting of hypophosphorous acid, salts of hypophosphorous acid, phosphorous acid, and salts and esters of phosphorous acid, preferably sodium hypophosphite or hypophosphorous acid, as described in said Nunn application, lighter colored or substantially colorless reaction products are obtained.

The nonionic surface active agents employed for reaction with P_2O_5 are well known in the art and are disclosed along with suitable methods for their preparation in numerous patents and other publications. In general, they may be obtained by condensing a polyglycol ether containing the required number of alkenoxy groups or an alkylene oxide such as propylene oxide, butylene oxide, or preferably ethylene oxide, or mixtures thereof, with an organic compound containing at least 6 carbon atoms and a reactive hydrogen atom. As such compounds containing a reactive hydrogen atom there may be mentioned alcohols, phenols, thiols, primary and secondary amines, and carboxylic and sulfonic acids and their amides. These compounds may obviously contain more than one reactive hydrogen atom, i.e. more than one hydroxy, mercapto, amino, amido, carboxylic, sulfonic or sulfonamido group, each such group in the compound being reactive with the alkylene oxide in suitable proportions. The amount of alkylene oxide or equivalent condensed with the reactive hydrogen-containing compound, i.e. the length of the polyoxyalkylene chain, will depend primarily upon the particular compound with which it is condensed. As a convenient rule of thumb, an amount of alkylene oxide or equivalent should be employed which will result in a condensation product containing about 20 to 85% by weight of combined alkylene oxide. How-

ever, the optimum amount of alkylene oxide for attainment of the desired hydrophobic-hydrophilic balance may be readily determined in any particular case by preliminary test and routine experimentation.

The reaction between the reactive-hydrogen-containing organic compound and the alkylene oxide in the production of the above described nonionic surface active agents is well known in the art, being preferably carried out at elevated temperatures and pressures and catalyzed by quaternary hydroxides, amines, acids and/or coordinating type compounds although strong alkaline catalysts such as KOH or NaOH and the like are preferred because of fewer by-products formed and the more easily controlled reaction conditions. The reaction is substantially quantitative, although it will be understood that the product of this reaction between the alkylene oxide, preferably ethylene oxide, and the organic reactive hydrogen-containing compound will be a mixture of polyoxyalkylene derivatives of varying oxyalkylene chain lengths, the average of which substantially corresponds to the amount of alkylene oxide reactant. Such product will of course always contain an average of at least one hydroxy group (in a terminal $-C_2H_4OH$ group) per molecule.

In the production of the above described nonionic surface active agents, the following are illustrative examples of types of organic compounds containing a reactive hydrogen atom:

(1) Aromatic mono- and poly-hydroxy compounds such as phenols, naphthols, benzene and naphthalene diols, triols and tetrols and the like. In this group, alkyl phenols are preferred containing 1 to 3 alkyl substituents of from 4 to 20 carbon atoms each. Some examples of such compounds are the normal and isomeric mono-, di-, and tri-butyl-, -nonyl, and octadecylphenols and cresols, and phenols and cresols substituted by a plurality of different such alkyl groups.

(2) Straight and branched chain, saturated and unsaturated aliphatic monohydric and polyhydric alcohols of natural or synthetic origin. Among this group are the alcohols derived from animal and vegetable sources such as lauryl alcohol, stearyl alcohol, and the like. Also included are the diol precursors of the Pluronic type nonionic surface active agents, generally prepared by polyoxyethylenation of a polymerized alkylene oxide of at least 3 carbon atoms, preferably propylene oxide, or of the reaction product of a plurality of moles of propylene oxide or substituted propylene oxide with alkylene diamines such as ethylene diamine and propylene diamine, polyalkylene polyamines, and alkane diols such as ethylene glycol, hexamethylene glycol, and the like. These agents of the Pluronic type may range in molecular weight from about 300 to 10,000. This group also includes the primary aliphatic alcohols containing a plurality of side chains. Such multi-branched chain alcohols may be produced by various methods, preferably by subsection of an olefin containing at least 7 carbon atoms and at least 2 side chains, such as tripropylene, tetrapropylene, pentapropylene, diisobutylene, triisobutylene and the like to the Oxo process, involving the catalytic reaction of the olefin with carbon monoxide and hydrogen to form an aldehyde followed by catalytic reduction of the aldehyde to the corresponding primary alcohol. Other alcohols in this group are the essentially straight chain alcohols produced from Fischer-Tropsch olefins by the Oxo process or those produced by oxidation of Ziegler type polymer intermediates. Such intermediates, or mixtures thereof, made by polymerizing ethylene with a metal (e.g. aluminum) alkyl, have an even number of carbon atoms averaging 10 to 24 per molecule in the chain.

(3) Higher fatty acids of animal and vegetable origin and mixtures containing the same, such as lauric acid, oleic acid, stearic acid, the animal and vegetable fats and oils containing same, or the acids derived by oxidation of suitable petroleum fractions.

(4) Aliphatic and aromatic mono- and poly-mercapto

compounds including cetyl mercaptan, dodecyl mercaptan, alkyl benzomercaptan, alkyl thiophenol, thionaphthol, and the like.

(5) Aliphatic and aromatic mono- and polyamines, including laurylamine, stearylamine, alkyl benzylamine, alkyl naphthylamine, dodecylene diamine, tetrapropylene pentamine, and the like.

(6) Carboxylic acid amides such as lauric acid amide, stearic acid amide and the like.

(7) Sulfonamides such as dodecyl sulfonamide, dodecylbenzene sulfonamide, and the like.

These and other types of organic compounds containing reactive hydrogen atoms suitable for reaction with alkylene oxides are disclosed for example in United States Patents 1,970,578, 2,002,613, 2,085,706, 2,174,761, 2,205,021, 2,213,477, 2,266,141, 2,593,112, 2,674,619, 2,677,700, 2,766,212 and others.

The following is an illustrative, non-limitative list of some specific examples of suitable nonionic surface active agents which may be employed as reactants in the present invention. In this list, "E.O." means "ethylene oxide" and the number preceding same refers to the number of moles thereof reacted with one mole of the given reactive hydrogen-containing compound.

Nonylphenol -----	+9-11 E.O.
Nonylphenol -----	+2 E.O.
Dinonylphenol -----	+7 E.O.
Dodecylphenol -----	+18 E.O.
Castor oil -----	+20 E.O.
Tall oil -----	+18 E.O.
Oleyl alcohol -----	+18 E.O.
Lauryl alcohol -----	+4 E.O.
Lauryl alcohol -----	+15 E.O.
Hexadecyl alcohol -----	+12 E.O.
Hexadecyl alcohol -----	+20 E.O.
Octadecyl alcohol -----	+20 E.O.
Oxo tridecyl alcohol (from tetrapropylene) -----	+7 E.O.
Oxo tridecyl alcohol (from tetrapropylene) -----	+10 E.O.
Oxo tridecyl alcohol (from tetrapropylene) -----	+15 E.O.
Dodecyl mercaptan -----	+9 E.O.
Soya bean oil amine -----	+10 E.O.
Rosin amine -----	+32 E.O.
Cocoonut fatty acid amine -----	+7 E.O.
Cocoa fatty acid -----	+10 E.O.
Dodecylbenzene sulfonamide -----	+10 E.O.
Decyl sulfonamide -----	+6 E.O.
Oleic acid -----	+5 E.O.
Polypropylene glycol (30 oxypropylene units) -----	+10 E.O.

In general, the nonionic surface active agents preferred herein for the production of the desired reaction products with P_2O_5 are the polyoxyethylenated derivatives of alkyl phenols and aliphatic alcohols containing at least 10 carbon atoms, such as the polyoxyethylene ethers of coco alcohols containing an average of 12 carbon atoms, nonyl phenol, dodecyl phenol, dinonyl phenol, and Oxo tridecyl alcohol as derived from tetrapropylene or triisobutylene.

It has also been determined that reaction products in the range of about 2 to 3.5 and preferably 2 to less than 3 hydroxy groups in the nonionic surface active agent per mole of P_2O_5 have increased solubility and the use of such reaction products is accordingly preferred when formulating detergent composition in accordance with this invention which are to be supplied in the form of a liquid concentrate. However, it will be understood that reaction products in the range of 2 to 4.5 hydroxy groups in the nonionic per mole of P_2O_5 may be employed in producing detergent compositions in accordance with this invention in any desired form such as liquid concen-

trates, powders, shaped compositions, pastes, and the like. It will also be understood that such phosphate ester reaction products may be employed in the form of the free acid or soluble salts thereof with alkali metals, ammonium or organic amines. Optimum proportions of nonionic: P_2O_5 , selection of nonionic precursor, identity of the alkali metal polyphosphate, proportions of components and the like for any specific end use may be readily determined by routine experimentation.

It is well known that fibrous materials such as textile fibers, paper and the like are difficult to provide and maintain in bright white shades, since such shades normally have or develop a yellowish shade which cannot be removed by ordinary methods of bleaching, washing or the like. The heretofore employed methods of "bluing" white materials with blue pigments or fugitive blue dyestuffs have already become obsolete and superseded by methods employing fluorescent optical bleaching agents or brighteners as additives to or in the material or to the washing bath or other treating solution. These optical brightening agents may be classed as colorless dyes in that they are generally substantive to the fiber and perform their desired function by absorption of the ultraviolet light present in ordinary daylight and conversion and reemission of this light in part or in whole within the visible region of the spectrum. The converted light is preferably in the blue range of the spectrum whereby the yellowness in the white material is neutralized and a purer, brighter white shade obtained.

A great many optical brightening agents of various different chemical constitutions have been proposed and employed for use in detergent compositions for washing white fibrous materials. As examples of such agents there may be mentioned stilbenes, diamino stilbenes, acylated, cyanuric and triazolyl derivatives of such stilbenes, diphenyl derivatives, dibenzothioephene derivatives, aminocoumarone salts, derivatives of diazotized amino-containing benzoxazole, benzthiazole and benzimidazole compounds, and the like. These and other optical brightening agents are disclosed in U.S. Patents 2,171,427, 2,563,493, 2,563,795, 2,581,059, 2,612,501, 2,618,636, 2,643,198, 2,666,062, 2,668,777, 2,713,054, 2,713,055, 2,713,056, 2,715,630, 2,715,632, 2,784,183 and 2,817,665, application Serial No. 381,856, published May 11, 1943, by the A.P.C., British Patent 584,484 and other patents. These agents are more or less soluble in water, increased solubility usually being accomplished by inclusion of one or more water solubilizing groups such as sulfonic acid, carboxylic acid, phosphoric acid or other anionic radicals. In formulating heavy duty detergent compositions containing alkali metal polyphosphates and optical brightening agents, it has been very often found that on further inclusion in such compositions of synthetic organic surface active agents such as organic sulfonates, nonionic surface active agents of the type described above, and the like, the substantivity of the brightening agents for the fibrous material is undesirably reduced whereby a relatively high proportion of the brightening agent in the wash bath is not adsorbed by the fibrous material but is instead lost in the rinse water.

It has been unexpectedly found that the use of the above defined reaction products of nonionic surface active agents with P_2O_5 in detergent compositions containing alkali metal polyphosphates and optical brightening agents soluble to the extent of less than about 0.1% in water at 25° C. results in a substantial relative increase in the amount or proportion of brightening agent remaining in the washed fibrous material as compared with compositions containing other organic surface active agents, for example the described nonionic surface active agents, instead of the defined reaction products of such nonionic agents with P_2O_5 . This relative improvement in substantivity is peculiarly restricted to those brightening agents having the defined low solubility, the substantivity of the more soluble brightening agents being unaffected

and in some cases even reduced. Brightening agents of the sulfonated stilbene derivative type are preferred for use in the present compositions, although it will be understood that any other type of brightening agent may be employed having the defined solubility characteristics. In general, the brightening agent may be employed in proportions of about 0.025 to 3%, based on the weight of the defined nonionic- P_2O_5 reaction product.

The compositions of this invention may also include other usual constituents of heavy duty detergent compositions as for example 0 to 5 parts of one or a mixture of water soluble inorganic salts effective for adjustment of pH values, buffering, corrosion resistance, and the like such as sodium and potassium tetraborates, perborates, phosphates, carbonates, sequicarbonates, bicarbonates, chlorides, sulfates, silicates, and the like; 0 to 1 part of one or a mixture of soil suspending agents, these being generally water soluble polymeric materials such as cellulose glycollic acid, cellulose ethane sulfonic acid, hydroxyethyl methyl cellulose, starch, hydroxyethyl starch, starch glycollic acid, lichenin, xylan, polymeric carboxylic acids such as copolymers of maleic anhydride with styrene, vinyl methyl ether, and vinyl ethyl ether, polyvinyl pyrrolidone, etc.; and any desired amount of deodorants, disinfectants, coloring matters, tarnish and corrosion inhibitors, caustic for adjustment of pH, sequestrants such as ethylene diamine tetracetic acid, sodium gluconate and polyhydric sugar acids, foam stabilizers such as dialkanolamides of fatty acids, etc.

There may also be included in the above described heavy duty detergent compositions small proportions of hydrotropes or solubilizers such as sodium xylene sulfonate, sodium toluene sulfonate and the like although the necessity for their use is minimized in accordance with this invention. Further, these compositions may also contain other organic surface active agents of the anionic or nonionic type such as the well known alkyl (e.g. lauryl) sulfates, alkylaryl (e.g. dodecylbenzene) sulfonates, sodium taurides, fatty acid soaps, nonionic agents of the type described above, and the like. Generally, proportions of these additive surface active agents are no higher than those of the P_2O_5 reaction products described above, to obtain maximum advantage of the basic concepts of this invention. It has further been found that the above described P_2O_5 reaction products with nonionic surface active agents exert a solubilizing effect upon alkylaryl sulfonates and other such surface active agents in the presence of alkali metal polyphosphates whereby the necessity for using a hydrotrope is minimized or eliminated.

In view of the improved properties and functions of the detergent compositions of this invention, they may be employed with advantage for a number of different end uses including liquid floor and wall cleaners, waxed surface cleaners, scrub soaps, controlled foam heavy duty liquid and powder detergents for washing fibrous materials and the like, all purpose cleaners, wax strippers, dairy cleaners, and the like.

The following examples are only illustrative of the present invention and are not to be regarded as limitative. All parts and proportions referred to herein and in the appended claims are by weight unless otherwise indicated. As appears in the examples, "P.E." means phosphate ester; "STPP" means sodium tripolyphosphate; "TSPP" means tetrasodium pyrophosphate; "TSP" means trisodium phosphate; "TKPP" means tetrapotassium pyrophosphate; "E.O." means ethylene oxide, its proportion in the defined nonionic surface active agent being expressed in moles per mole of reactive hydrogen containing compound and/or in weight percent in the nonionic surfactant. All compositions exemplifying the invention have, in 0.3% aqueous solution, a pH of about 8 to 12.

The constitution of representative phosphate ester surfactants is disclosed in Table A. All are prepared by reaction between P_2O_5 and the designated nonionic sur-

factant precursor in the stated molar proportions and in the presence of sodium hypophosphite following the procedure described in the examples in said Nunn application Serial No. 856,367.

TABLE A

Nonionic Surfactant Precursor

Phosphate Ester	Reactive Hydrogen-Containing Compound (1 mole)	Moles E.O.	Percent E.O.
I	Nonyl Phenol		45
II	do.	6	54
III	do.	9	65
IV	do.	15	75
V	do.		80
VI	do.		86
VII	do.	100	
VIII	Dodecyl Phenol	6	50
IX	do.	11.5	75
X	Dinonyl Phenol	17	65
XI	Oxo Tridecyl Alcohol (from tetrapropylene)	3.5	
XII	do.	7	59
XIII	do.	10	68
XIV	do.	15	77
XV	Oleyl Alcohol	7	54
XVI	Lauryl Alcohol	4	49
XVII	Pluronic L-62 [HO(C ₂ H ₄ O) ₅ (C ₃ H ₆ O) ₃₀ (C ₂ H ₄ O) ₅ H]	10	

TABLE 1

Viscosity in Centipoises of Clear Aqueous Solutions

Example	Polyphosphate	Phosphate Ester II				
		4%	6%	8%	10%	25%
1	2% STPP	9	16	34	154	
2	2% TSPP					
3	3% STPP					
4	3% TSPP	59	162	269	337	
5	4% STPP					
6	4% TSPP					
7	6% STPP	107	158	191	208	
8	6% TSPP					
9	None					
10	3% TSP		238			
11	3% TSPP					
12	3% STPP					
13	10.4% TSP		250			
14	5.5% STPP					
15	0.5% STP					
16	5% STPP		133			
17	1% TSP					
18	6% STPP					
19			200			596
20						
21						

The results appearing in Table 1 were obtained with a Brookfield viscosimeter LV model, Serial No. 832. The examples in the table show that compositions may be produced in accordance with the invention having a predetermined viscosity depending upon the proportions of components and the like, although it will be understood that the identity of the phosphate ester employed will also be a factor. The phosphate ester II used in the above examples is the reaction product of 1 mole of P_2O_5 with 4.0 moles of the nonionic precursor. The solutions in these examples, in common with other compositions included in this invention have a very low corrosive action on metal surfaces. These solutions are highly effective scrub soaps for hard surfaces such as floors, walls, metal articles, and the like. By proper adjustment of concentrations and proportions of components, the solutions may be employed as wax strippers or as wax cleaners. Thus, the solution of Example 8 is highly effective as a wax cleaner, having a very high cleaning efficiency in addition to the desirable property of removing only a very small proportion of the wax. The solution may be shipped in unlined mild steel containers without danger of corrosion. No. 1006 steel panels immersed in this solution for two days at room temperature and at 130° F. showed no signs of rusting.

TABLE 2

Solubility of 10% of Phosphate Esters in Aqueous TKPP Solutions

Example	Phosphate Ester	Mole Ratio Non-ionic:P ₂ O ₅	Percent TKPP							
			5	10	12	15	17	20	25	30
12	II	4.0:1	Sol	54	Sol	Sep				
13	II	3.0:1	Sol	Sol	Sol	Sol	40	Sep		
14	II	2.9:1	Sol	Sol	Sol	Sol	47	Sep		
15	II	2.8:1	Sol	Sol	Sol	Sol	63	Sep		
16	II	2.7:1	Sol	Sol	Sol	Sol	70	Sep		
17	II	2.6:1	Sol	Sol	Sol	Sol	67	Sep		
18	II	2.5:1	Sol	Sol	Sol	Sol	68	Sep		
19	II	2.2:1	Sol	Sol	Sol	Sol	64	Sep		
20	II	2.0:1	Sol	Sol	Sol	Sol	49	Sep		
21	I	4.0:1		Sep						
22	II	4.0:1	Sol	54		Sep				
23	III	4.0:1	Sol	0	Sol	33		Sep		
24	III	2.7:1	Sol	Sol	Sol	Sol	Sol	35	Sep	
25	IV	4.0:1	Sol	85		Sep				
26	IV	3.0:1	Sol	5		Sep				
27	IV	2.5:1	Sol	Sol	Sol	85	Sep			
28	V	4.0:1	Sol	46		Sep				
29	VI	4.0:1		Sep						
30	VII	4.0:1		Sep						
31	VIII	2.5:1				Sol		Sep		
32	IX	2.7:1	Sol	Sol		Sep				
33	X	2.7:1				42		Sep		
34	XI	4.0:1		Sep						
35	XII	4.0:1	Sol	84				Sep		
36	XIII	4.0:1	Sol	74				Sep		
37	XIV	4.0:1	Sol	85		Sep				
38	XI	2.7:1		Sep						
39	XII	2.7:1	Sol	Sol	Sol	Sol	Sol	46	Sep	
40	XIII	2.7:1	Sol	Sol	Sol	Sol	Sol	65	Sep	
41	XIV	2.7:1	Sol	Sol	Sol	Sol	85	Sep		
42	XVI	4.0:1	Sol	Sol	Sol	Sol	Sol	45	Sep	
43	XVI	2.5:1	Sol	Sol	Sol	Sol	Sol	Sol	72	Sep
44	XV	2.5:1	Sol	Sol	Sol	Sol	Sol	Sol	60	Sep
45	XVII ¹	4.0:1	45							

¹ Nonionic precursor, Pluronic L-62, is insoluble in 5% TKPP solution.

In common with the base nonionics, the solubility of these phosphate ester surfactants decreases with increasing temperatures. Therefore, as the solubility limit is

approached, the mixtures show a cloud point, i.e., become cloudy at a temperature which is a unique function of the concentrations and the phosphate ester. The numbers in the above Table 2 refer to the maximum temperature (° C.) at which the phosphate ester surfactant is completely soluble and the solution clear. The term "Sol." indicates solubility to give a clear solution at temperatures up to the boiling point. The term "Sep." means that a separation of the phosphate ester from solution has occurred, usually in the form of a hazy or cloudy suspension. The examples in the above table show the unusual compatibility of these phosphate esters with aqueous solutions of TKPP. The table also shows the effect of variation in oxyethylene content of the base nonionic upon the solubility in TKPP of the corresponding phosphate ester, and the effect of decreasing ratios of base nonionic to P₂O₅. In general, it is apparent that, other things being equal, highest solubilities are obtained with propor-

TABLE 3
Detergency Test

Example	Phosphate Ester	Mole Ratio Non-ionic: P ₂ O ₅	Final Reflectance								
			50 p.p.m. Water					300 p.p.m. Water			
			T.F. No. 26	A.C.H. No. 115	P.H.D.	Average	Redeposition	T.F.	P.H.D.	Redeposition	
46	II	4:1	33.3	49.6	73.0	53.6	75.8	36.9	70.0	73.7	
47	II	3.0:1	32.4	47.6	71.9	50.6	77.3	39.7	70.0	75.5	
48	II	2.9:1	33.7	46.6	73.6	52.3	79.0	37.1	69.6	75.8	
49	II	2.8:1	33.2	47.5	73.1	52.9	78.6	37.7	69.5	76.2	
50	III	2.7:1	38.4	49.9	72.1	53.5	76.5	36.9	71.7	76.7	
51	IV	3.0:1	39.5	51.9	72.0	54.5	77.0	37.9	73.0	77.3	
52	XII	2.7:1	38.1	47.4	71.4	52.3	75.0	36.1	69.9	74.3	
53	XIII	2.7:1	41.6	47.1	72.3	53.7	75.3	33.8	70.3	75.2	
54	XVI	2.5:1						35.8	73.0	77.5	
55	XV	2.5:1						36.2	73.0	76.8	
56	VIII	2.5:1						35.5	73.5	75.8	
57	None		31.3	44.1	70.0	48.5	77.0	29.0	64.1	74.3	

approached, the mixtures show a cloud point, i.e., become cloudy at a temperature which is a unique function of the concentrations and the phosphate ester. The numbers in the above Table 2 refer to the maximum temperature (° C.) at which the phosphate ester surfactant is completely soluble and the solution clear. The term "Sol." indicates solubility to give a clear solution at temperatures up to the boiling point. The term "Sep." means that a separation of the phosphate ester from solution has occurred, usually in the form of a hazy or cloudy suspension. The examples in the above table show the unusual compatibility of these phosphate esters with aqueous solutions of TKPP. The table also shows the effect of variation in oxyethylene content of the base nonionic upon the solubility in TKPP of the corresponding phosphate ester, and the effect of decreasing ratios of base nonionic to P₂O₅. In general, it is apparent that, other things being equal, highest solubilities are obtained with propor-

In the examples in the above Table 3, formulations consisting of 20% TKPP in water with and without 10% phosphate ester surfactant were tested as industrial laundry detergents in a Terg-O-Tometer (U.S. Testing Company) test washer operated at 125 r.p.m. for 10 minutes using 0.3% detergent formulation in 50 p.p.m. (Easton, Pennsylvania), tap water and in 300 p.p.m. water at 120° F. for washing soiled cloths at a cloth:liquor ratio of 1:20 followed by a thorough cold water rinse. ACH (American Conditioning House) No. 115 and T.F. (Test Fabrics) No. 26 are standardized soiled cloths made available to the trade for detergency tests and the like. These soiled cloths are described in "Detergency Evaluation and Testing" by J. C. Harris, Interscience Publishers, Inc., New York, 1954, at, respectively, pages 84 and 88. In these tests the cloths are employed in the form of 1½" x 3" swatches. The "P.H.D." soiled cloths are 1½" x 3" cotton swatches soiled by padding with hotel dirt obtained

from sweepings of a local (Easton, Pennsylvania) hotel. The initial reflectances of the soiled cloths as measured with a reflectometer were 25 or less. The washed swatches were measured with the reflectometer to determine soil removal and redeposition. Reflectance values vary directly with the cleanliness of the cloths (inversely with the proportion of soil on the cloths).

The higher reflectance values shown in Examples 46 to 56 as compared with Example 57 in which no phosphate ester surfactant was employed establishes the improvements in detergency attainable by the use of the compositions of this invention.

TABLE 4

Brightener Retarding on Indianhead Cotton

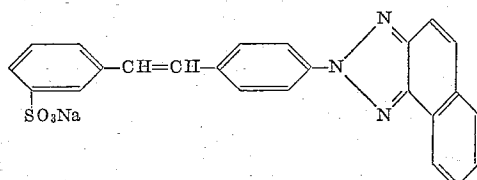
Example	Surfactant	Mole Ratio Nonionic: P ₂ O ₅	Brightener					
			I	II	III	IV	V	VI
58.....	Nonionic Precursor of P.E. III.....	-----	24.0	25.0	48.5	7.0	49.0	66.5
59.....	Nonionic Precursor of P.E. IV.....	-----	34.5	-----	-----	-----	-----	-----
60.....	Nonionic Precursor of P.E. XIII.....	-----	40.0	23.0	-----	12.0	55.5	48.0
61.....	P.E. II.....	4:1.....	47.0	-----	-----	-----	-----	-----
62.....	P.E. II.....	2.8:1.....	54.0	-----	46.0	-----	-----	-----
63.....	P.E. III.....	2.7:1.....	53.0	35.0	48.0	33.0	61.5	35.0
64.....	P.E. IV.....	4:1.....	48.5	-----	-----	-----	-----	-----
65.....	P.E. X.....	2.7:1.....	49.0	-----	-----	-----	-----	-----
66.....	P.E. XII.....	2.8:1.....	57.0	-----	-----	-----	-----	-----
67.....	P.E. XIII.....	2.8:1.....	52.0	43.0	-----	36.0	64.0	29.0

In the examples in the above Table 4, the test method consists of washing clean cotton 7" x 7" swatches weighing about 10 g. in a Terg-O-Tometer (U.S. Testing Company) in 1000 ml. of detergent solution containing 0.25% of the formulation being tested. The ratio of cloth to detergent solution is 1 g. to 100 ml. Since the normal ratio of cloth to detergent solution is 1 to 20, this test is equivalent (as a measure of dyeing efficiency) to washing the material five times in succession using fresh detergent solution each time.

The amount of brightener or fluorescent dye deposited from the detergent solution onto the cloth is determined by means of a fluorescent photometer which is described in Beiswanger and Hemmendinger, "Photometric Evaluation of Brightening Agents," Soap and Sanitary Chemicals, 1951, and the use of which for evaluation of treated swatches is described in Beiswanger and Sherburne, "Textile Application of Brighteners," Am. Dyestuff Reporter, 41, 144-148 (1952). The brightener units read by the photometer and shown in the table are a function of the logarithm (base C) of the concentration of brightener on the cloth; a two fold increase in brightness units represents about four times as much brightener on the cloth. A difference of 10 units is readily discernible by the average individual in sunlight. A difference in five units is discernible under ultra-violet light. In Table 4, the various surfactants and brighteners were employed in the following formulation:

Brightener	Parts
Surfactant	0.088
STPP	12.0
TSPP	22.5
Sodium sulfate	22.5
SMS (sodium metasilicate)	45.5
Sodium carbonate	6.0
CMC (carboxymethylcellulose)	3.0
	0.5

In the above table, brightener I has the formula



Brightener II is the compound described in Example 5 of U.S. 2,784,183. Brightener III is the compound described in Example 16 of application No. 381,856, published May 11, 1943, by the Alien Property Custodian. Brightener IV is the compound described in Example 16 of U.S. 2,171,427. Brightener V is the compound described in Example 1 of U.S. 2,618,636. Brightener VI is the compound of claim 5 of U.S. 2,488,094 after-treated with epichlorhydrin. Brighteners I, II, IV and V are soluble to the extent of less than about 0.1% in water at 25° C. whereas brighteners III and VI are relatively more soluble. The table shows that on Indianhead

cotton, compositions of the present invention enable the attainment of surprisingly increased brightener efficiency (increased build-up of brightener on the cloth) as compared with corresponding compositions containing as surfactant the nonionic precursor of the indicated phosphate ester when the brightener is soluble to the extent of less than about 0.1% in water at 25° C., but not when the brightener is relatively more soluble.

TABLE 5

Brightener Retarding on Resin-Treated Cotton

Example	Surfactant	Mole Ratio Nonionic: P ₂ O ₅	Brightener	
			V	IV
68.....	Nonionic Precursor of P.E. XIII.....	-----	15.0	6.0
69.....	Nonionic Precursor of P.E. III.....	-----	13.0	1.0
70.....	P.E. XIII.....	2.7:1.....	21.0	19.0
71.....	P.E. III.....	2.7:1.....	21.5	20.0

The above Table 5 shows results of a brightener retarding test similar to that employed in the examples in Table 4, but applied to resin treated (wash-and-wear) cotton. This table also shows the improved brightener efficiencies attainable by use of the compositions of this invention as compared with similar compositions containing as surfactant the nonionic precursor of the indicated phosphate ester, although brightener efficiencies attainable with resin treated cotton are notably inferior to those attainable with Indianhead cotton, at least with the tested formulations.

Additional formulations representative of the compositions of this invention are given in the following examples:

EXAMPLE 72

70	P.E. XVI, nonionic:P ₂ O ₅ =2.5:1.....	Parts
	TKPP	10
	SMS	20
	Water	3
75	KOH sufficient to adjust pH to 11.5.	67

13

EXAMPLE 73

P.E. XVI, nonionic: P ₂ O ₅ =2.5:1	7.47
TKPP	15.00
Potassium silicate (1:3.92)	2.47
CMC	0.23
Sodium xylene sulfonate	0.74
KOH	1.87
Water	72.00

EXAMPLE 74

P.E. III, nonionic: P ₂ O ₅ =2.7:1	10
TKPP	15
SMS	3
Water	72
KOH sufficient to adjust to pH 12.0.	

EXAMPLE 75

P.E. II, nonionic: P ₂ O ₅ =2.8:1	10
TKPP	10
SMS	2
Water	78
KOH sufficient to adjust to pH 12.1.	

The formulations of Examples 72 to 75 are all stable clear solutions suitable for detergent uses as described above. Addition to such formulations of a small amount, e.g. .05 to .5 part of a brightening agent, preferably of limited solubility as described above, results in highly effective heavy duty liquid household detergent compositions for clothes washing and the like.

In the following examples, the "surfactant" employed is the phosphate ester surfactant of Example 74, although it will be understood that other of the above defined phosphate ester surfactants may be substituted.

EXAMPLE 76.—ALL PURPOSE LIQUID CLEANER

Surfactant	5
Tall oil	10
NaOH	2.5
TKPP	10.0
Water	72.5

TABLE 6

All Purpose Liquid Cleaners

Examples	83	84	85	86	87	88	89	90
Surfactant	5.0	5.0	5.0	4.55	5.0	5.0	5.0	5.0
Tall Oil Fatty acids	10.0	10.0	10.0	9.10	10.0		10.0	
NaOH	2.5		2.5	2.30	2.5		2.5	
Triethanolamine		7.5						
Coco Acid Diethanolamide						1.0		1.0
Solvesso No. 1 ¹	10.0	10.0		9.10				
Ethyl Cellosolve			10.0	9.10				
Water	62.5	57.5	62.5	56.80	77.5	69.0	72.5	74.0
TKPP	10.0	10.0	10.0	9.10			10.0	5.0
STPP					5.0	10.0		
Ultrawet 35KX ²						15		15.0
Properties	opaque, very viscous.	opaque, very viscous.	clear, viscous.	clear, viscous.	clear, sep. with 10% STPP.	clear, also clear with 5% STPP.	clear, also clear with 5% TKPP.	clear, sep. with 10% TKPP.
Viscosity ³					20,800	400 ³ 320 ⁴	12,200 ³ 720 ⁴	320.

¹ Highly refined mineral oil with high flash point.

² Aqueous solution containing 30% sodium dodecylbenzene sulfonate, 5% sodium xylene sulfonate.

³ Viscosity with 10% polyphosphate salt.

⁴ Viscosity with 5% polyphosphate salt.

⁵ Centipoises, Brookfield Viscosimeter LV Model Serial No. 832.

EXAMPLE 77.—ALL PURPOSE LIQUID CLEANER

Surfactant	5
Sodium dodecylbenzene sulfonate	5
Lauroyl diethanolamide	1
STPP	10
Water	79

14

EXAMPLE 78.—LIQUID FLOOR-WALL CLEANER

Surfactant	3
Tall oil	2
NaOH	0.5
STPP	10
Water	84.5

EXAMPLE 79.—LIQUID WAX STRIPPER

Surfactant	5
SMS	10
STPP	5
Water	80

EXAMPLE 80.—HEAVY DUTY CLEANING POWDER

Surfactant	5
SMS	60
STPP	10
Sodium sesquicarbonate	15
TSP	10

EXAMPLE 81.—DAIRY CLEANING POWDER

Surfactant	10
STPP	15
TSPP	25
SMS	30
Sodium sesquicarbonate	20

EXAMPLE 82.—EMULSION OR DISPERSION TYPE
HEAVY DUTY LIQUID DETERGENT

Surfactant	10
TKPP	25
Sodium oleate	7.2
Sodium xylene sulfonate	5
SMS	3
PVM/MA	1
CMC	0-0.5
KOH	2.5

This heavy duty liquid detergent contains a highly effective anti-redeposition mixture and constitutes an excellent clothes washing detergent, particularly for cotton. The PVM/MA is a copolymer of vinyl methyl ether and maleic anhydride having a K value of about 30.

This invention has been disclosed with respect to certain preferred embodiments and various modifications and variations thereof will become obvious to the person skilled in the art. It is to be understood that such modifications and variations are to be included within the spirit and scope of this invention.

We claim:

1. An alkaline cleaning composition which in the form

of an 0.3% by weight aqueous solution has a pH of about 8 to 12, consisting essentially of approximately by weight, 1 to 10 parts of an alkali metal polyphosphate, and 1 to 10 parts of the reaction product consisting essentially of a mixture of primary and secondary phosphate esters, of P_2O_5 with a nonionic surface active agent having the molecular configuration of a condensation product of at least 1 mole of ethylene oxide, and up to an amount sufficient to provide said agent with about 95% by weight of combined ethylene oxide, with 1 mole of a compound containing about 6 to 150 carbon atoms and a reactive hydrogen atom and selected from the group consisting of phenol, alkyl phenols, aliphatic alcohols, fatty acids, fatty amines, fatty amides, rosin amines, long chain sulfonamides, long chain-substituted aryl sulfonamides, and high molecular weight mercaptans, in a ratio of 1 mole of P_2O_5 for each 2 to 4.5 hydroxy groups in said nonionic agent.

2. A composition as defined in claim 1 in which said alkali metal polyphosphate is sodium tripolyphosphate.

3. A composition as defined in claim 1 in which said alkali metal polyphosphate is tetrasodium pyrophosphate.

4. A composition as defined in claim 1 in which said alkali metal polyphosphate is tetrapotassium pyrophosphate.

5. A composition as defined in claim 1 in which said compound containing at least 6 carbon atoms and a reactive hydrogen atom is an alkyl phenol of at least 10 carbon atoms.

6. A composition as defined in claim 1 in which said compound containing at least 6 carbon atoms and a reactive hydrogen atom is an aliphatic alcohol of at least 10 carbon atoms.

7. An alkaline cleaning composition which in the form of an 0.3% by weight aqueous solution has a pH of about 8 to 12, consisting essentially of approximately by weight, 1 to 10 parts of an alkali metal polyphosphate, 1 to 10 parts of the reaction product consisting essentially of a mixture of primary and secondary phosphate esters, of P_2O_5 with a nonionic surface active agent having the molecular configuration of a condensation product of at least 1 mole of ethylene oxide, and up to an amount sufficient to provide said agent with about 95% by weight of com-

bined ethylene oxide, with 1 mole of a compound containing about 6 to 150 carbon atoms and a reactive hydrogen atom and selected from the group consisting of phenol, alkyl phenols, aliphatic alcohols, fatty acids, fatty amines, fatty amides, rosin amines, long chain sulfonamides, long chain-substituted aryl sulfonamides, and high molecular weight mercaptans, in a ratio of 1 mole of P_2O_5 for each 2 to 4.5 hydroxy groups in said nonionic agent, and about 0.25 to 3% based on the weight of said reaction product of a fiber-substantive optical brightening agent soluble to the extent of less than about 0.1% in water at 25° C.

8. A composition as defined in claim 7 in which said alkali metal polyphosphate is sodium tripolyphosphate.

9. A composition as defined in claim 7 in which said alkali metal polyphosphate is tetrasodium pyrophosphate.

10. A composition as defined in claim 7 in which said alkali metal polyphosphate is tetrapotassium pyrophosphate.

11. A composition as defined in claim 7 in which said compound containing at least 6 carbon atoms and a reactive hydrogen atom is an alkyl phenol of at least 10 carbon atoms.

12. A composition as defined in claim 7 in which said compound containing at least 6 carbon atoms and a reactive hydrogen atom is an aliphatic alcohol of at least 10 carbon atoms.

13. A composition as defined in claim 1 dissolved in water.

14. A composition as defined in claim 1 in the form of a dry particulate mixture.

References Cited in the file of this patent

UNITED STATES PATENTS

1,970,578	Schoeller et al.	Aug. 21, 1934
2,213,477	Steindorff et al.	Sept. 3, 1940
2,365,215	Rhodes	Dec. 19, 1944
2,522,447	Harris	Sept. 12, 1950
2,677,700	Jackson et al.	May 4, 1954
3,004,056	Nunn et al.	Oct. 10, 1961

FOREIGN PATENTS

719,445	Great Britain	Dec. 1, 1954
---------	---------------------	--------------

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,122,508

February 25, 1964

Richard A. Grifo et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 69, for "composition" read -- compositions --; column 7, line 15, for "sequicarbonates" read -- sesquicarbonates --; line 64, for "examples." read -- examples, --; column 8, TABLE 1, second column, opposite Example 9, for "0.5% STP" read -- 0.5% TSP --.

Signed and sealed this 21st day of January 1969.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents