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3,168,478

HIGHLY ALKALINE SURFACE ACTIVE COMPOSITIONS

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This invention relates to highly alkaline surface active compositions, and more particularly to such compositions containing an organic surface active agent.

A great number of highly alkaline compositions are known in the art based upon the use of one or a mixture of alkaline reacting substances which are principally inorganic alkali metal hydroxides and salts of relatively weak acids. In these compositions, the alkalinity serves the function of cleaning, emulsifying, saponifying, peptizing, descaling, derusting, paint and/or wax stripping and the like.

It has also been customary to include in such composition one or more synthetic organic surface active agents to provide a wetting, dispersing, foaming or similar function and to contribute to the primary function of the alkaline reacting substance. Nonionic surface active agents have been employed for this purpose, being substantially insensitive to heavy metals or alkaline earth metal ions and having excellent wetting, dispersing and/or emulsifying properties. However, such non-ionic agents discolor badly when mixed with such alkaline reacting substances in dry form such as powders, shaped products and the like. The liquid nonionic agents dedust dry alkali compositions at first, but lose this power after about two weeks or so whereby such mixes thereafter dust badly. In addition, the nonionic agents exhibit very little solubility in highly alkaline solutions, thereby greatly limiting their usefulness. The sulfate esters of such nonionic surface active agents do not have any substantially higher solubility in alkaline solutions.

Alkylaryl sulfonates have also been commonly employed in dry alkaline compositions, and while they do not discolor as do the nonionic surface active agents, they are substantially insoluble in the presence of large concentrations of calcium or aluminum ions normally present in many cleaning operations, such as dairy bottle washing and the like. Further, they do not have any dedusting action.

It is an object of this invention to provide a highly alkaline surface active composition in dry or liquid form which will not be subject to the above disadvantages attributable to the previously employed synthetic organic surface active agents. 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 a highly alkaline surface active composition containing the reaction product of P_2O_5 with a nonionic surface active agent having the molecular configuration of a condensation product of at least one mole of ethylene oxide, and up to an amount sufficient to provide said agent with about 95% by weight of combined ethylene oxide, with one mole of a compound containing about 6 to 150 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 said nonionic agent, and an amount of an alkaline reacting inorganic alkali metal substance sufficient to yield with said reaction product an aqueous solution having a pH of more than about 12 when the combined concentration of said reaction product and said alkali metal substance in the solution is about 0.3% by weight.

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 disad-

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vantages. They may be employed for the production of homogeneous liquid concentrates containing relatively high proportions of inorganic alkali metal substance and the defined surface active reaction product. When provided in dry or particulate form, the compositions of this invention have improved resistance to dusting, discoloration and/or decomposition of the components of the composition. Further, these compositions have highly desirable low or controlled foaming properties, relatively high wetting, dispersing, emulsifying, and/or detergency properties, and reduced corrosive action on metal, vitreous, ceramic, and other surfaces with which they may come in contact.

As the alkaline reacting substance to be employed in the present compositions, the alkali metal (sodium, potassium) hydroxides and silicates are preferred although other sodium or potassium salts may be employed such as the phosphates, carbonates, borates, and the like. Instead of or in addition to these strong alkali metal salts, there may also be employed relatively weaker salts such as the sodium or potassium polyphosphates, sulfides, cyanides, acetates and the like, the basic requirement being that the alkali metal substance, whether a single compound or a mixture of compounds, be employed in an amount sufficient to supply a concentration of alkali metal ion effective to yield a pH of more than about 12 when the compositions of this invention are dissolved in aqueous solution in a concentration of 0.3%.

As specific examples of inorganic alkali metal substances, there may be mentioned sodium and potassium hydroxide, phosphate, carbonate, sesquicarbonate, bicarbonate, tetraborate, perborate, sulfide, cyanide, acetate, orthosilicate, metasilicate, polyphosphates, and the like. Those alkali metal silicates are preferred having a mole ratio of $M_2O:SiO_2$ of at least about 0.7:1 and up to 2:1 or the like, where M means Na or K. These ortho- and metasilicates are highly effective strong alkaline reacting substances.

The alkali metal polyphosphates 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 such as the triphosphates, tetraphosphates, hexametaphosphates, decaphosphates and the like. As representative 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.

The above defined reaction product of P_2O_5 with a nonionic 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 nonionic 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 continu-

ously during the addition of the P_2O_5 and is preferably followed by maintenance of the reaction mixture at ambient temperatures up to $110^\circ C$. 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 nonionic 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 hydrophosphorous 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 95% by weight of combined alkylene oxide. However, 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 length, 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, to produce the corresponding water insoluble polypropylene glycol having a molecular weight of up to about 3600, 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 naphthylamine, alkyl thiophenol, thionaphthol, and the like.

(5) Aliphatic and aromatic mono- and poly-amines, 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 and 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.

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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.
From tetrapropylene -----	+10 E.O.
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, nonylphenol, dodecylphenol, dinonylphenol, 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 a lower proportion of free unreacted (non-phosphated) nonionic. Since increasing proportions of nonionic in dry alkali formulations yield increased discoloration, the use of such reaction products is preferred when formulating alkaline compositions in accordance with this invention, particularly when a dry formulation or a highly soluble formulation is desired. However, it will be understood that reaction products in the broader range of 2 to 4.5 hydroxy groups in the nonionic per mole of P_2O_5 may be employed, that such reaction products may be used in the form of the free acid or soluble salts thereof with alkali metals and the like, and that the compositions of this invention may be provided in any desired form such as liquid concentrates, powders, shaped compositions, pastes and the like.

For most purposes, the objects of this invention may be attained with mixtures, in dry or particulate form or in aqueous solution, of about 0.002 to 25 parts of the above defined phosphate ester reaction products for each part by weight of the alkaline reacting substance.

The compositions of this invention may also include 0 to about 25% by weight of one or more of the other usual constituents of highly alkaline cleaning and/or surface active compositions, as for example one or more neutral inorganic salts such as sodium and potassium chloride and sulfate and the like; 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, polyvinylpyrrolidone and the like; perfumes; deodorants; disinfectants; corrosion inhibitors; sequestrants such as ethylenediamine tetracetic acid, sodium gluconate and polyhydric sugar acids and the like; foam stabilizers such as dialkanolamides of fatty acids and the like; hydrotropes or solubilizers such as sodium xylene and toluene sul-

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fonate and the like; other anionic or nonionic surfactants such as higher alkyl (e.g. lauryl) sulfates, alkylaryl sulfonates (e.g. dodecylbenzene sulfonate), sodium tau-rides, fatty acid soaps, nonionics described above, etc.

The highly alkaline surface active compositions are useful and highly effective as electrolytic cleaners, metal processing cleaners, alkaline descaling and derusting agents, steam cleaners, metal soak cleaners, aluminum cleaners, aluminum milling agents, alkaline dairy cleaners, bottle washing agents, paint strippers, wax strippers, heavy duty industrial cleaners and degreasers (for fabrics, industrial clothing, curtains, belting, floors, castings, engines, railroad cars, trucks, buses), paper digester additives (for wetting, peptizing and dispersing action), paper de-inking agents (for dispersing and emulsifying action), 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. All these exemplified compositions have, in 0.3% aqueous solution, a pH of more than 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 surfactant 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. "E.O." means "ethylene oxide," its proportion in the defined nonionic surfactant being expressed in moles per mole of reactive hydrogen containing compound and/or in weight percent in the nonionic surfactant.

Table A

NONIONIC SURFACTANT PRECURSOR

Phosphate Ester	Reactive Hydrogen-Containing Compound (1 Mole)	Moles E.O.	Percent E.O.
I.-----	Nonyl Phenol.-----	6	54
II.-----	do.-----	9	65
III.-----	do.-----	15	75
IV.-----	do.-----	100	-----
V.-----	Dodecyl Phenol.-----	6	50
VI.-----	do.-----	11.5	75
VII.-----	Dinonyl Phenol.-----	17	65
VIII.-----	Oxo Tridecyl Alcohol (from tetra propylene).-----	3.5	-----
IX.-----	do.-----	7	59
X.-----	do.-----	10	68
XI.-----	do.-----	15	77
XII.-----	Oleyl Alcohol.-----	7	54
XIII.-----	Lauryl Alcohol.-----	4	49
XIV.-----	Pluronic L-62.-----	10	-----
	$[H(O(C_2H_4O)_5(C_2H_5O)_{38}(C_2H_4O)_5H)]$		

In Table B below, the solubilities of varying concentrations of phosphate ester surfactants employed in the present compositions are disclosed in varying concentrations of aqueous solutions of sodium hydroxide and sodium metasilicate. In the table, "SMS" means sodium metasilicate, "sol." means soluble giving a clear solution at temperatures up to boiling, and "sep." means that a separation of the phosphate ester from solution has occurred, usually in the form of a hazy or cloudy suspension. In common with the nonionic surfactant precursors, the solubility of the corresponding phosphate ester surfactants generally decreases with increasing temperatures. Where a number appears in the table, it refers to the maximum temperature in degrees centigrade at which the phosphate ester surfactant is completely soluble and the solution clear. The examples in the table show the unusual solubility and compatibility of the indicated phosphate esters in aqueous solutions of sodium hydroxide and sodium metasilicate. The table also shows the effect of variation in oxyethylene content of the nonionic surfactant precursor upon the solubility in alkalies of the corresponding phosphate ester and the effect of decreasing ratios of nonionic to P_2O_5 . In general, it is apparent that, other things being equal, highest solubilities are obtained

with proportions of nonionic precursor to P_2O_5 below 3.5:1 and ranging from about 2.5:1 to 2.8:1 for the compositions tested. In contrast, the nonionic surfactant precursors of phosphate esters II and X and their corresponding sulfate esters, illustratively, are substantially insoluble at room temperature in 5% NaOH and 5% SMS.

in general, other things being equal, optimum color stability is obtained with proportions of nonionic precursor to P_2O_5 below 3:1 and ranging from about 2.5:1 to 2.85:1 for the compositions tested. The unusual color stability of these dry alkali mixes is further established by the fact that the white appearance of the compositions

Table B

PHOSPHATE ESTER SOLUBILITY IN AQUEOUS ALKALI

Example	Phosphate Ester	Mole Ratio Nonionic: P ₂ O ₅	Alkali	Percent Phosphate Ester: Percent Alkali														
				0.1:5	1:5	1:10	5:10	10:10	15:10	0.1:10	1:15	5:15	10:15	15:15	0.1:15	1:20	5:20	10:20
1	IX	4:1	SMS NaOH					49 sep.					sep. sep.	sep. sep.				
2	X	2.7:1	SMS NaOH			sol. 65		sol. 65					69 sep.	64 sep.		sep. sep.		
3	X	4:1	SMS NaOH		99 74	55 27		51 sep.					sep. sep.					
4	XI	2.7:1	SMS NaOH			sol. 67		sol. 63					sep. sep.			sep. sol.		
5	XII	2.7:1	SMS NaOH			sol. 66		sol. 65					sep. sep.			50 sep.		
6	VI	2.7:1	SMS NaOH				75 43		60 32									
7	VII	2.7:1	SMS NaOH				50 sep.	sol. sep.						sep. sep.				
8	XIII	2.5:1	SMS NaOH	sol.	sol.	sep. sol.		sep. sol.					sol. sep.			sol. sep.		50
9	I	2.8:1	SMS NaOH				52 67		74 83	sol.			sep.					
10	III	3:1	SMS NaOH				96 60	98 53	97 52		sep. sol.	sep. 58						
11	IX	2.8:1	SMS NaOH	sol.	sol.	sol.		59 30	sol. 34				42 35	46 85	34 85		sep. sep.	
12	II	2.7:1	SMS NaOH	sol.	sol.	sol.			98 30		sol. 47	58			45 84	66	sep.	

The following Table C shows the color stability of dry mixes of alkali and various nonionic surfactants and

containing the indicated phosphate ester surfactant lasted indefinitely.

Table C

COLOR STABILITY OF DRY ALKALINE MIXES

Example	Surfactant	Percent Surfactant Mixed with dry Alkali	Mole Ratio of Nonionic: P_2O_5	Alkali	Conditions	Appearance
13a	Nonionic Precursor of P.E.III	3		NaOH	55° C., 1 hr.	Brown.
13b	P.E.III	3	3:1	NaOH	55° C., 40 hrs.	Tan.
14a	Nonionic Precursor of P.E.IV	10		SMS	55° C., 40 hrs.	Do.
14b	P.E.IV	10	2.85:1	NaOH	50° C., 10 days.	Brown.
15a	Nonionic Precursor of P.E.XIV	5		NaOH	50° C., 10 days.	White.
15b	P.E.XIV	5	2.5:1	NaOH	59° C., 16 hrs.	Discolored.
16a	Nonionic Precursor of P.E.XIII	5		NaOH	50° C., 16 hrs.	White.
16b	P.E.XIII	5	2.5:1	NaOH	50° C., 16 hrs.	Discolored.
17a	Nonionic Precursor of P.E.VII	5		NaOH	50° C., 16 hrs.	White.
17b	P.E.VII	5	2.7:1	NaOH	50° C., 16 hrs.	Discolored.
18a	Nonionic Precursor of P.E.IX	5		NaOH	50° C., 24 hrs.	White.
18b	P.E.IX	5	2.7:1	NaOH	50° C., 170 hrs.	Brown.
19a	Nonionic Precursor of P.E.II	5		SMS	50° C., 2 hrs.	Do.
				SOS	50° C., 2 hrs.	White.
19b	P.E.II	5	2.7:1	SMS	50° C., 2 wks.	Do.
				SOS	50° C., 2 wks.	White.
20a	Nonionic Precursor of P.E.IX	5		SMS	50° C., 2 hrs.	Brown.
				SOS	50° C., 2 hrs.	Do.
20b	P.E.IX	5	2.7:1	SMS	50° C., 2 wks.	White.
				SOS	50° C., 2 wks.	Do.
21	P.E.I	5	4:1	NaOH	R.T., 2 wks.	Red-brown.
				NaOH	60° C., 24 hrs.	Do.
22	P.E.I	5	3:1	NaOH	R.T., 2 wks.	Tan.
				NaOH	60° C., 24 hrs.	Do.
23	P.E.I	5	2.8:1	NaOH	R.T., 2 wks.	White.
				NaOH	60° C., 24 hrs.	Do.
24	P.E.I	5	2.7:1	NaOH	R.T., 2 wks.	Do.
				NaOH	60° C., 24 hrs.	Do.
25	P.E.IV	5	3.7:1	NaOH	R.T., 2 wks.	Brown.
				NaOH	60° C., 24 hrs.	Do.
26	P.E.IV	5	2.85:1	NaOH	R.T., 2 wks.	White.
				NaOH	60° C., 24 hrs.	Do.

phosphate ester surfactants of the type employed in the present compositions. In the table, "P.E." means phosphate ester; "SOS" means sodium orthosilicate; and "R.T." means room temperature. The examples in the table show the unexpected superiority in color stability of the indicated phosphate ester surfactants as compared with the corresponding nonionic surfactant precursors in the presence of dry alkalies. The table also shows that

In the examples in the following Table D, formulations consisting of sodium metasilicate with and without surfactants and CMC (carboxymethylcellulose) were tested as industrial laundry detergents in a Terg-O-Tometer (U.S. Testing Co.) test washer operated at 125 r.p.m. for 30 minutes using 1.0% detergent formulation in tap water at 180° F. for washing soiled cloths at a cloth:liquor ratio of 1:25, followed by a thorough cold

water rinse. ACH (American Conditioning House) No. 115 and 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., N.Y., 1954 at, respectively, pages 84 and 88. In these tests the cloths are employed in the form of 1½" x 3" swatches. The "Grease Spot" soiled cloths are 8" x 8" cotton twill swatches soiled with oil dag plus auto grease in 2" diameter circular areas. 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

The following Table F shows the dusting characteristics of dry sodium metasilicate powder alone and mixed with 0.5% surfactant. The mixtures were prepared by pouring 0.5% surfactant onto the SMS in a sample bottle and rolling the sample bottle for one hour. The appearance of the various mixtures after storage at 50° C. for the periods indicated in the table establish the unexpected superiority of the compositions of this invention as compared with compositions containing the corresponding non-ionic surfactant precursors with respect to dusting. Thus, Examples 31b and 32b, prepared in accordance with this invention, show little or no dusting during the test periods as compared with Examples 31a, 32a and 32c.

Table F
DUSTING

Ex.	Surfactant	Mole Ratio Nonionic: P ₂ O ₅	Appearance			
			2 weeks	1 month	5 weeks	8 weeks
31a.....	Nonionic Precursor of P.E. IX.....		Slight dust.....	Dusty.....	Very dusty.....	Very dusty.
31b.....	P.E. IX.....	2.7:1	No dust.....	No dust.....	Trace dust.....	Trace dust.
32a.....	Nonionic Precursor of P.E. II.....		Dusty.....	Dusty.....	Very dusty.....	Very dusty.
32b.....	P.E. II.....	2.7:1	No dust.....	No dust.....	No dust.....	No dust.
32c.....	None (SMS alone).....		Dusty.....	Dusty.....	Very dusty.....	Very dusty.

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 27b and 30

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

Table D

Example	Detergent	Mole Ratio Nonionic: P ₂ O ₅	Final Reflectance After Washing			
			ACH No. 115	Test Fabrics No. 26	Grease Spot	Redepo- sition
27a.....	80% SMS plus: 20% Nonionic Precursor of P.E. II.		39.0	46.0	63.0	69.0
27b.....	20% P.E. II.	2.7:1	50.0	50.5	65.5	74.0
28a.....	79.5% SMS 0.5% CMC plus: 20% Nonionic Precursor of P.E. II.		56.0	56.0	74.0	73.0
28b.....	20% P.E. II.	2.7:1	60.5	57.5	75.0	82.5
28c.....	100% SMS.		42.0	46.0	63.0	72.5

28b as compared with Examples 27a, 28a and 28c establishes the improvements in detergency attainable by the use of the compositions of this invention.

In the following Table E, soiled 1" x 8" cotton swatches were washed using a typical industrial laundry detergent formulation containing 20% surfactant, 79.5% SMS and 0.5% CMC. The washed swatches were subjected to a water absorption test by suspending them from a holder so that about ½" was immersed in tap water at room temperature. The time required for the water to rise on the swatch to a predetermined height is shown in the table. The water absorption rate by capillary action is an indication of the amount of residual soil remaining in the laundered swatch. The more rapid the rise the cleaner the swatch. The detergency superiority of the formulation of Example 30, formulated in accordance with this invention, as compared with Example 29 is established by the faster absorption rates shown in the table.

Table E

RATE OF WATER ABSORPTION

Example	Surfactant	Mole Ratio Nonionic: P ₂ O ₅	Time in Seconds to Rise—	
			1.5 inches	2.0 inches
29.....	Nonionic Precursor of P.E. II.		36	78
30.....	P.E. II.	2.7:1	30	72

EXAMPLE 33

	Parts
Phosphate ester III (nonionic:P ₂ O ₅ =3:1)	10
SMS	10
STPP (sodium tripolyphosphate)	5
Water	75

This is a clear solution useful as a paint stripper and the like.

EXAMPLE 34

	Parts
Phosphate ester XII (nonionic:P ₂ O ₅ =2.7:1)	0.3
NaOH	10.5
Na ₂ CO ₃	4.0
Na ₂ S	4.0
Na ₂ SO ₄	0.5
Water	80.7

This is a clear solution typical of digester solutions in the paper industry, the phosphate ester surfactant functioning further as an aid in reduction of resin content.

In the following examples, the "surfactant" employed is of phosphate ester II with a mole ratio of nonionic:P₂O₅ of 2.7:1 although it will be understood that other of the above defined phosphate ester surfactants may be substituted.

EXAMPLE 35

Liquid metal soak cleaner

	Parts
Surfactant	1
NaOH	6
Water	93

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This is a clear solution with no decrease in cloud point temperature even after maintenance at a rolling boil for two weeks.

EXAMPLE 36

Powdered metal soak cleaner

	Parts
Surfactant	3
TSP (trisodium phosphate)	10
Sodium carbonate	26
NaOH	61

This composition may be used at dilutions of 1 to 10% or more in water as an immersion type soak cleaner for metal parts such as in electrolytic cleaning of steel prior to electroplating. The concentrate and diluted solutions remain clear and stable at 160° C.

EXAMPLE 37

Liquid steam cleaner

	Parts
Surfactant	5
SMS	15-20
Sodium xylene sulfonate	1-2
Water	73-79

EXAMPLE 38

Liquid paint stripper

	Parts
Surfactant	5
NaOH	15
Sodium xylene sulfonate	1-2
Water	78-79

EXAMPLE 39

Liquid white wall tire cleaner

	Parts
Sulfactant	5
TSP	8
SMS	2
Water	85

EXAMPLE 40

Powdered cleaner

	Parts
Surfactant	6
SMS	30
NaOH	64

This is a powder which may be dissolved in water to form a 15 to 20% stable liquid concentrate, or it may be used at about 8 oz. per gallon or the like at temperatures from 120° F. to the boil as a steam cleaner, electrolytic cleaner, immersion type soak cleaner, etc.

EXAMPLE 41

Powdered cleaner

	Parts
Surfactant	0.5
Sodium tetraborate	95.5

This mixture was thoroughly stirred in a sigma-blade mixer and then stored at 120° F. for two weeks. Another mixture was similarly prepared as a control using as the surfactant the nonionic precursor of this phosphate ester surfactant. At the end of two weeks, the control dusted as much as the sodium tetraborate alone whereas the formulation employing the phosphate ester surfactant was dust free.

EXAMPLE 42

Powdered alkaline dip cleaner

	Parts
Surfactant	5
SMS	50
NaOH	20
TSP	20

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EXAMPLE 43

Powdered bottle washing compound

	Parts
5 Surfactant	0.5
Sequestant (sodium gluconate, polyhydric sugar acids, etc.)	1.5
NaOH	98

EXAMPLE 44

Powdered electrolytic cleaner

	Parts
Surfactant	2
15 SOS	50
NaOH	28
Sodium carbonate	20

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. A highly alkaline surface active composition consisting essentially of

(1) 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, and

(2) an alkaline reacting inorganic alkali metal substance selected from the group consisting of sodium and potassium hydroxides, silicates, tribasic phosphates, polyphosphates, carbonates, borates, sulfides and cyanides,

the amount by weight of component (2) being within the range of 1 part for each 0.002 to 25 parts of component (1) and sufficient to yield an aqueous solution having a pH of more than 12 when the combined concentration of components (1) and (2) in the solution is about 0.3% by weight.

2. A composition as defined in claim 1 in which said alkali metal substance is an alkali metal hydroxide.

3. A composition as defined in claim 1 in which said alkali metal substance is a sodium silicate having a mole ratio of $Na_2O:SiO_2$ of about 0.7:1 to 2:1.

4. A composition as defined in claim 1 in which the said ratio is 1 mole of P_2O_5 for each 2 to less than 3 hydroxy groups in said nonionic surface active agent.

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

8. An aqueous solution containing a composition as defined in claim 1.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,168,478

February 2, 1965

Andrew Stefcik 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 3, line 21, for "hydrophosphorous" read -- hypophosphorous --; column 5, line 32, for "dinoylphenol" read -- dinonylphenol --; column 9, Table D, first and second columns should appear as shown below instead of as in the patent:

Example	Detergent
27a	80% SMS plus: 20% Nonionic Precursor of P.E. II
27b	20% P.E. II
28a	79.5% SMS 0.5% CMC plus: 20% Nonionic Precursor of P.E. II
28b	20% P.E. II
28c	100% SMS

Signed and sealed this 14th day of January 1969.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents