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3,310,496

ALKALI STABLE AND SOLUBLE SURFACTANTS
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This application is a continuation-in-part of our application Ser. No. 195,953, which was filed on May 18, 1962, and has since been abandoned.

This invention relates to improvements in the art of cleaning objects, particularly those made of metal, glass, etc.

Broadly stated, the invention pertains to alkaline cleaning and, more particularly, to surfactants for use in alkaline metal cleaning baths.

An object of the invention is to improve the cleaning efficiency of alkaline metal cleaners.

Other objects of the invention will in part be obvious and will in part be disclosed hereinafter.

Alkaline cleaners are the most widely used means in industry for cleaning metal, glass, certain plastics, etc. They are primarily used to prepare metals such as steel, brass, and copper for plating, painting, enameling, rust-proofing, pickling, and other operations. Such preparation includes the removal of various types of soil such as cutting oils, grinding, buffing, stamping, and drawing compounds used in various metal-forming operations, as well as rust preventatives, lubricating greases, and various forms of dirt. The alkaline cleaning solutions may be used for soaking, spraying, or electrolytic types of cleaning. Of these, the soaking or tank cleaning techniques is most important because of its widespread use in industry.

In the soaking method of cleaning, the article to be cleaned usually is dipped in or slowly transported through a hot alkaline solution with little or no agitation present. The cleaning solutions employed generally are made of materials consisting of between about 88 to 99 percent by weight of various alkalies, such as caustic soda, sodium metasilicate, soda ash, trisodium phosphate, sodium tripolyphosphate, sodium orthosilicate, tetrasodium pyrophosphate, and tetrapotassium pyrophosphate, and from about 1 to 12 percent by weight of a surfactant. Previously, the most widely used surfactants for this purpose have been alkylaryl sulfonates and rosin soaps. Usually, the concentration of the cleaning materials (alkali plus surfactant) in the tank or bath is maintained between 2 and 10 percent of the cleaning solution.

As oil, grease, and other soils are caused to be separated from the part being cleaned in the tank, a scum-like layer collects at the top of the bath. If the surfactant employed is not thoroughly soluble in hot alkaline solution, it also will tend to accumulate in this surface layer. When the accumulation of scum in the surface layer becomes so great that it tends to coat the otherwise clean part as it is withdrawn from the bath, it becomes necessary to skim the soil and undissolved surfactant from the top of the tank. Each time this is done, a considerable amount of the surfactant is removed and, of course, this tends to lower the concentration of the effective cleaning agents in the bath to a point where the operation of the bath becomes unsatisfactory much sooner than it otherwise would if such losses could be minimized or eliminated. One obvious

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solution to this problem is to employ only surfactants that are soluble in hot alkaline solutions.

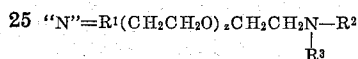
In addition to (1) solubility in hot alkaline solution, other important requisites of alkaline cleaners include (2) stability on solid caustic and other alkalies and (3) stability in highly alkaline solutions. It is also desirable that there be essentially no discoloration on solid caustic and other alkalies. No known prior art detergents, which are very effective metal cleaners, have all of the above-listed important properties as well. The present invention, by comparison, provides an extremely efficient metal cleaner that possesses all of these characteristics to an unusually high degree.

The attainment of the above general objects and specific properties has been made possible through a unique process by which novel compositions have been prepared. The compositions may be defined as blends of about 65 to 95% of "M" and about 35 to 5% of "N" where

"M"=the reaction product (and salt thereof) of



and polyphosphoric acid, and



In the above formulas

R and R¹=C₁₀₋₁₅ alkoxy groups, or alkylphenoxy groups with C₄₋₁₀ alkyl groups,

x=about 5 to about 25,

z=about 4 to about 25, and

R² and R³=H or small alkyl groups with a total number of carbon atoms (R²+R³) of at least 1 and less than 8.

Only when the blends are formed from certain ratios of their components can a useful combination of the above-described properties be obtained. The results of forming these critical combinations are unobvious and unpredictable from mere knowledge of the properties of each component, for each ingredient has certain limitations which appear to indicate a lack of utility for the purpose desired. For example, the phosphated portion is highly soluble in hot alkaline solutions, and satisfactorily stable on alkali and in alkaline solutions, but is not an effective cleaner. By contrast, the amine-terminated portion is a highly effective cleaner and is stable but is not sufficiently soluble in built alkaline solutions. But, when blended together in accordance with the present invention, the end products are highly soluble in concentrated hot alkaline solutions, stable on alkali and in alkaline solutions, and very effective as a cleaning agent.

The use of the divalent phosphate terminating group in part "M" of the unique blends affords the desired solubility and stability factors in a satisfactory manner which is incapable of achievement by other anionic components such as the sulfated, sulfonated or carboxy analogs. For part "N" other types of nonionic components also do not give the desired properties. Blends with unterminated nonionics, such as alkylphenoxy polyethoxy compounds, have proven unstable and do not give satisfactory cleaning. Nonionics terminated with amides or esters are not stable on caustic and are of questionable value as cleaners. Only the amine-terminated blends provide both stability on caustic and satisfactory detergency.

Part "M" of the unique blend, it should be pointed out, is a novel phosphate ester made according to a novel process disclosed in copending application Ser. No. 255,173, which was filed on Jan. 31, 1963, by Richard C. Mansfield. (That application, incidently, is a continuation-in-part of Ser. No. 195,952, which was filed on May 18, 1962, and since abandoned). Although not all of the phosphate esters disclosed in those applications are useful in the present invention, a large number of them are. In any event the contents of the specifications of both those applications are incorporated herein by reference since they disclose in detail the process of making many products which are employed in the present invention.

In brief, the novel phosphate ester, "M," which consists of at least 85% primary phosphate (i.e. monoester phosphate) components, is prepared by reacting from

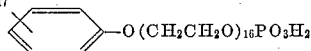
about 0.6 mol to about 2.0 mols of polyphosphoric acid with 1.0 mol of a condensation product having the formula $R(CH_2CH_2O)_xH$ as indicated above. The polyphosphoric acid which is used is a mixture of phosphoric acids with a phosphoric acid anhydride content corresponding to about 73 to 85 percent expressed as P_2O_5 .

In Table I, which follows, data are given comparing the performance characteristics of the present inventive composition, those of the components of our novel blend, those of several commonly used and widely accepted surfactants, as well as those of prior art materials with chemical compositions that are somewhat analogous to the compositions of the present invention. It can be readily seen from these data that compositions outside of the present invention (namely, B to J, inclusive) are unsatisfactory, either because of poor solubility in caustic, poor detergency, poor stability on solid caustic or in caustic solution, or a combination thereof.

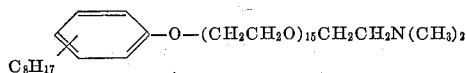
TABLE I

Composition ¹	Solubility, Max. percent NaOH which 1% Surf. is Soluble from 60-100° C.	Detergency, percent Cleaner ²	Stability on Solid NaOH ³	Stability in Caustic Solution ⁴	Discoloration on Solid Caustic ⁵
A-----	10.5	100	No loss-----	Stable-----	Very slight.
B-----	15.0	30	do-----	do-----	None.
C-----	< 0	100	do-----	do-----	Very slight.
D-----	4.0	38	do-----	do-----	None.
E-----	< 0	100	Large loss-----	do-----	Considerable.
F-----	4.0	0	do-----	do-----	None.
G-----	5.5	100	Some loss-----	Unstable-----	Considerable.
H-----	7.7	13	No loss-----	Stable-----	Very slight.
I-----	6.7	21	do-----	do-----	do-----
J-----	18.0	18	do-----	do-----	do-----
K-----	-----	0	do-----	Stable-----	do-----

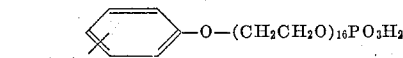
¹ A=Blend of 8 parts C_8H_{17}



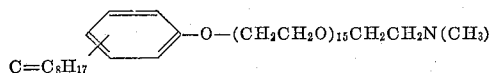
and 2 parts



C_8H_{17}

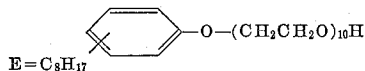


B= C_8H_{17}



C= C_8H_{17}

D=Sodium dodecylbenzene sulfonate



E= C_8H_{17}

F=Tall Oil Soap.

G=Sodium salt of a sulfated oxyethylated t-C₁₂-C₁₅ aliphatic amine.

H=A commercially available phosphated nonionic surfactant.

I=A phosphated nonionic surfactant prepared by the reaction of an octylphenoxy (polyethoxy)₁₁₋₁₅ ethanol and P_2O_5 by the procedure described in U.S. Patent 3,004,056.

J=A sodium dodecyl diphenyl ether disulfonate.

K=A blank.

² Removal of mineral oil (Sun 150 Brightstock) from solvent precleaned steel panels. The panels are rotated for 5 minutes at 28 r.p.m. in a bath of 5% of a base (made from 40.0% NaOH, 28.5% Na_2CO_3 , 31.5% sodium etasilicate pentahydrate) and 0.1% active surfactant maintained at 82° C. Each value represents this average percent of clean area on both sides of 3 panels.

³ Two (2) percent surfactant (active) was blended on crystal flake caustic and stored in open jars for 2-3 weeks at 60° C.; detergency was evaluated before and after storage in order to determine stability.

⁴ One (1) percent surfactant (active) was stored in caustic solutions (5-10%) at 60° C. for 2-3 weeks. The cloud point was measured before and after storage.

⁵ Two (2) percent surfactant (active) was blended into crystal flake caustic and stored at 25° C. in a sealed container for at least one week.

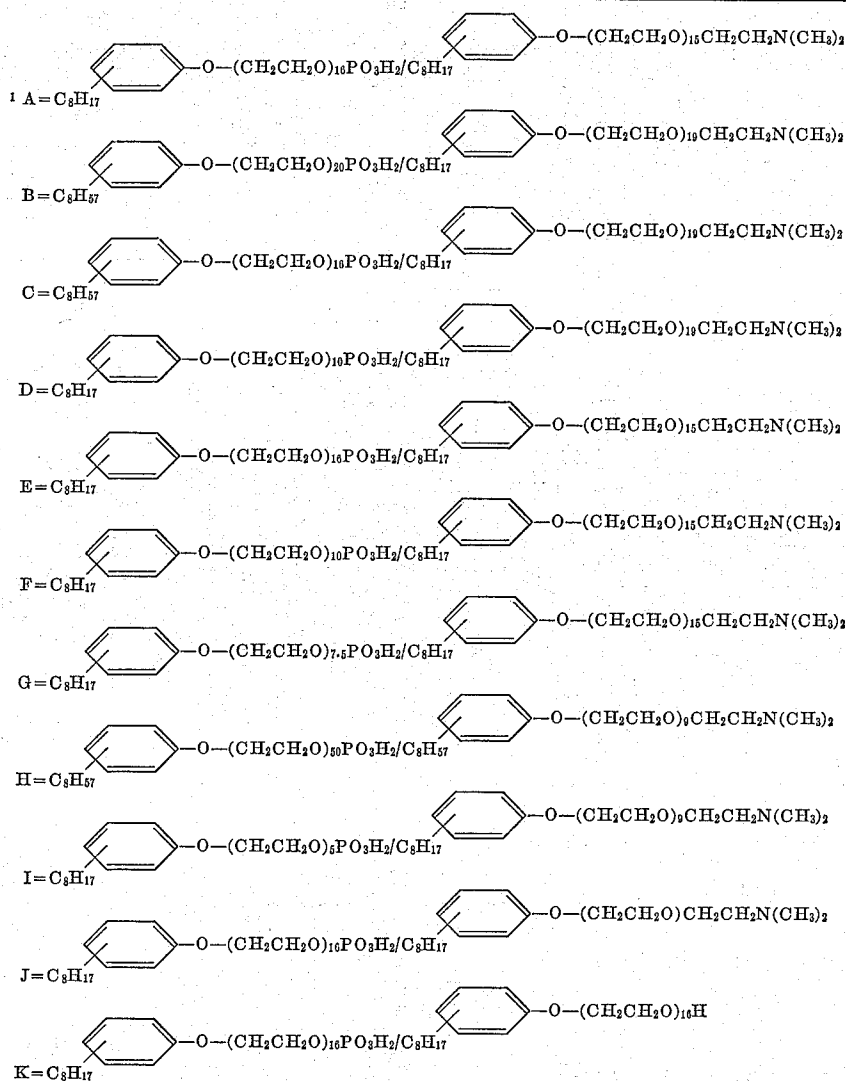
⁶ Does not give a clear solution from 60-100° C. in water (percent NaOH).

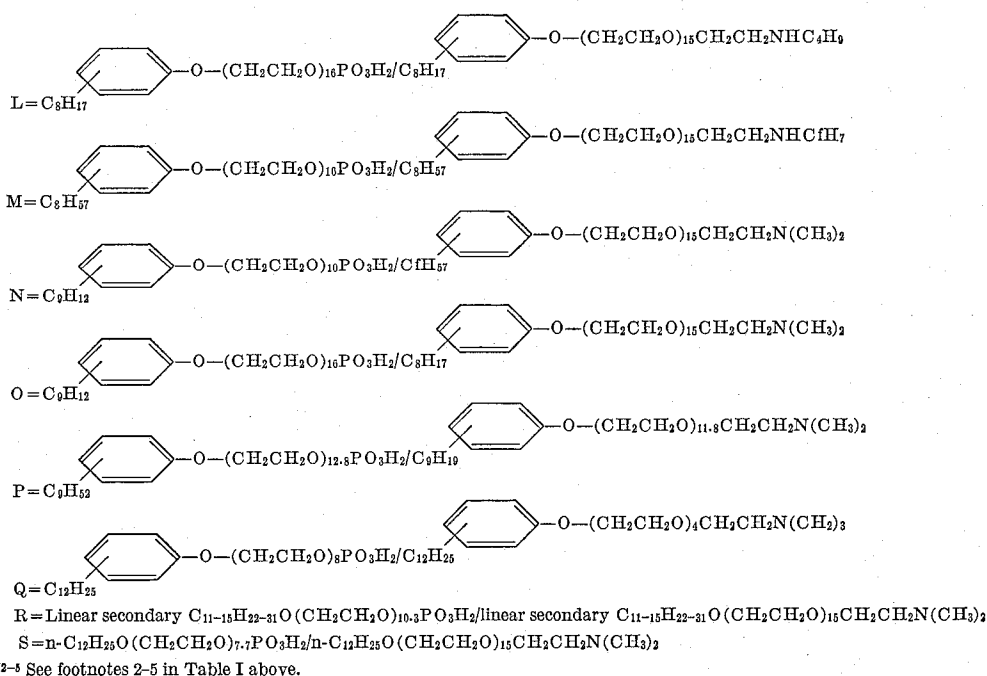
As indicated above, the compositions of the present inventions are comprised of blends of 65–95% of “M” (the phosphorylated component) and 35 to 5% of “N” (the amine-terminated component). These ratios are critical to the successful functioning of the present invention. With less than 5 percent of component “N” inadequate detergency is obtained. With more than 35% of

“N” the solubility of the end product in builder solutions is inadequate. By the term “inadequate” is meant that the blend will not give a clear solution in 5% caustic over the range of 60–100° C. Table II, which follows, shows the importance of having the ratio of “M”:“N” within the designated limits.

TABLE II

Components of Blends ¹	Ratio “M”/“N”	Solubility, Percent NaOH	Detergency ²	Stability on Solid NaOH ³	Stability in Caustic Solution ⁴	Discoloration on Solid Caustic ⁵
A.....	100/10	15.0	30	No loss.....	Yes.....	None.
A.....	95/5	12.5	93	do.....	Yes.....	Very slight.
A.....	90/10	11.6	100	do.....	Yes.....	Do.
A.....	80/20	10.5	100	do.....	Yes.....	Do.
A.....	70/30	10.0	100	do.....	Yes.....	Slight.
A.....	60/40	4.0	100	do.....	Yes.....	
B.....	80/20	9.5	99	do.....	Yes.....	Very slight.
C.....	80/20	11.0	100	do.....	Yes.....	Do.
D.....	80/20	9.9	100	do.....	Yes.....	Do.
E.....	80/20	10.5	100	do.....	Yes.....	Do.
F.....	80/20	12.8	100	do.....	Yes.....	Do.
G.....	80/20	11.5	100	do.....	Yes.....	Do.
H.....	80/20	12.5	99	do.....	Yes.....	Do.
I.....	80/20	11.1	88	do.....	Yes.....	Do.
J.....	80/20	12.5	45	do.....	Yes.....	Do.
K.....	80/20	8.8	73	Some loss.....	Yes.....	Do.
L.....	80/20	10.5	100	No loss.....	Yes.....	Do.
M.....	80/20	12.9	76			
N.....	80/20	10.7	97	No loss.....	Yes.....	Do.
O.....	80/20	10.7	92	do.....	Yes.....	Do.
P.....	80/20	10.8	89	do.....	Yes.....	Do.
Q.....	80/20	6.0	24	do.....	Yes.....	
R.....	80/20	11.3	99			None.
S.....	80/20	12.0	100			Do.





In the test for detergency in Table II, a value of 85 or higher is considered acceptable. All the detergency values represent tests made before the stability tests were run. The table does not reflect it, but, after the stability tests were run, detergency tests were run again to see how much of an effect the exposure to caustic had upon the composition's detergency abilities. For example, the blend of components A, at the 80/20 ratio, showed no change from 100% cleaning after storage on solid caustic at 60° C. for 2-3 weeks on a 0.1% active surfactant basis. When the test was made more severe by using only 0.03% surfactant, there was no significant change in detergency from about 90% cleaning as a result of exposure to solid caustic.

As another example, note the blend of components K, which lacks the amine-terminated portion and is, therefore, outside the scope of the present invention. It shows a poor detergency value of 73 for its 80/20 ratio of components. When the same composition was altered to a 70/30 ratio, and tested on a 0.1% active surfactant level, its detergency value was 83 before being tested on solid caustic. After one week of exposure at 60° C. to the caustic, the detergency value dropped to 42, showing clearly the importance of the amine-terminated portion to the composition.

Compositions which include components A, at the 100/0 ratio, and at the 60/40 ratio, and also those which include components J, M and Q are examples of other materials which are just outside the ranges of the compositions of the present invention. Each is shown to illustrate the unacceptable detergency or stability on caustic, or solubility in NaOH, which results if the proper formulation is not made as herein disclosed.

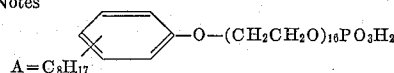
In Table III, which follows, further comparisons are made between the present invention and analogous combinations of ingredients disclosed in the closest known prior art. In some of the combinations a compound of the types "M" or "N," per the present invention, was used. The ratio of components employed, 80/20, is the same as that used for most of the examples in Table II for the ratio of components "M"/"N." The tests to which these various combinations were submitted are the same

as those employed in the comparisons between the present invention and other products set forth in Table I.

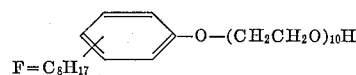
TABLE III

Components of Blend	Ratio of Components	Solubility, Max. percent NaOH in which 1% Surf. Soluble. 60-100° C.	Percent Detergency	Discoloration on Solid Caustic
A+B-----	80/20	-----	9	
C+B-----	80/20	<1	-----	
D+B-----	80/20	4.6	-----	
C+E-----	80/20	<1	-----	
D+E-----	80/20	4.4	-----	
A+F-----	80/20	-----	-----	Considerable.
A+G-----	80/20	-----	-----	Do.
M'+N'-----	80/20	10.5	100	Very slight.

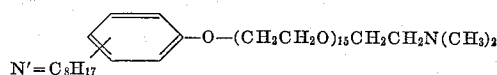
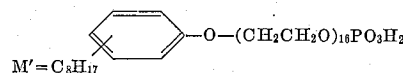
Notes



- Corresponds to compound "M" in type formula given above.
 B = $\text{C}_6\text{H}_{17}\text{C}_6\text{H}_5\text{O} (\text{CH}_2\text{CH}_2\text{O})_2 \text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$. Corresponds to compound prepared in accordance with Bruson, U.S. Patent 2,229,024.
 C = (Oxo) hexadecyl polyethoxy phosphate (with 10 mols of ethylene oxide) prepared by the method of Chiddix, U.S. Patent 3,033,880.
 D = Octylphenoxypolyethoxy phosphate (with 12.5 mols of ethylene oxide) prepared using P_2O_5 by the procedure of Nunn, U.S. Patent 3,004,057.
 E = Octylphenoxypolyethoxy phosphate dimethyl amine (with 16 mols of ethylene oxide). Corresponds to compound "N" in type formula given above.



as disclosed in Steindorff, U.S. Patent 2,213,477.
 G = $t\text{-C}_{14}\text{H}_{25}\text{N}(\text{CH}_2\text{CH}_2\text{O})_{15} \text{H}$ prepared by the general method disclosed in Schoeller, U.S. Patent 1,970,578.



The data in Table III demonstrate the following:

(1) The amine of Bruson U.S. Patent 2,229,024 mixed with component "M" of the present invention exhibits unsatisfactory detergency properties in accordance with the standards specified in the present application which our invention meets and exceeds.

(2) The amine of Bruson U.S. Patent 2,229,024 mixed with either a phosphate prepared by the method of Chiddix U.S. Patent 3,033,889 or a phosphate prepared by the method of Nunn U.S. Patent 3,004,057 exhibits solubility in caustic which is unsatisfactory as measured by the standards specified in the present application which our invention meets and exceeds.

(3) The amines utilized in the present invention, represented by "N" in the general formula given above, when mixed with phosphates prepared either by the method of Chiddix U.S. Patent 3,033,889 or by the method of Nunn U.S. Patent 3,004,057, exhibit solubility in caustic which is below the minimum of acceptability specified in the present application, which minimum the present invention meets and exceeds.

(4) The mixtures of the phosphate ester utilized in the present invention, represented by "M" in the general formula given above, with either a nonionic prepared by the method of Steindorff U.S. Patent 2,213,477 or by the method of Schoeller U.S. Patent 1,970,578, exhibit poor stability on solid caustic as shown by the extensive discoloration, and are far inferior than the present invention in this respect.

The novel compositions can be prepared by either of two procedures. In method I the nonionic phosphate and the nonionic amine can be prepared separately and then blended together. In method II the nonionic and the nonionic amine can be blended together first, and then the blend is phosphated. Method II is preferred since it has the advantage of terminating by phosphorylation any hydroxyl groups remaining in the nonionic amine. Substantially complete termination of hydroxyl groups is essential for good stability of the product on solid caustic.

When method I is used, a mixture of 1 mol of the nonionic surfactant and about 1 to about 2 mols of polyphosphoric acid is first heated to about 80–110° C. until the cloud point in caustic solution ceases to rise. A preferred range is about 1.0 to 1.3 mols of polyphosphoric acid to 1 mol of nonionic surfactant. The indicated mols of polyphosphoric acid is based upon the percentage of phosphoric acid anhydride, expressed as percent P_2O_5 , in the polyphosphoric acid. A more complete disclosure as to the nature of method I and the resultant products therefrom is set forth in copending application Ser. No. 255,173 and its since abandoned parent application Ser. No. 195,952, both cited above. The phosphorylated product made in this first step of method I is then, in step 2, mechanically blended with the amine component which has itself been prepared by any of numerous well-known methods from the desired nonionic surfactant. One such method is to react the surfactant with thionyl chloride and then react the product thereof with dimethylamine.

In the preferred method II, the nonionic surfactant and the amine-terminated nonionic surfactant are mixed together and the blend is phosphated with polyphosphoric acid at 80–110° C. It is necessary, as in method I, to use about 1–2 mols of the polyphosphoric acid for each hydroxyl equivalent present in the mix, with 1–1.3 mols being preferred. In both methods greater amounts of polyphosphoric acid give darker products, and this is generally to be avoided, particularly since they are unnecessary for complete termination. Lesser amounts result in incomplete termination and usually require prolonged heating to get the reaction to go to completion.

Optionally, small amounts of an oxidizing agent, such as hydrogen peroxide, can be added before the phosphorylation step to give lighter-colored products, if desired. An additional option, instead of using an oxidizing agent, is to use a reducing agent such as hydrazine hydrate.

Illustrative of the practice of this invention are the following examples. It should be understood, of course, that they are merely explanatory and not limiting. The true limits of the invention, and those within which we agree to bound, are those defined by the claims which follow the examples, it being understood that there will be many optional modes of practicing our invention without having to depart from the spirit and scope thereof.

Example I

To a stirred mixture of 207.5 parts (0.246 mol) of an oxyethylated p, t-octylphenol having a hydroxyl number of 66.4, which corresponds to a molecular weight of 843, 65 parts of the corresponding dimethylamine, prepared by converting a similar oxyethylated octylphenol to the corresponding chloro compound with thionyl chloride and reacting that with dimethylamine in the presence of alkali, which had a neutral equivalent of 893, corresponding to 94.5% conversion, and 10 drops of 30% hydrogen peroxide solution was added in a nitrogen atmosphere over a period of ½ hour, during which the temperature rose to 50° C., 52.8 parts (0.312 mol as P_2O_5) of 115% ortho equivalent polyphosphoric acid (82–84% P_2O_5). The mixture was then gradually heated to 105° C. during another 1½ hours and stirred at 105–110° C. for 5½ hours while the cloud point in 12% aqueous sodium hydroxide solution gradually rose to and leveled off at 74° C. The color of the product was 12—on the Varnish Color Scale.

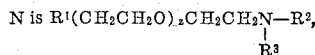
Example II

To a stirred mixture of 709 parts (1.152 m.) of an oxyethylated p-t-octylphenol having a hydroxyl number of 91.2, which corresponds to a molecular weight of 615, 230 parts of a dimethylaminoethyl-terminated oxyethylated p-t-octylphenol prepared as described in Example I from an oxyethylated p-t-octylphenol with a molecular weight of about 819, and having a neutral equivalent of 864, which corresponds to a purity or conversion of 97.9%, and 1.88 parts of 30% hydrogen peroxide was added in a nitrogen atmosphere during ½ hour 245 parts (1.449 m. as P_2O_5) of 115% ortho equivalent polyphosphoric acid (82–84% P_2O_5) while the temperature rose to and was controlled below 50° C. The mixture was then gradually heated to 105° C. during another 1½ hours and stirred at 105–110° C. for 4 hours while the cloud point in 14% aqueous sodium hydroxide solution gradually rose to and leveled off at 58° C. The color of the product was 12—on the Varnish Color Scale.

We claim:

1. An alkali-stable and soluble surfactant composition consisting essentially of a blend of about 65 to 95 percent of a component M with about 35 to 5 percent of a component N, where

M is a surface-active composition, which contains upwards of 85% primary phosphate esters, of the class consisting of the condensation product, and the salts of said product, of the reaction of $R(CH_2CH_2O)_xH$ and polyphosphoric acid,



R and R^1 are members of the class consisting of alkoxy groups having from 10 to 15 C atoms in the alkyl portion thereof, and alkylphenoxy groups having 4 to 10 C atoms in the alkyl portion thereof,

R^2 and R^3 are members of the class consisting of H and small alkyl groups whose entire carbon atoms ($R^2 + R^3$) total between 1 and 7, inclusive,

x is a number in the range of from about 5 to about 25, and

z is a number in the range of from about 4 to about 25; the said phosphate ester, M, being prepared by reacting from about 0.6 mol to about 2.0 mols of polyphosphoric acid with each mol of said condensation

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product; and the said polyphosphoric acid being a mixture of phosphoric acids with a phosphoric acid anhydride content corresponding to about 73 to 85 percent expressed as P_2O_5 .

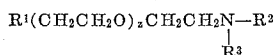
2. The surfactant of claim 1 in which M essentially is a divalent phosphate-terminated alkylphenoxypolyethoxy compound whose alkylphenoxy portion contains an alkyl group having 4 to 10 C atoms and whose polyethoxy portion contains 5 to 25 condensed ethylene oxide units; and N is an alkylphenoxypolyethoxy compound which is terminated with an aminoethyl group in which the nitrogen has attached thereto two members of the class consisting of H and lower alkyl groups whose entire total of carbon atoms ranges between 1 and 7, inclusive, the alkylphenoxy portion of N containing an alkyl group having 4-10 C atoms, and its polyethoxy portion containing 4-25 condensed ethylene oxide units.

3. The surfactant of claim 1 in which M essentially is a divalent phosphate-terminated alkoxy-polyethoxy compound whose alkoxy portion contains an alkyl group having 10-15 C atoms and whose polyethoxy portion contains 5-25 condensed ethylene oxide units; and N is an alkoxy-polyethoxy compound which is terminated with an aminoethyl group in which the nitrogen has attached thereto two members of the class consisting of H and lower alkyl groups whose entire total of carbon atoms ranges between 1 and 7, inclusive, the alkoxy portion of N containing an alkyl group having 10-15 C atoms, and its polyethoxy portion containing 4-25 condensed ethylene oxide units.

4. The process of manufacturing the surfactant defined by claim 1 in which the nonionic surfactant



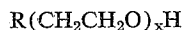
is blended with the amine-terminated nonionic surfactant



and the blend then in phosphated with polyphosphoric acid, the values for R, R^1 , R^2 , R^3 and z being the same as in claim 1.

5. The process of claim 1 in which M is prepared by heating together 1 mol of the nonionic surfactant $R(CH_2CH_2O)_xH$ with from 1 to 2 mols of polyphosphoric acid to about 80° to 110° C. until the cloud point in caustic solution ceases to rise, and N is prepared by reacting a thionyl halide with a nonionic surface-active material of the formula $R'(CH_2CH_2O)_xH$, and then reacting the product thereof with dimethylamine, the value for R' being the same as the value for R, and the values for R and x being the same as in claim 1.

6. The process of claim 5 in which the polyphosphoric acid is used in quantities of between about 1 and 2 mols of it for each mol of the nonionic surfactant



7. The process of claim 4 in which the phosphorylating agent is polyphosphoric acid and it is used in quantities of between about 1 and 2 mols of it for each mol of the nonionic surfactant $R(CH_2CH_2O)_xH$, and the phosphorylation is carried out at a temperature of about 80-110° C.

8. The process of claim 5 in which a small amount of hydrogen peroxide is added before the phosphorylation step to promote lighter-colored products.

9. The process of claim 7 in which a small amount of hydrogen peroxide is added before the phosphorylation step to provide lighter colored products.

10. The process of claim 5 in which a small amount of hydrazine hydrate is added before the phosphorylation step to provide lighter-colored products.

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11. The process of claim 7 in which a small amount of hydrazine hydrate is added before the phosphorylation step to provide lighter-colored products.

12. A cleaning composition consisting essentially of a mixture of about 88 to 99 percent by weight of an alkali metal salt from the class consisting of caustic soda, sodium metasilicate, soda ash, trisodium phosphate, sodium triphosphate, sodium orthosilicate, tetrasodium pyrophosphate and tetrapotassium pyrophosphate, and about 1 to 12 percent by weight of the surfactant of claim 1.

13. A cleaning composition consisting essentially of a mixture of about 88 to 99 percent by weight of an alkali metal salt from the class consisting of caustic soda, sodium metasilicate, soda ash, trisodium phosphate, sodium triphosphate, sodium orthosilicate, tetrasodium pyrophosphate and tetrapotassium pyrophosphate, and about 1 to 12 percent by weight of the surfactant of claim 2.

14. A cleaning composition consisting essentially of a mixture of about 88 to 99 percent by weight of an alkali metal salt from the class consisting of caustic soda, sodium metasilicate, soda ash, trisodium phosphate, sodium triphosphate, sodium orthosilicate, tetrasodium pyrophosphate and tetrapotassium pyrophosphate, and about 1 to 12 percent by weight of the surfactant of claim 3.

15. A cleaning bath essentially consisting of an aqueous alkaline solution having dissolved therein a mixture of about 88 to 99 percent by weight of an alkali metal salt from the class consisting of caustic soda, sodium metasilicate, soda ash, trisodium phosphate, sodium triphosphate, sodium orthosilicate, tetrapotassium pyrophosphate and tetrasodium pyrophosphate, and at least about 1 to 12 percent by weight of the surfactant composition of claim 1.

16. A cleaning bath essentially consisting of an aqueous alkaline solution having dissolved therein a mixture of about 88 to 99 percent by weight of an alkali metal salt from the class consisting of caustic soda, sodium metasilicate, soda ash, trisodium phosphate, sodium triphosphate, sodium orthosilicate, tetrapotassium pyrophosphate and tetrasodium pyrophosphate, and at least about 1 to 12 percent by weight of the surfactant composition of claim 2.

17. A cleaning bath essentially consisting of an aqueous alkaline solution having dissolved therein a mixture of about 88 to 99 percent by weight of an alkali metal salt from the class consisting of caustic soda, sodium metasilicate, soda ash, trisodium phosphate, sodium triphosphate, sodium orthosilicate, tetrapotassium pyrophosphate and tetrasodium pyrophosphate, and at least about 1 to 12 percent by weight of the surfactant composition of claim 3.

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