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3,328,309

## STABILIZED LIQUID HEAVY DUTY DETERGENT COMPOSITION

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20 Claims. (Cl. 252—137)

This case is a continuation of Ser. No. 202,098, filed June 13, 1962, now abandoned.

This invention relates to new composition of matter and to methods for making same, and in particular to stabilized liquid heavy duty detergent compositions.

Liquid detergent compositions comprise as the major components thereof a surface active detergent ingredient in a liquid medium. The liquid medium is usually water, and the detergent may be any of the commonly used surfactants of the nonionic and anionic types and mixtures thereof. In general, the detergents themselves, whether in the form of a liquid or solid, are generally sufficiently soluble in the aqueous medium to form relatively stable and usually clear solutions. In preparing so-called heavy duty detergent compositions, however, to the water detergent combination there are added various inorganic salts of an alkaline nature, which combination is then characterized as a heavy duty detergent. The presence of the alkaline salts resulting in a relatively high pH of the aqueous detergent composition gives to the composition its so-called heavy duty cleansing characteristics.

The heavy duty liquid detergent compositions have become of increasing importance and permanence, particularly in the home laundering field. This is, of course, not to say that heavy duty detergent compositions are not of great utility in many other commercial and industrial applications, and while in the latter two fields unquestionably, stability of the detergent compositions is an important consideration, in the consumer market which would be the primary outlet for home laundry use, the stability of the liquid heavy duty detergent composition is of great importance. The particular stability mentioned above refers to the homogeneity of the various ingredients. As pointed out above, the three major ingredients of a heavy duty liquid detergent composition are water, detergent, and inorganic alkaline salt. The presence of the salt, especially in relatively large amounts, results in the insolubilization of the detergent in the water medium. This phenomenon is well known and is referred to as a salting out effect. Since most of the detergents employed, especially of the nonionic type, are liquid materials, the emulsions which are produced by the presence of a separate detergent liquid phase should be stable for extended periods of time and under varying ambient conditions of temperature lest there result a complete separation of the detergent as a distinct oil phase and perhaps some precipitation of the inorganic salt. This would not only be intolerable from an aesthetic point of view for the consumer but would obviously render the composition sadly deficient if the materials were not homogeneously distributed throughout the water carrier.

In order to effect the formulation of satisfactory emulsions containing inorganic salts and detergent in water, various thickeners and stabilizers have been resorted to. To date there has been no satisfactory product for producing liquid heavy duty detergent compositions of the type above described which have any significant degree of stabilization of the emulsion system, and this includes not only stability under uniform conditions of temperature but also stability under varying conditions of temperature which

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would include a range of temperatures from freezing up to about 120° F.

It is therefore an object of the present invention to provide new and useful liquid heavy duty detergent compositions which are outstandingly stable.

It is a further object of the present invention to provide new and useful stabilized liquid heavy duty detergent compositions comprising as the detergent nonionic, anionic detergents and mixtures thereof.

It is still a further object of the present invention to provide liquid heavy duty detergent compositions which form stable emulsions and/or suspensions.

It is still a further object of the present invention to provide detergent compositions which are characterized as heavy duty due to the presence of inorganic alkaline salts and which form with water stable emulsions or suspensions.

It is still another further object of the present invention to provide processes for accomplishing the foregoing objects.

Other objects will appear hereinafter as the description proceeds.

It has now been discovered that the objects set forth above may be accomplished by preparing liquid heavy duty detergent compositions containing minor amounts of polymeric partial esters which result in the detergent compositions having outstanding stability.

The polymeric partial esters which are used to effect the stabilization of the liquid heavy duty detergent compositions hereinafter to be described are prepared by the interaction of hydroxy-containing micelle forming surface active compounds with ethylenically unsaturated polymeric anhydrides, and preferably  $\alpha,\beta$ -unsaturated polymeric anhydrides. The partial esters herein contemplated are water soluble products which contain up to about 5 mole percent of the potential carboxyl groups in the polymeric anhydride as ester groups, and preferably no more than about 3 mole percent as ester groups. As little as 0.01% ester groups in the polymeric anhydride produces a partial ester which functions outstandingly well as a stabilizer for the compositions employed in this invention.

The hydroxyl-containing micelle forming surface active agents comprise the nonionic hydroxyl containing compounds as well as anionics containing an hydroxyl grouping. The micelle forming surface active agents are well-known and as illustrative of the hydroxyl-containing compounds, mention may be made of the following:

(A) Alkylene oxide condensation products with an active hydrogen-containing hydrophobe.

The alkylene oxide condensates are prepared from an alkylene oxide or a precursor thereof and a hydrophobe containing an active hydrogen. The alkylene oxides include precursors as well having from 2 to 4 carbon atoms such as ethylene oxide, propylene oxide and the like. Mixtures of such oxyalkylating reagents may also be used simultaneously or in sequence. Examples of such products may be found in U.S. Patents 1,970,578 directed to derivatives of carboxylic acids, alcohols and amines; 2,085,706, directed to derivatives of amides; 2,205,021, directed to derivatives of mercaptans; and 2,213,477, directed to derivatives of ring substituted isocyclic hydroxyl compounds. The number of oxyalkyl groups may range from 1 to about 200 or more.

The following illustrate typical reactive-hydrogen compounds:

nonylphenol (propylene trimer)  
octylphenol (diisobutylene)  
dodecylphenol (propylene tetramer)  
diamylphenol  
dibutylphenol  
alkylphenols, where alkyl is  $C_4$  to  $C_{18}$

alkyl cresols, where alkyl is  $C_4$  to  $C_{18}$

mixed "coco" alcohols

lauryl alcohol (85%  $C_{12}$  alcohol)

castor oil

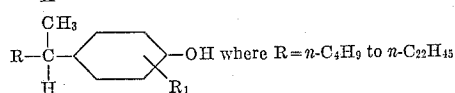
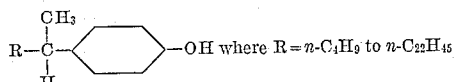
lauryl alcohol (92%  $C_{12}$  alcohol)

tridecyl (oxo) alcohol

oleyl alcohol

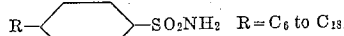
hydrogenated tallow alcohol

$R-OH$  prepared from olefins of  $C_{12}$  to  $C_{22}$  by the "oxo" process, i.e., addition of  $H_2C=O$  and hydrogenation to the alcohol  $R-OH$  where  $R=C_8$  to  $C_{22}$



$R-SH \quad R=C_8 \text{ to } C_{22}$

$R-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2 \quad R=C_8 \text{ to } C_{22}$   
 $R-\text{SO}_2\text{NH}_2 \quad R=C_8 \text{ to } C_{14}$



polypropylene oxide of M.W. about 800 to about 2500  
 $H_2N-CH_2CH_2NH_2$  + propylene oxide to M.W. 800 to 2500

$X-NH_2$  or  $X(NH)_2$  + propylene oxide to M.W. 800 to 2500

$X$  or  $(OH \text{ or } X-(OH)_2)$  + propylene oxide to M.W. 800 to 2500

$X$  = residue of active hydrogen compound

(B) Alkylolamine condensation products with fatty acids or esters. Suitable alkylolamines include:

diethanolamine

monoethanolamine

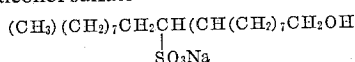
isopropanolamine

di-n-propanolamine

(C) Glycol and polyol esters of fatty acids.

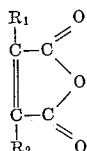
(D) Anionic surface active agents containing hydroxyls, e.g.,

- (1) sodium salt of  $\alpha$ -hydroxy stearic acid
- (2) sulfated fatty acid esters of glycols and polyols
- (3) alkali salts of sulfate ester of (B)
- (4) oleyl alcohol sulfate



- (5) salts of ricinoleic acid, and the like
- (6) sulfate and phosphate esters and neutral salts thereof of the nonionic products described in (A) above.

The polymeric anhydrides which are herein contemplated are interpolymers of at least one ethylenically unsaturated monomer with an anhydride containing an ethylenic linkage. The preferred anhydrides are the  $\alpha,\beta$ -unsaturated dicarboxylic acid anhydrides and particularly those of the maleic anhydride series having the formula:



wherein  $R_1$  and  $R_2$  are independently selected from the group consisting of hydrogen, halogen, alkyl, aryl, aralkyl, substituted alkyl, aryl or aralkyl, or  $-\text{SO}_3\text{H}$ .

Examples of such compounds are:

maleic anhydride

chloromaleic anhydride

citraconic anhydride (methyl maleic)

fumaric anhydride

mesaconic anhydride

phenyl maleic anhydride

benzyl maleic anhydride

sulfomaleic anhydride

5 aconitic anhydride

In addition, other unsaturated anhydrides such as

itaconic

methylene malonic

10 allyl succinic, and the like may be used.

The copolymerizable monomers containing a  $>C=CH_2$  group which may be employed with the above described anhydride included all of the known ethylenically unsaturated copolymerizable compounds such as:

15 vinyl ethers e.g.,

vinyl methyl ether

vinyl ethyl ether

vinyl n-propyl ether

vinyl iso-propyl ether

20 vinyl n-butyl ether

vinyl iso-butyl ether

vinyl iso-octyl ether

vinyl phenyl ether

$\alpha$ -chlorovinyl phenyl ether

25 vinyl  $\beta$ -naphthyl ether

vinyl esters, e.g.,

vinyl acetate

vinyl propionate

vinyl butyrate

vinyl caproate

vinyl stearate, etc.

vinyl halides, e.g.,

vinyl chloride

vinyl fluoride

vinyl bromide

acrylic acid and esters, e.g.,

methyl acrylate

ethyl acrylate

propyl acrylate

40 acrylic acid derivatives, e.g.,

methacrylic acid and esters

$\alpha$ -haloacrylic acid and esters

acrylonitrile

methacrylonitrile

45 acrylamide

methacrylamide

N-alkyl acrylamides

N-aryl acrylamides

N-vinyl heterocycles, e.g.,

50 N-vinyl pyrrolidone

N-vinyl-3-morpholinones

N-vinyl oxazolidone

N-vinyl imidazole

styrene

55 alkyl styrenes, e.g.,  $\alpha$ -methyl styrene

vinylidene chloride

vinyl ketones, e.g., methyl vinyl ketone

olefins such as

ethylene

60 propylene

isobutylene

butene-1

2,4,4-trimethyl pentene-1

hexene-1

65 3-methyl-butene-1, and the like.

The anhydride-ethylenically unsaturated interpolymers preferably contain the two moieties in equimolar amounts whereby the repeating unit in the interpolymers contains

70 1 anhydride and 1 comonomer moiety.  
 Examples of specific interpolymers which may be employed are:

vinyl methyl ether-maleic anhydride

vinyl ethyl ether-maleic anhydride

75 styrene-maleic anhydride

$\alpha$ -methyl styrene-maleic anhydride  
ethylene-maleic anhydride  
vinyl methyl ether-citraconic anhydride  
vinyl methyl ether-itaconic anhydride  
vinyl methyl ether-chloromaleic anhydride  
vinyl chloride-maleic anhydride  
vinyl acetate-maleic anhydride  
vinyl chloride-vinyl acetate-maleic anhydride  
styrene-vinyl acetate-maleic anhydride

The interpolymers above described may vary in molecular weights from as low as about 400 to several million (e.g., 2,000,000) or more. Viscosity measurements are commonly used as an indication of the average molecular weight of the polymeric composition. The K value (Fikentscher) of any particular mixture of polymers is calculated from viscosity data and is useful as an indication of the average molecular weight of such mixture. Its determination is fully described in "Modern Plastics" 23, No. 3, 157-61, 212, 214, 216, 218 (1945) and is defined as 1000 times  $k$  in the empirical relative viscosity equation:

$$\log_{10} \eta_{rel} = \frac{75k^2}{1 + 1.5kC} + k$$

wherein  $C$  is the concentration in grams per hundred cc. of polymer solution and  $\eta_{rel}$  is the ratio of the viscosity of the solution to that of pure solvent. The  $K$  values are reported as 1000 times the calculated viscosity coefficient in order to avoid the use of decimals. The preferred interpolymers employed in the present invention have  $K$  values of from about 10 to about 200.

$K$  values and specific viscosities ( $\eta_{sp}$ ) are interconvertible and are related through relative viscosity ( $\eta_{rel}$ ). Thus, when viscosity measurements are taken on solutions which have a concentration of 1.00 gram of polymer per deciliter of solution at 25° C. ( $C=1$ ), the relationships are as follows:

$$\eta_{rel} = \eta_{sp} + 1$$

Relative viscosity = specific viscosity plus one

$$\text{Relative viscosity} = 10^{(0.001K + 0.000075K^2 / (1 + 0.0015K))}$$

$$\text{Hence } \eta_{sp} = -1 + 10^{(0.001K + 0.000075K^2 / (1 + 0.0015K))}$$

Relative viscosity, specific viscosity and  $K$  are dimensionless, whereas inherent viscosity

$$\frac{(\log_e \eta_{rel})}{C}$$

and intrinsic viscosity (the limit of inherent viscosity as  $C$  approaches zero) have the dimensions of dilution, i.e., the reciprocal of concentration. Intrinsic viscosity and  $K$  are intended to be independent of concentration. The preferred interpolymers are those having a specific viscosity ranging from about 0.1 to about 4.5.

The partial esters employed as stabilizers in the compositions of the present invention may be prepared in various ways. The partial esters may be prepared in an aqueous medium or in a non-aqueous solvent medium. Where water is used as the medium for reaction, the polymeric anhydride must not be in contact with the water except when there is present surface active hydroxy compounds. Thus, where water is used as the reaction solvent medium, the anhydride must be added to the hydroxy compound in water solution, the hydroxy compound being present at a concentration greater than its critical micelle concentration. Alternatively, the solution of the hydroxy compounds may be added to the anhydride, for example, in the dry state. Where a non-reactive solvent is used such as acetone, either reactant or both may be in solution, and either may be added to the other. When employing water as the reaction medium, the amount of water to be used should not be greater than about 99.7%, i.e., 0.25% reactants. The minimum water content is governed primarily by viscosity considerations relating to handling problems. It is, however, desirable to maintain a minimum water content of about 2%. The preferred range of water

is from about 8% to about 98%. In preparing the partial esters the ratio of the reactants may vary widely. As little as about 0.01% on a molar basis of surface active agent per mole of polymeric anhydride yields partial esters suitable for the present invention. The surface active agent may also be present in large excess. While there is no theoretical mass ratio of surface active agent to polymer anhydride from the practical point of view, it is preferred to employ a molar ratio of no more than about 100:1. It is of course clear that the weight ratios will vary in accordance with the above depending upon the particular polymeric anhydride used and the particular surface active agent employed.

In non-aqueous systems the lower limit of surfactant is similar to that described above for the aqueous systems but in contradistinction to the aqueous system, the upper limit of the surface active material is about 1.5 to 2 moles thereof per mole of polymeric anhydride.

As pointed out above, the two essential ingredients of the heavy duty detergent composition are the surface active agent and the inorganic salt. The surface active agent may be a non-ionic surfactant, an anionic surfactant or a mixture of these. Suitable nonionic surfactants and anionic surfactants include those described above as useful in the preparation of the partial esters in the preparation of the stabilizers used in the compositions of this invention. In addition, since the surface active compounds described above all contain hydroxyl groups, one may employ other surface active materials as organic detergent ingredients of the heavy duty liquid composition, as for example, sodium lauryl sulfate, dodecyl benzene sulfonates and the like.

Since the characteristic of the "heavy duty" compositions lies in the presence generally of inorganic salts alkaline in nature, the salts which are herein contemplated are usual alkaline reacting inorganic materials employed in such compositions and include alkali metal polyphosphates alone or in combination with other neutral or alkaline reacting inorganic salts such as alkali metal silicates, carbonates, bicarbonates, phosphates, sulfates, borates, hydroxides, etc. In many applications, the polyphosphates may not be present, and instead, one or more of the other mentioned inorganic salts is present as the inorganic constituent of the detergent composition.

A number of other auxiliary agents may also be included in such compositions to adapt them to certain specific applications. These include optical brighteners, foam stabilizers, defoaming agents, soil suspending agents, and the like. Additionally, there may be employed coloring materials, perfumes, and corrosion inhibitors. The alkali metal polyphosphates which are the preferred inorganic salts 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 in 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 representative of commonly employed alkali metal polyphosphates, there may be mentioned tetrasodium and tetrapotassium pyrophosphates, sodium and potassium triphosphates, tetraphosphates, pentaphosphates, hexameta phosphates, and mixtures of two or more thereof. Ammonium and amine salts of the above described compounds are to be regarded as the equivalents of the alkali metal products recited.

The concentrations of the various ingredients of the compositions of the present invention are not critical except that certain practical limits are advantageous. Since the object of this invention is to prepare a stable emulsion of detergent, water and inorganic salt, any combinations of these three which does not produce a single phase,

homogenous system will be stabilized by the partial esters used and described herein.

The amount of partial ester may vary between about 0.1% to about 5%, with a range of about 0.4% to about 2.0% being preferred.

The amount of detergent may vary widely with the preferred range for all-purpose dishwashing and clotheswashing compositions being from about 5% to about 20%. Similarly, the inorganic salts may vary in amounts from about 7% to about 40% with the preferred limits being from about 15% to about 30%. The other additives mentioned above comprise but a minor portion of the total solids, i.e., less than about 5%, leaving as the balance for the amount of water a range of from about 35% to about 85%.

The following examples will serve to illustrate the present invention without being deemed limitative thereof. Parts are by weight unless otherwise indicated.

#### EXAMPLE 1

Operating at room temperature (about 25° C.), 38 g. of vinyl methyl ether-maleic anhydride interpolymers (mole ratio 1:1; specific viscosity 1.6) is added to a solution of 2 grams of a surface active product (made by reacting nonyl phenol with 10 moles of ethylene oxide) in 60 g. of water. The product becomes extremely viscous.

2.5 g. of the above reaction product is added to the following liquid detergent:

##### Formulation A

Water	62.5
Nonyl phenol+10 moles ethylene oxide surfactant	10.0
Tetrapotassium pyrophosphate	25.0

The pH of finished Formula A is 8.9, the viscosity is 1100 cps. and the resulting emulsion is completely stable after 100 minutes in a centrifuge at 500 r.p.m. and overnight there is still 100% emulsion stability.

#### EXAMPLE 2

Example 1 is repeated except that the reaction product is prepared from 39.6 g. of interpolymers and 0.4 g. of surface active agent. In finished Formulation A the pH is 8.7, the viscosity 200 cps. and the stability similar to Example 1.

#### EXAMPLE 3

Example 2 is repeated except that the reaction product is added to a liquid detergent of the following composition:

##### Formulation B

Water	40
Carboxymethyl cellulose (5% solution in water)	10
KOH	2
Sodium silicate-H <sub>2</sub> O solution (36% solids)	10
Surface active agent of formulation A	10
Tetrapotassium pyrophosphate	25

The pH of the finished formulation is 11.9, viscosity 1600 cps. and stability as in Examples 1 and 2.

In the absence of the reaction product the Formulations A and B after 15 minutes on the centrifuge have only 10% emulsion. With 1.0% interpolymers (unreacted), the stability of the emulsion is only 25% after 15 minutes in the centrifuge.

The interpolymers-surfactant reaction products of Examples 1 and 2 have, respectively, about 0.3% and 0.1% of the total potential carboxyl groups of the interpolymers present as ester groups.

#### EXAMPLE 4

A heavy duty liquid detergent composition is prepared as follows:

(A) To a solution of 0.05 g. of a nonyl phenol plus 15 moles of ethylene oxide condensate (surface active agent) in 7.5 g. of water are added 4.95 g. of a vinyl

methyl ether-maleic anhydride copolymer (1:1 ratio; specific viscosity=1.6). The mixture is stirred while being heated on a steam bath for 45 minutes and then 153 g. of water are added and the reaction mixture stirred until solution is complete.

(B) There are then added:

	G.
1% aqueous solution of Blancophor RG-96 (brightener)	50.5
5% aqueous solution of a low viscosity carboxymethylcellulose	50
KOH	9
36% aqueous sodium silicate	50
Nonyl phenol+10 moles ethylene oxide surface active condensation product	50
Tetrapotassium pyrophosphate	125

The resultant composition has a pH of 12 and is a readily pourable emulsion of excellent stability. Viscosity=400 cps.

#### EXAMPLE 5

Example 4 is repeated except that the partial ester stabilizer is reduced to 0.75% active in the final composition, employing 3.75 g. of anhydride copolymer and 0.0038 g. of surfactant.

#### EXAMPLE 6

A stabilizer (partial ester) is prepared as in Example 4(A). There are then added the same ingredients as in Example 4(B) except in place of the 50 g. of nonyl phenol+10 moles of ethylene oxide condensate, there are used 40 g. of the sodium salt of the sulfate ester of nonyl phenol+6 moles of ethylene oxide and 10 g. of lauric diethanolamide. This results in a stable emulsion similar to Example 4 but containing a major amount of an anionic surfactant.

The stabilizer of Examples 4 through 6 has about 0.1% of the carboxyl groups as ester groups.

#### EXAMPLE 7

Example 2 is repeated employing as the interpolymers an ethylene-maleic anhydride copolymer of specific viscosity 0.6 (Monsanto DX840-21) and is used in formulation B of Example 3. A stable emulsion is produced.

#### EXAMPLE 8

5 g. of the interpolymers of Example 1 is added to a solution of 5 g. of the surface active product of Example 1 in 90 g. of water. The mixture is heated on a steam bath for 1 hour with stirring.

To the following detergent composition there is added 1% (active basis) or 10% of the above solution:

	Percent
Low viscosity carboxymethyl cellulose	0.5
Sodium silicate (36% aqueous solution)	10.0
Sodium xylene sulfonate (40% aqueous solution)	12.5
Oleic acid	2.0
Surface active agent of nonyl phenol+10 moles ethylene oxide	10.0
Tetrapotassium pyrophosphate	25
Ethanol	4
Balance water and KOH to a pH=12.	

The resultant emulsion is very stable and has a viscosity of 1500 cps. The partial ester stabilizer contains about 0.7% ester groups based on total carboxyls present or potential.

#### EXAMPLE 9

Example 8 is repeated except that the surface active hydroxy compound used to prepare the partial ester is

- nonyl phenol+6 moles ethylene oxide (0.6% ester groups)
- nonyl phenol+15 moles ethylene oxide (0.5% ester groups)

9

10

- (c) non phenol+30 moles ethylene oxide  
 (d) tridecyl alcohol+6 moles ethylene oxide (0.5% ester groups)

## EXAMPLE 10

The partial ester stabilizer of Example 9(b) is used in the following formulations:

Formula	1	2	3	4	5	6	7	8	9	10
KOH	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
CMC <sup>1</sup>	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Stabilizer <sup>2</sup>	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.25	2.0	1.0
Silicate <sup>3</sup>	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Sodium xylene sulfonate (40% aq. sol.)		12.5	12.5		12.5	12.5	12.5	12.5	12.5	
Oleic acid		2.0	2.0		2.0	2.0	2.0	2.0	2.0	
Detergent A <sup>4</sup>	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	
TKPP <sup>5</sup>	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
Ethanol					4.0	4.0	4.0	4.0	4.0	
Detergent B <sup>6</sup>										
Viscosity(cps.)	1,850	1,600	1,840	440	9,000	7,600	3,000	3,800	3,300	16.7
Stability					All excellent					1,400

<sup>1</sup> Low viscosity carboxy methyl cellulose.

<sup>2</sup> Stabilizer of Example 9(c) (0.7% ester groups).

<sup>3</sup> 36- sodium silicate in water.

<sup>4</sup> Nonyl phenol+10 moles ethylene oxide.

<sup>5</sup> Tetrapotassium pyrophosphate.

<sup>6</sup> Sodium dodecyl benzene sulfonate.

## EXAMPLE 11

Example 8 is again repeated except that 9.9 g. of surface active agent and only 1 g. of interpolymer is used. This stabilizer contains 3% ester groups. The resultant liquid detergent composition is very stable.

## EXAMPLE 12

0.3 g. of the detergent composition containing stabilizer of Example 4 is added to 1 liter of water (150 p.p.m. hardness) at 120° F. in a stainless steel beaker and evaluated for cotton detergency in a standard Terg-O-Tometer test (125 r.p.m.) using 4 samples each of three different soiled fabrics: (1) U.S. Testing Co.; (2) Test Fabrics soiled cotton No. 26, and (3) American Conditioning House No. (115) and three samples of unsoiled Indian-head Cloth. The soiled (1½" x 3½") and unsoiled samples are added to the water at 120° F. and washed for 10 minutes, wrung hand dry and rinsed for five minutes with one liter water (150 p.p.m. hardness) at 100° F. in same beaker. The swatches are then dried and the reflectance is measured using a model 610 photometer (Photovolt Corp.) containing a tristimulus green filter on the search unit. The unit is calibrated so that the standard white ceramic plate gives a reading of 86. Similar tests are run using a commercial liquid detergent (A) and a commercial powder detergent (B). The results are tabulated below.

Detergent	Reflectance Readings Soiled Fabrics			Redeposition (unsoiled)
	(1)	(2)	(3)	
Example 4	40.8	37.5	42.5	80.0
(A)	34.0	36.5	42.3	81.0
(B)	39.5	37.5	42.8	79.0

The above results clearly establish that the detergent qualities of the heavy-duty liquid formulation are excellent and compare favorably with other commercially available products.

## EXAMPLE 13

Example 3 is repeated except that the stabilizer is prepared as in Example 1 using a ratio of polymer anhydride to surfactant of 199:1. The viscosity of the detergent formulation is 280 cps. and the stability is the same as in Example 3.

## EXAMPLE 14

Example 3 is again repeated using a ratio of polymer

anhydride to surfactant of 399:1. The viscosity of the detergent formulation is 140 cps. and the stability is excellent.

## EXAMPLE 15

Example 1 is repeated except that the ratio of polymer anhydride to surfactant is 3:1 (i.e., 30 g. anhydride:10 g.

surfactant). The viscosity of the detergent formulation A is 490 cps. and the stability is excellent.

## EXAMPLE 16

Example 1 is again repeated using a polymer anhydride to surfactant ratio of 9:1. The finished formulation has a pH of 9.1, a viscosity of 3600 cps. and is excellently stabilized.

## EXAMPLE 17

Using equal weights of the polymer anhydride and surfactant of Example 1, stabilizers are prepared in water at solids contents of 5%, 10%, 20%, 40%, 60% and 80% following the procedure of Example 8. The viscosities of detergent formulations (formulation A of Example 1) are 120 cps., 130 cps., 100 cps., 220 cps., 100 cps. and 55 cps. respectively. All emulsions are stable.

## EXAMPLE 18

Example 3 is repeated except that instead of 1% active stabilizer, the following amounts (active bases) are used and the viscosities and stabilities given below.

Percent Stabilizer	Viscosity of Detergent (cps.)	Stability
2.00	5,400	Excellent.
0.50	180	Do.
0.25	130	Do.

## EXAMPLE 19

The procedure of Example 8 is repeated in the preparation of the stabilizer using, however, an interpolymer of specific viscosity 0.1. To detergent formulation B of Example 3 there is added 10% by weight of the stabilizer solution (1% active in final formulation) based on weight of detergent formulation B. The viscosity of the final stabilized formulation is 140 cps.

## EXAMPLES 20-25

Example 19 is repeated except that the interpolymers used have the indicated viscosity characteristics.

Example	Specific Viscosity of Interpolymer	Viscosity of Final Formulation (cps.)
20	0.5	200
21	1.1	350
22	2.0	1,100
23	3.2	2,000
24	3.8	3,800
25	4.5	5,200

## 11

## EXAMPLE 26

A stabilizer is prepared by adding in one minute 79.2 g. of the anhydride interpolymers of Example 1 to 0.8 g. of surfactant of Example 4 (nonyl phenol+15 ethylene oxide) in 320 g. of water at 87° C. and stirring for 45 minutes. The product contains 0.32% ester groups and is added to (1% active) formulation B of Example 3. The results are similar to Example 3.

## EXAMPLE 27

The procedures of Examples 1 and 8 are repeated for preparing the stabilizer using the following polymer anhydrides and comonomers in equimolar amounts:

- (1) Chloromaleic anhydride-vinyl methyl ether (K=30);
- (2) Chloromaleic anhydride-vinyl methyl ether (K=60);
- (3) Citraconic anhydride-vinyl methyl ether (K=40);
- (4) Methylene malonic anhydride-vinyl methyl ether (K=20);
- (5) Benzyl maleic anhydride-vinyl methyl ether (K=35);
- (6) Maleic anhydride-vinyl ethyl ether (K=20);
- (7) Maleic anhydride-vinyl ethyl ether (K=90);
- (8) Maleic anhydride-vinyl isobutyl ether (K=40);
- (9) Maleic anhydride-vinyl acetate;
- (10) Maleic anhydride-vinyl stearate;
- (11) Maleic anhydride-vinyl chloride;
- (12) Maleic anhydride-vinyl chloride (80%)-vinyl acetate (20%);
- (13) Maleic anhydride-acrylonitrile;
- (14) Maleic anhydride-methyl acrylate;
- (15) Maleic anhydride-N-vinyl pyrrolidone;
- (16) Maleic anhydride-styrene;
- (17) Maleic anhydride-propylene.

## EXAMPLE 28

Example 7 is repeated using a styrene-maleic anhydride interpolymers (M.W.=2300).

## EXAMPLE 29

The products of Example 27 are employed (1% active) in detergent formulations as in Examples 1, 3 and 8. Excellent stabilities are forthcoming.

## EXAMPLE 30

Example 27 is repeated employing as the esterifying surfactant in place of the one used in Examples 1 and 8, the following:

- (a) castor oil+20 moles ethylene oxide
- (b) castor oil+30 moles ethylene oxide
- (c) castor oil+180 moles ethylene oxide
- (d) dinonyl phenol+150 moles ethylene oxide
- (e) dodecyl phenol+18 moles ethylene oxide
- (f) dodecyl phenol+33 moles ethylene oxide
- (g) dodecyl phenol+200 moles ethylene oxide
- (h) polypropylene oxide (M.W. 1200)+10 moles ethylene oxide
- (i) sodium  $\alpha$ -hydroxy stearate
- (j) monophosphate ester of nonyl phenol+6 moles ethylene oxide.
- (k) ammonium sulfate of nonyl phenol+10 moles ethylene oxide

## EXAMPLE 31

A stabilizer composition is prepared as in Example 8 using as the surfactant, however, a nonyl phenol+15 moles of ethylene oxide condensate.

One percent (active) of the stabilizer is added to a liquid detergent formulation of:

	Percent
Nonyl phenol+10 moles ethylene oxide	10.0
Tetrapotassium pyrophosphate	20.0
Sodium silicate (36% aqueous)	10.0
Water balance.	

## 12

0.25g. of the above detergent formulation is employed in a Terg-O-Tometer test as in Example 12.

A similar formulation without the stabilizer is also tested in the same manner. The results are in the following table:

Detergent Product	Reflectance Readings			Redeposition (unsoiled)
	(1)*	(2)*	(3)*	
With stabilizer	37.0	38.0	46.0	74.0
Without stabilizer	37.0	38.0	46.0	74.0

\*Indicates same fabrics as tested in Example 12.

The data demonstrates that there is no loss in detergency due to the presence of the stabilizer.

## EXAMPLE 32

Example 1 is again repeated employing 9 g. of anhydride and 36 g. of surfactant (ratio 1:9). A well stabilized detergent formulation is obtained.

## EXAMPLE 33

Example 1 is once again repeated employing 0.4 g. of anhydride and 39.6 g. of surfactant (ratio 1:99). A well stabilized product is obtained.

Other variations in and modifications of the described processes which will be obvious to those skilled in the art can be made in this invention without departing from the scope or spirit thereof.

We claim:

1. A stabilized liquid alkaline detergent composition consisting essentially of water, a water-soluble organic detergent compound selected from the group consisting of anionic and non-ionic compounds and mixtures thereof and a water-soluble inorganic alkaline salt, the said detergent forming a separate liquid phase, with from about 0.1% to about 5% based on the weight of the total composition of a water-soluble partial ester of

(a) a hydroxyl-containing micelle-forming surface active agent selected from the group consisting of anionic surface active agents, alkaline oxide condensation products with an active hydrogen-containing hydrophobe, alkylolamine condensation products with fatty acids, alkylolamine condensation products with fatty esters, and glycol and polyol esters of fatty acids and

(b) an alkaline-soluble interpolymers with an  $\alpha,\beta$ -unsaturated carboxylic acid anhydride with an ethylenically unsaturated monomer selected from the group consisting of vinyl esters, vinyl ethers and  $\alpha$ -olefins, said interpolymers having a K value of from about 10 to about 200 and said partial ester containing from about 0.01% to about 5% of the carboxyl groups present as ester groups.

2. A composition as defined in claim 1, wherein the anhydride is maleic anhydride.

3. A composition as defined in claim 2, wherein the ethylenically unsaturated monomer is methyl vinyl ether.

4. A composition as defined in claim 2, wherein the ethylenically unsaturated monomer is an olefin.

5. A composition as defined in claim 2, wherein the ethylenically unsaturated monomer is ethylene.

6. A composition as defined in claim 2, wherein the ethylenically unsaturated monomer is styrene.

7. A composition as defined in claim 1, wherein the hydroxyl-containing micelle-forming surface active agent is an alkaline oxide condensation product of an active hydrogen-containing hydrophobe.

8. A composition as defined in claim 1, wherein the hydroxyl-containing micelle-forming surface active agent is an anionic surface active agent.

9. A composition as defined in claim 7, wherein the surface active agent is an alkyl phenol-ethylene oxide condensate.

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10. A composition as defined in claim 7, wherein the surface active agent is an aliphatic alcohol-ethylene oxide condensate.

11. A composition as defined in claim 7, wherein the alkaline salt is an alkali polyphosphate.

12. A composition as defined in claim 7, wherein the alkaline salt is tetrapotassium pyrophosphate.

13. A composition as defined in claim 7, wherein the alkaline salt is sodium metaphosphate.

14. A stabilized aqueous detergent composition consisting essentially of from about 7% to about 40% by weight of a water-soluble inorganic alkaline salt, from about 5% to about 20% by weight of a water-soluble organic detergent compound selected from the group consisting of anionic and nonionic compounds and mixtures thereof, and from about 0.1% to about 5% by weight, the said weights based upon the weight of the total composition, of a water-soluble partial ester of

(a) a hydroxyl-containing micelle-forming surface active agent selected from the group consisting of anionic surface active agents, alkaline oxide condensation products with an active hydrogen-containing hydrophobe, alkylolamine condensation products with fatty acids, alkylolamine condensation products with fatty esters, and glycol and polyolesters of fatty acids and

(b) an alkali-soluble interpolymer with an  $\alpha,\beta$ -unsaturated carboxylic acid anhydride with an ethylenically unsaturated monomer selected from the group consisting of vinyl esters, vinyl ethers and  $\alpha$ -olefins, said interpolymer having a K value of from about 10 to about 200 and said partial ester containing from

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about 0.01% to about 5% of the carboxyl groups present as ester groups.

15. A composition as defined in claim 14, wherein the surface active agent is an alkyl phenol-ethylene oxide condensate.

16. A composition as defined in claim 14, wherein the surface active agent is an aliphatic alcohol-ethylene oxide condensate.

17. A composition as defined in claim 14, wherein the alkaline salt is an alkali polyphosphate.

18. A composition as defined in claim 14, wherein the interpolymer is an alkyl vinyl ether-maleic anhydride interpolymer.

19. A composition as defined in claim 15, wherein the interpolymer is an alkyl vinyl ether-maleic anhydride interpolymer.

20. A stabilized aqueous detergent composition consisting essentially of from about 7% to about 40% by weight of an alkali polyphosphate, from about 5% to about 20% by weight of a water-soluble organic non-ionic detergent and from about 0.1% to about 5% by weight of a water-soluble partial ester of an alkyl phenol-ethylene oxide surface active condensate and an alkyl vinyl ether-maleic anhydride interpolymer, the said weights based upon the weight of the total composition and said partial ester containing from about 0.01% to about 5% of the carboxyl groups present as ester groups.

No references cited.

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,328,309 Dated June 27, 1967

Inventor(s) Richard A. Grifo and Fred E. Woodward

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 12, lines 42 and 68, and column 13, line 21, for "alkaline", read -- alkylene --.

Signed and sealed this 12th day of June 1973.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

ROBERT GOTTSCHALK  
Commissioner of Patents