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3,629,125

LIQUID DETERGENT COMPOSITIONS

Thomas Aquinas Payne, Jr., Teaneck, and Warren Eric Olson, Verona, N.J., assignors to Lever Brothers Company, New York, N.Y.

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14 Claims

ABSTRACT OF THE DISCLOSURE

A phase-stable, pourable, heavy-duty, liquid detergent emulsion composition which does not exhibit a substantial change in viscosity on standing comprising a nonionic synthetic detergent, an alkali metal pyrophosphate, a combination of a first stabilizer which is a hydrolyzed linear copolymer of ethylene and maleic anhydride and a second stabilizer which is a hydrolyzed cross-linked copolymer of ethylene and maleic anhydride, and the balance substantially water.

This application is a continuation of application Ser. No. 685,273, filed Nov. 24, 1967, now abandoned, which is a continuation-in-part of application Ser. No. 362,489, filed Apr. 24, 1964, now abandoned.

The invention relates to liquid cleansing compositions and more particularly to an improvement in preparing stable, heavy-duty, liquid detergent formulations.

Heavy-duty liquid detergent compositions particularly suited for laundry purposes are well known. Many of these products tend to be unstable and their components separate into layers upon standing for a period of time. This is objectionable from the consumer's standpoint since measured amounts of the detergent do not always contain the same proportion of cleansing ingredients and the result in many instances is an inefficient washing performance.

Another problem in the production of heavy-duty liquid detergents is that the viscosity of the product is not always desirable from the consumer's standpoint. Thus, the viscosity of many formulations is so low that the resulting product is thin and watery. In others, the viscosity is unduly excessive so that the detergent is difficult to pour.

These difficulties have, to a large extent, been obviated by the development disclosed and claimed in co-pending application Ser. No. 301,957, filed Aug. 14, 1963, now abandoned. However, it has been observed that detergent formulations prepared by the method of Ser. No. 301,957 exhibit a gradual change in viscosity over an extended period of time. The addition of a hydrotrope further accelerates the change in the viscosity of detergent compositions manufactured in accordance with the procedure disclosed in said application.

It is an object of this invention to provide an improved procedure for preparing stable, heavy-duty, liquid detergents having an acceptable viscosity and satisfactory detergent properties.

Another object is to provide phase-stable, heavy-duty liquid detergents having viscosities that do not change substantially with time and having satisfactory detergent properties.

These and other objects and advantages of the invention are attained by hydrolyzing a combination of a linear and a cross-linked copolymer of ethylene and maleic anhydride in the presence of a synthetic organic nonionic surface active agent of the polyoxyalkylene type to provide the requisite stability and viscosity to liquid detergent compositions of the heavy-duty type. It is especially

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preferred to utilize the mixture of copolymers in combination with a hydrotrope to produce formulations which exhibit improved stability, particularly at elevated temperatures.

The products of the invention contain four ingredients which are essential and which should be employed within a specified range of proportions if a composition having the desirable properties enumerated above is to be obtained. One component is water which acts as a suspending medium for the remaining ingredients in the composition.

Another necessary component is at least one nonionic synthetic non-soap detergent of the polyoxyalkylene type used in proportions ranging from about 6% to about 15% based on the weight of the total formula. These nonionic materials are formed by condensing several moles of an alkylene oxide such as ethylene oxide or propylene oxide with a hydrophobic base such as alkyl phenols, long chain aliphatic alcohols and mercaptans, propylene oxide-propylene glycol condensates, etc. Typical examples of suitable nonionics are shown in the following table:

TABLE I

Trade name	Hydrophobe	Average ethylene oxide content
Sterox DJ	Dodecylphenol	10 moles.
Sterox MJ-b	n-Dodecylphenol	Do.
Triton X-100	Octylphenol	Do.
Igepal CO-530	Nonylphenol	6 moles.
Igepal CO-730	Nonylphenol	15 moles.
Igepal RC-520	Dodecylphenol	6 moles.
Igepal RC-760	Dodecylphenol	11 moles.
Igepal DJ-890	Dinonylphenol	85 percent.
Adol 42-10EO	Tall oil alcohol	9 moles.
	Unhardened tallow alcohol	10 moles.
Alfonic 1418-6	n-C ₁₄ -C ₁₈ alcohols	62.5 percent.
Tergitol 15-S-7.5	n-C ₁₄ -C ₁₈ secondary alcohols	7.5 moles.

Other suitable nonionics include the polyoxyethylene polyoxypropylene ethanols having the empirical formula $\text{HO}-(\text{C}_2\text{H}_4\text{O})_a(\text{C}_3\text{H}_6\text{O})_b(\text{C}_2\text{H}_4\text{O})_c\text{H}$ prepared by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol where b is an integer from 26 to 30 and a plus c is an integer such that the molecule contains from 0% to 10% ethylene oxide ("Pluronic L-60"), or from 10% to 20% ethylene oxide ("Pluronic L-61").

Another critical ingredient of the heavy-duty detergents of this invention is at least one alkali metal pyrophosphate which should be employed in amounts ranging from about 17% to about 35% by weight of the mixture. Examples of the pyrophosphates include tetrapotassium pyrophosphate, tetrasodium pyrophosphate, and blends of these materials in which the tetrasodium pyrophosphate comprises up to about 20% by weight of the blend.

The remaining critical ingredient in the liquid detergents of this invention functions as a stabilizer to maintain the nonionic active and the pyrophosphate components in the aqueous medium without allowing phase separation of the emulsion formed in the process. The stabilizer comprises a combination of a linear and a cross-linked copolymer of ethylene and maleic anhydride and is employed in the liquid detergent in an amount sufficient to provide both the desired stability and viscosity to the product. A suitable level of this combination of copolymers ranges from about 0.60% to about 0.9% by weight of the total composition.

Suitable linear copolymers of ethylene and maleic anhydride are available from the Monsanto Chemical Company under the designations "DX-840-21," "DX-840-31," "DX-840-4118," etc. Cross-linked copolymers are available under the designations "DX-840-61," "DX-840-71," "DX-840-81," "DX-840-91" and similar materials in this series. In general, the monomers are polymerized in a

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1:1 ratio, the resins having molecular weights ranging from about 1500 and upwards. The cross-linked copolymers are generally cross-linked with a diamine, an alkylene polyamine, or a diolefinic material such as an ether, ester or a hydrocarbon, etc. Examples of polyamine cross-linking agents include diethylene triamine, triethylene tetramine, tetraethylene pentamine, and higher molecular weight polyethylene polyamines. Exemplary diolefinic cross-linking agents include divinyl benzene, diallyl ether, diallyl esters and the like. Other suitable cross-linking agents are set forth in U.S. Pats. Nos. 3,165,486 and 3,235,505 of Monsanto Company and include the preferred vinyl esters of olefinically unsaturated aliphatic carboxylic acids having from 3 to 24 carbon atoms, e.g., vinyl crotonate, vinyl linoleate, divinyl itaconate, vinyl acrylate and the like. The linear and cross-linked copolymers which have been successfully utilized in preparing formulations of this invention include the following:

	Specific viscosity*	Molecular weight
Linear resin:		
DX-840-21.....	0.6	Intermediate.
DX-840-31.....	1.0	High.
DX-840-4118.....	1.8	Very high.
	Viscosity in cps.**	
Cross-linked resin:		
DX-840-61.....	12,000	
DX-840-71.....	40,000	
DX-840-81.....	80,000	
DX-840-91.....	160,000	

* Determined on a 1% solution of the resin in dimethyl formamide at 25° C.

** Measurements made at 25° C. on a 1% aqueous solution, adjusted to pH 9 with ammonium hydroxide, using a Brookfield viscometer, No. 6 spindle at 5 r.p.m.

If desired, the compositions of the invention may contain various additives in amounts which do not deleteriously affect the stability and pourability of the liquids. For example, the liquid detergent formulas may contain about 2 to 10% by weight of inorganic silicate solids such as sodium or potassium silicates.

Furthermore, hydrotropes such as methyl Carbitol and the alkali metal salts of lower alkylaryl sulfonates may be present. The latter include sodium xylene sulfonate, sodium toluene sulfonate and mixtures thereof containing 0-25% sodium toluene sulfonate based on the combined weight of sodium toluene sulfonate and sodium xylene sulfonate. The proportions of hydrotrope in the formulations range from 0 to about 5% based on the weight of the composition. Preferably, about 2% of a hydrotrope is employed based on the weight of the total formulation.

Other suitable additives include fluorescent dyes, colorants, perfumes, germicides, bacteriostats, soil-suspending agents such as sodium carboxymethyl-cellulose and about 0.5 to about 3% of a suds-controlling nonionic surfactant such as the aforementioned "Pluronics."

In order to provide stable, pourable and substantially homogeneous heavy-duty liquid detergents, the aforementioned necessary components should be present within the range of proportions discussed above.

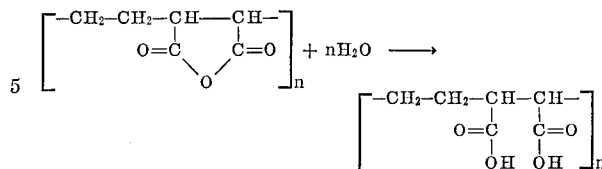
Moreover, the objectives of the invention can be attained most successfully by observing certain precautions in preparing the formulations of this invention.

Thus, to obtain liquid detergent products having desirable viscosities and acceptable stability, the linear and cross-linked ethylene-maleic anhydride copolymers in substantially anhydrous form must be rapidly dispersed in an aqueous solution in the presence of the synthetic nonionic surfactant. It is preferred that the copolymers be dispersed in an aqueous solution which already contains the nonionic. However, the copolymers and nonionic can be simultaneously dispersed in the aqueous solution, the main requirement being that the copolymers are hydrolyzed in the presence of the nonionic component.

Preferably, the aqueous solution is at an elevated temperature to accelerate hydration of the anhydride portion of the copolymers to the acid form in the presence of the

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nonionic surfactant according to the following reaction:



where n represents an integer. If the copolymers are dispersed in water in the absence of the nonionic surfactant, the viscosity and stability of the final composition will be adversely affected at the use levels recommended above.

It is preferred that the ethylene-maleic anhydride copolymers be added to the aqueous solution of nonionic active of the polyoxyalkylene type as rapidly as possible with stirring and heating. For best results it has been observed that extraneous alkaline materials should not be present during hydration of the copolymers. After hydrolysis the pH of the solution should be definitely on the acid side (pH of about 2.5-3.2) to insure maximum stability.

In preparing the formulations of this invention, there are other precautions which must be observed, if acceptable products are to be obtained. For example, it has been found that if the copolymers are not rapidly dispersed in the aqueous mixture, the viscosity of the resultant product may be too low from the standpoint of preparing a commercially acceptable product. In general the stability is less at the lower viscosities. The polymers, either singly or in combination, may be added gradually to the aqueous mixture or all at once; however, each addition should be rapidly admixed with the aqueous phase.

It is a necessary feature of the invention that the finished formula be homogenized to attain the desired stability and viscosity. The finished product preferably is homogenized immediately although homogenization may be delayed up to about 48 hours without deleteriously affecting the composition. A product having optimum properties has been obtained within a homogenization temperature range of room temperature to about 170° F. and homogenization pressures of about 500 to about 3,000 pounds. It is obvious, however, that the conditions under which the aqueous mix is homogenized can be varied so long as the finished product has suitable viscosity and stability characteristics. Thus, lower temperatures can be used during homogenization if the pressure is increased.

The following examples illustrate the preparation of compositions in accordance with the principles of this invention. It will be understood, however, that these examples are included merely for illustrative purposes and are not intended to limit the scope of the invention as described therein unless otherwise specifically indicated.

EXAMPLE I

(Basic formulation)

In the following formulas "Sterox DJ," "Pluronic L-60," "Alfonic 1418-6," "DX-840-21" and "DX-840-61" have been identified above. The designations TKPP and TSP refer to tetrapotassium pyrophosphate and tetrasodium pyrophosphate respectively. Methyl Carbitol is diethyleneglycol monomethyl ether. For all examples, laboratory size batches of about 2,000 grams were prepared.

Mixing formula for 100 gms. of finished product

Component:	Gms.
Distilled (zeolite) water	48.00
"Sterox DJ"	8.00
"DX-840-21"	0.20
"DX-840-61"	0.60
TKPP (60% soln.)	41.70
Water to balance to 100.00.	

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Main mixing procedure

The water was heated to a temperature of about 150° F. and the "Sterox DJ" was added with agitation. The anhydrous resins were then added to the well-agitated mixture at a temperature of 150–160° F. and the stirring and temperature were maintained for 1.5 hours.

At the end of this time the tetrapotassium pyrophosphate solution (60%) was slowly added while maintaining agitation at a temperature of 160–170° F. After a short period of mixing, the mixture was homogenized at a pressure of 3,000 p.s.i.g. and at a temperature of about 153–158° F.

EXAMPLE II

Addition of hydrotrope (2%)

The formulation and procedure described in Example I was repeated except that 2% by weight of sodium xylene sulfonate was fed to the aqueous phase with the necessary water adjustment for the finished formulation. The hydrotrope (solution) preferably is added before the addition of the copolymers. A product was obtained which had acceptable viscosity and stability characteristics.

To main mixing vessel (in order of addition) for 100 grams of finished product

Component:	Gms.
Distilled (zeolite) water	43.00
"Sterox DJ"	8.00
Sodium xylenesulfonate (40%)	5.00
"DX-840-21"	0.20
"DX-840-61"	0.60
TKPP (60% soln.)	41.70
Water to balance to 100.00.	

EXAMPLE III

(1% "Pluronic L-60"+2% hydrotrope)

The formulation and procedure described in Example II was repeated except that 1% by weight of "Pluronic L-60" was added to the aqueous phase with the necessary adjustment for the finished formulation. In accordance with the preferred procedure, the "Pluronic L-60" was added before the resins.

To main mixing vessel (in order of addition) for 100 grams of finished product

Component:	Gms.
Distilled (zeolite) water	42.00
"Sterox DJ"	8.00
Sodium xylenesulfonate (40%)	5.00
"Pluronic L-60"	1.00
"DX-840-21"	0.20
"DX-840-61"	0.60
TKPP (60% soln.)	41.70
Water to balance to 100.00.	

EXAMPLE IV

Addition of fluorescent dye and methyl carbitol to the formulation in Example III with necessary water adjustment.

Mixing formula for 100 grams of finished product

Mix No. I:	Gms.
Methyl Carbitol	0.195
Fluorescent dye	0.015
Mix No. II:	
"Sterox DJ"	8.00
Mix No. I	0.21
Mix No. III:	
Methyl Carbitol	0.575
Fluorescent dye	0.096

To main mixing vessel (in order of addition)

Component:	Gms.
Distilled (zeolite) water	40.00

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Mix No. II (containing Mix No. I)	8.21
"Pluronic L-60"	1.00
Sodium xylenesulfonate (40% soln.)	5.00
"DX-840-21"	0.20
"DX-840-61"	0.60
TKPP (60% soln.)	41.70
Mix No. II	0.67
Water to balance to 100.00.	

Mixing procedure

Mix No. I.—The methyl Carbitol was heated to about 190–200° F. with agitation. The fluorescent dye was then added and agitation continued until dispersion was substantially complete. Mixing was continued and the temperature maintained at 190–200° F. until ready for use.

Mix No. II.—The "Sterox DJ" was heated to 100–110° F. Mix No. I was added with agitation and maintained at this temperature with continued agitation until ready for use.

Mix No. III.—The methyl Carbitol was heated to a temperature of 190–200° F. with agitation until dispersion was complete. Mixing was continued and the above temperature maintained until the mix was ready for use.

Main mixing procedure

The water was heated to a temperature of about 150° F. and Premix No. II (which contained Premix No. I) was added with agitation. The "Pluronic L-60" was then added followed by the sodium xylenesulfonate. Then the anhydrous resins were rapidly added to the well-agitated mixture while maintaining the temperature at 150–160° F. for 1.5 hours.

At the end of this time the tetrapotassium pyrophosphate solution (60%) was slowly added while maintaining agitation and a temperature of 160–170° F. This was followed by the addition of Mix No. III and the entire reaction mixture was agitated at 160–170° F. for an additional 10 minutes. The mixture was homogenized at a pressure of 3,000 p.s.i.g. and a temperature of about 153–158° F.

EXAMPLE V

Addition of sodium silicate and potassium hydroxide to the formulation in Example IV with the necessary water adjustment.

Mixing formula for 100 grams of finished product

Mix No. I:	Gms.
Methyl Carbitol	0.195
Fluorescent dye	0.015
Mix No. II:	
"Sterox DJ"	8.00
Mix No. I	0.21
Mix No. III:	
Methyl Carbitol	0.575
Fluorescent dye	0.096

To main mixing vessel (in order of addition)

Distilled (zeolite) water	30.00
Mix No. II (containing Mix No. I)	8.21
"Pluronic L-60"	1.00
Sodium Xylenesulfonate (40% soln.)	5.00
"DX-840-21"	0.20
"DX-840-61"	0.60
TKPP (60% soln.)	41.70
Potassium hydroxide (45.5%)	1.80
Sodium silicate (37.0% solids; 1:25 ratio of Na ₂ O:SiO ₂)	8.10
Water to balance to 100.00.	

EXAMPLE VI

Addition of sodium carboxymethylcellulose, colorant and substitution of 8:1-TKPP:TSPP for TKPP in the formulation in Example V with the necessary water adjustment.

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Mixing formula for 100 grams of finished product

Mix No. I:	Gms.
Methyl Carbitol	0.195
Fluorescent dye	0.015
Mix No. II:	
"Sterox DJ"	8.00
Mix No. I	0.21
Mix No. III:	
Methyl Carbitol	0.575
Fluorescent dye	0.096
Colorant	0.025

To main mixing vessel (in order of addition)

Distilled (zeolite) water	28.00
Mix No. II (containing Mix No. I)	8.21
"Pluronic L-60"	1.00
Sodium xylenesulfonate (40% soln.)	5.00
"DX-840-21"	0.20
"DX-840-61"	0.60
8:1-TKPP:TSPP (55% soln.)	45.45
Potassium hydroxide (45.5%)	2.00
Sodium silicate (37.0% solids; 1:2.5 ratio of Na ₂ O:SiO ₂)	8.10
Sodium carboxymethylcellulose (75%)	0.50
Mix No. III	0.6
Perfume	0.10
Water to balance to 100.00.	

EXAMPLE VII

Increased level of TKPP (35%) and use of "Alfonic 1418-6" as the nonionic.

Mixing formula for 100 grams of finished product

Mix No. I:	Gms.
Methyl Carbitol	0.195
Fluorescent dye	0.015
Mix No. II:	
"Alfonic 1418-6"	8.00
Mix No. I	0.21
Mix No. III:	
Methyl Carbitol	0.595
Fluorescent dye	0.295
Colorant	0.025

To main mixing vessel (in order of addition)

Distilled (zeolite) water	27.50
Sodium xylenesulfonate (40%)	5.00
Mix No. II (containing Mix No. I)	8.21
"Pluronic L-60"	1.00
"DX-840-21"	0.20
"DX-840-61"	0.60
TKPP (60/soln.)	58.50
KOH (45.5% soln.)	1.80
Sodium silicate (37.0% solids; 1:2.5 ratio of Na ₂ O:SiO ₂)	8.10
Sodium carboxymethylcellulose (75% active)	0.50
Mix No. III	0.915
Perfume	0.10
Water to balance to 100.00.	

EXAMPLE VIII

Combination of 0.1% DX-840-4118 (linear) and 0.5% DX-840-61 (cross-linked) resins

Mixing formula for 100 grams of finished product

Mix No. I:	Gms.
Methyl Carbitol	0.195
Fluorescent dye	0.015
Mix No. II:	
"Sterox DJ"	8.00
Mix No. I	0.21
Mix No. III:	

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Methyl Carbitol	0.575
Fluorescent dye	0.307
Colorant	0.025
Water	0.500

To main mixing vessel (in order of addition)

Distilled (zeolite) water	27.50
Sodium xylenesulfonate (40%)	5.00
Mix No. II (containing Mix No. I)	8.21
"Pluronic L-60"	1.00
"DX-840-4118"	0.10
"DX-840-61"	0.50
TKPP:TSPP (8:1 ratio, 55% solids)	45.45
KOH (45.5% soln.)	1.80
Sodium silicate (37.0% solids; 1:2.5 ratio of Na ₂ O:SiO ₂)	8.10
Sodium carboxymethylcellulose (75% active)	0.50
Mix No. III	1.407
Perfume	0.10
Water to balance to 100.00.	

EXAMPLE IX

Combination of 0.20% DX-840-21 (linear) and 0.5% DX-840-91 (cross-linked) resins

Mixing formula for 100 grams of finished product

Mix No. I:	Gms.
Methyl Carbitol	0.195
Fluorescent dye	0.015
Mix No. II:	
"Sterox DJ"	8.00
Mix No. I	0.21
Mix No. III:	
Methyl Carbitol	0.575
Fluorescent dye	0.095
Colorant	0.025

To main mixing vessel (in order of addition)

Distilled (zeolite) water	28.00
Sodium xylenesulfonate (40%)	5.00
Mix No. II (containing Mix No. I)	8.21
"Pluronic L-60"	1.00
"DX-840-21"	0.20
"DX-840-91"	0.50
TKPP:TSPP (8:1 ratio, 55% soln.)	45.45
KOH (45.5% soln.)	1.50
Sodium silicate (37.0% solids; 1:2.5 ratio of Na ₂ O:SiO ₂)	8.10
Sodium carboxymethylcellulose (75% active)	0.50
Mix No. III	0.695
Perfume	0.10
Water to balance to 100.00.	

The properties of phase stability and viscosity stability over extended storage periods are readily demonstrated by comparing representative products prepared according to the procedure in Example VI above with similar products prepared by the same procedure but having only one stabilizing resin in place of the combination of resins as shown by the comparative data in Table II below.

Phase stability was determined by storing the products at room temperature (R.T.) and recording the time for a 5% rise or separation therein. Phase stability was also determined by an accelerated phase stability test wherein a sample of the detergent emulsion composition was placed in a centrifuge tube and the tube inserted into a centrifuge which was then rotated for 30 minutes at 5,000 r.p.m. which is equivalent to a centrifugal force of about 5,000 g. The percent phase separation was then recorded. The apparent viscosity measurements were made using a Brookfield LVF Viscometer, No. 3 spindle, at 30 r.p.m. for 30 seconds at room temperature (78-80° F.).

TABLE II

Number	Percent DX-840-21		Percent DX-840-61	Ratio 21/61	Percent total resins	Initial apparent viscosity	Apparent viscosity (cps.) with time (weeks)					Δ viscosity factor ¹	Storage stability time for 5% rise at R.T., weeks	Percent phase separation
	1	2					3	4	8	20	21			
A	0.8				0.8	910	930						16	3.0
B			0.6		0.6	380							6	16.0
C	0.2		0.6		1:3	850	1,020		1,105	885			60	3.0
D	0.45		0.15		3:1	335		410					20	9.0
E	0.45		0.35		1.29:1	900		840		325	270		36	3.0
F	0.50		0.50		1.67:1	975				760			36	3.0
G	0.56		0.34		1.66:1	1290		1,200		730			36	2.0
										950			1.5	
													36	
A	0.8				0.8	910	930						16	3.0
H			0.6		0.6	400	720	1,140			180		2	30.0
I	0.2		0.6		1:3	265	440	575					21	10.0
A	0.8				0.8	910	930						16	3.0
J			0.6		0.6	420	560	1,260			180		3	24.0
K	0.2		0.6		1:3	290	680	800					21	9.0
A	0.8				0.8	910	930						16	3.0
J			0.6		0.6	420	560	1,260			180		3	24.0
K	0.2		0.6		1:3	290	680	800					21	9.0

group consisting of sodium and potassium silicates is added after the pyrophosphate.

3. The method according to claim 1 wherein from about 0% to about 5% based on the weight of the composition of a hydrotrope selected from the group consisting of diethylene glycol monomethylether, sodium xylene sulfonate, sodium toluene sulfonate and mixtures thereof containing 0-25% sodium toluene sulfonate based on the combined weight of sodium toluene sulfonate and sodium xylene sulfonate is present in said aqueous mixture prior to the addition of said stabilizers.

4. The method according to claim 1 wherein the non-ionic synthetic detergent is a condensate of dodecyl phenol with from 6 to 11 moles of ethylene oxide.

5. The method according to claim 1 wherein the aqueous mixture is maintained at an elevated temperature of from about 150° F. to about 160° F. during the blending of the two stabilizers therewith.

6. The method according to claim 1 wherein the homogenizing is conducted at from room temperature at about 170° F. and at a pressure from about 500 to about 3,000 p.s.i.g.

7. The method according to claim 1 wherein about 0.5% based on the weight of the composition of sodium carboxymethyl cellulose is added after the silicate.

8. The method according to claim 1 wherein the weight ratio of said first stabilizer to said second stabilizer is from about 1:3 to about 1:1.

9. A phase-stable, pourable, heavy duty liquid detergent emulsion composition which does not exhibit a substantial change in viscosity on standing consisting essentially of from about 6% to about 15% by weight of at least one nonionic synthetic detergent condensate of an alkylene oxide with a hydrophobic base selected from the group consisting of higher alkyl phenols and alcohols; from about 17% to about 35% by weight of at least one alkali metal pyrophosphate selected from the group consisting of tetrapotassium pyrophosphate, tetrasodium pyrophosphate and blends of these materials in which the tetrasodium pyrophosphate comprises up to 20% by weight of the blend; from about 0.6% to about 0.9% by weight of a combination of a first stabilizer which is a hydrolyzed

linear copolymer of ethylene and maleic anhydride having a specific viscosity of from about 0.6 to about 1.8 and a second stabilizer which is a hydrolyzed copolymer of ethylene and maleic anhydride cross-linked with a vinyl ester of an olefinically unsaturated aliphatic carboxylic acid having from 3 to 24 carbon atoms, said copolymer having a viscosity of from about 12,000 centipoises to about 160,000 centipoises; and the balance substantially water; the weight ratio of said first stabilizer to said second stabilizer being from about 1:6 to about 3:1.

10. The composition according to claim 9 which also contains from about 2% to about 10% by weight of an alkali metal silicate selected from the group consisting of sodium and potassium silicates.

11. The composition according to claim 9 which also contains from about 0% to about 5% by weight of a hydrotrope selected from the group consisting of diethylene glycol monomethylether, sodium xylene sulfonate, sodium toluene sulfonate, and mixtures thereof containing 0-25% sodium toluene sulfonate based on the combined weight of sodium toluene sulfonate and sodium xylene sulfonate.

12. The composition according to claim 9 which also contains about 0.5% by weight of sodium carboxymethyl cellulose.

13. The composition according to claim 9 wherein the weight ratio of said first stabilizer to said second stabilizer is from about 1:3 to about 1:1.

14. The composition according to claim 9 wherein the cross-linking agent is vinyl crotonate.

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