

1

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HEAVY DUTY LIQUID DETERGENT COMPOSITIONS

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The present invention relates to a heavy duty liquid detergent composition in the form of a stable, free-flowing suspension having thixotropic properties.

Various types of liquid compositions in the form of lotions and liquid emulsions are known in the cosmetic art, including shampoo products. Such compositions comprise generally a suitable detergent and an opacifier, stabilizing agent or suitable waxy material in an aqueous solvent. Where soap is the detergent in a shampoo, it has been suggested to incorporate a very small amount of a water-softener such as various phosphate compounds in order to prevent formation of insoluble soaps during use of the product in hard water.

In the detergent art, however, it has been common practice to prepare detergent compositions in powdered form, as obtained by spray-drying a slurry of the detergent composition for example. In these powdered products, alkaline builder salts such as sodium tripolyphosphate and pyrophosphate have been incorporated in significant amounts to improve the detergency or washing power for the laundering of soiled textile materials. Other salts such as sodium silicate, carbonate, carboxymethylcellulose and the like have been employed also in the preparation of powdered heavy duty detergent compositions.

Within recent years, liquid detergent compositions having particular utility for washing of dishes and fine fabrics have been produced commercially. In general, such light-duty liquid compositions have been primarily a clear solution of a suitable detergent in an aqueous solvent.

Heretofore, heavy duty detergent compositions in liquid, free-flowing form have not been made as articles of commerce because of the difficulty in retaining substantial proportions of the ingredients in solution. For example, the mere admixture of substantial amounts of phosphate salts and an organic detergent in water results in a marked tendency for separation of the mixture into two or more immiscible phases, sometimes with the settling of the phosphate salts as hard non-redispersible cakes in the bottom of the container.

It has now been found that effective amounts of alkaline builder salts, such as sodium tripolyphosphate and/or tetrasodium pyrophosphate, can be incorporated and formed into a stable, free-flowing heavy duty liquid detergent composition by a careful choice of ingredients and their proportions, as hereinafter described and claimed.

In accordance with the present invention, such a heavy duty liquid detergent composition comprises a water-soluble organic synthetic detergent and water-soluble inorganic alkaline builder salt, particularly polyphosphate salt, in an aqueous alcoholic medium, the amount of said inorganic salt being in excess of its normal solubility in the amount of water present and maintained in a permanently non-caking suspension in the presence of minor proportions of a wax substantially insoluble in water and in the aqueous-alcoholic solvent of the compositions, a substantially water-insoluble colloidal material, and a water-soluble nitrogen compound selected from the group

2

consisting of urea and thiourea. By reference to a stable or non-caking suspension, it is meant that the undissolved ingredients are essentially retained in the product in suspension or are re-dispersible upon light shaking.

These novel liquid detergent compositions are characterized by many desirable properties. The product is in the form of a substantially homogeneous opaque suspension which exhibits a satisfactory degree of stability upon aging. It exhibits thixotropic properties which assure suspension of the dense, substantially undissolved builder salts during storage life of the composition. By virtue of this thixotropy and other peculiar physical properties, the composition has sufficient viscosity, when at rest, to maintain the ingredients and particularly the dispersed alkaline builder salts in homogeneous suspension, but the composition becomes highly fluid upon light shaking and may be poured freely from the container. In addition the composition exhibits a washing power during laundering that is comparable to the commercial heavy-duty detergents in powdered form.

In the formulation of such product, the ingredients should be selected and proportioned so as to form a suspension having the foregoing qualities. As indicated the suspension is free-flowing upon light shaking of the container at room temperature. The viscosity of the suspension may be varied accordingly but the product should have an apparent viscosity from about 50 to about 5000 centipoises and preferably about 500 to about 3000 centipoises, for optimum results. The above references to viscosity and any others set forth in this application are determined by a Brookfield viscometer, Model HAF, using a No. 2 spindle at 10 r.p.m. and at room temperature, i.e. 20° C. The suspension may be employed in any suitable container or packaging material such as metal, glass or plastic in the form of bottles, cans, drums or bags.

For the sake of simplicity, the several ingredients will be described individually to some extent but the final desired qualities of the product are the resultant or unitary effects produced by the inter-action of the ingredients within the indicated proportions.

These novel compositions contain an organic detergent selected from the group consisting of the water-soluble anionic organic sulfate and sulfonate, and non-ionic organic detergents. These materials are known and have sufficient water solubility or dispersibility to form foaming and deterative aqueous solutions in the concentrations which are suitable for use, e.g. in washing dishes, laundry and the like. They may be used individually or in any desired combination. A suitable synthetic detergent is a water-soluble higher alkyl aryl sulfonate detergent, particularly those having about 8 to 15 carbon atoms in the alkyl group. It is preferred to use the higher alkyl benzene sulfonate detergent for optimum effects, though other similar detergents having a mononuclear aryl nucleus, such as toluene, xylene, or phenol, may be used also. The higher alkyl substituent on the aromatic nucleus may be branched or straight-chained in structure, examples of such group being nonyl, dodecyl and pentadecyl groups derived from polymers of lower mono-olefins, decyl, keryl, and the like.

Examples of suitable aliphatic detergents are the normal and secondary higher alkyl sulfate detergents, particularly those having about 8 to 15 carbons in the fatty alcohol residue, such as lauryl (or coconut fatty alcohol) sulfate. Other suitable detergents are the sulfuric acid esters of polyhydric alcohols incompletely esterified with higher fatty acids, e.g. coconut oil monoglyceride monosulfate; the higher fatty acid esters of low molecular weight alkylol sulfonic acids, e.g. oleic acid ester of isethionic acid; the higher fatty acid (e.g. coconut) ethanolamide sulfate; the higher fatty acid amide of amino alkyl sulfonic acids, e.g. lauric acid amide of taurine; and the like.

These sulfate and sulfonate detergents are used in the form of their water-soluble salts, such as the alkali metal and nitrogen-containing, e.g. lower alkylolamine, salts. Examples are the sodium, potassium, ammonium, isopropanolamine, mono- and tri-ethanolamine salts of said higher alkyl benzene sulfonate, higher alkyl sulfate and the like. In commercial practice, it is preferred to use the alkali metal salts.

Examples of suitable non-ionic detergents are the water-soluble non-ionic polyalkylene oxide detergents. In general, these detergents are the products produced by the introduction of a controlled number of alkylene oxide groups into an organic hydrophobic compound or group, usually of an aliphatic or aromatic structure. The hydrophobic organic group contains usually at least about 8 carbons, and preferably up to 30 carbons, condensed with at least about 5 and usually up to about 50 alkylene oxide groups. It is preferred to use the polyoxyethylene condensates derived from ethylene oxide, although other lower alkylene oxides such as propylene oxide, butylene oxide and the like have generally similar properties and may be substituted therefor.

Among the non-ionic detergents, it is preferred to use the polyalkylene oxide condensates of alkyl phenol, such as the polyoxyethylene ethers of alkyl phenols having an alkyl group of at least about six, and usually about 8 to 12 carbons, and an ethylene oxide ratio (No. of moles per phenol) of about 7.5, 8.5, 11.5 and 20, though the number of ethylene oxide groups will be usually from about 8 to 18. The alkyl substituent on the aromatic nucleus may be di-isobutylene, diamyl, polymerized propylene, dimerized C_6-C_7 olefin, and the like.

Further suitable detergents are the polyoxyalkylene esters of organic acids, such as the higher fatty acids, rosin acids, tall oil acids, or acids from the oxidation of petroleum, etc. These polyglycol esters will contain usually from about 12 to about 30 moles of ethylene oxide or its equivalent and about 8 to 22 carbons in the acyl group. Suitable products are refined tall oil condensed with 16 or 20 ethylene oxide groups, or similar polyglycol esters of lauric, stearic, oleic acids, etc.

Additional non-ionic agents are the polyalkylene oxide condensates with higher fatty acid amides, such as the higher fatty acid primary amides, mono- and di-ethanolamides. Suitable agents are coconut fatty acid amide condensed with about 10 to 50 moles of ethylene oxide. The fatty acyl group will have similarly about 8 to 22 carbons, and usually about 10 to 18 carbon atoms, in such products. The corresponding sulfonamides may be used also if desired.

Other suitable polyether non-ionic detergents are the polyalkylene oxide ethers of higher aliphatic alcohols. Suitable fatty alcohols having a hydrophobic character, preferably 8 to 22 carbons, are lauryl, myristyl, cetyl, stearyl and oleyl alcohols which may be condensed with an appropriate amount of ethylene oxide, such as at least about 6, and preferably about 10-30 moles. A typical product is oleyl alcohol condensed with about 12, 15 or 20 moles of ethylene oxide. The corresponding higher alkyl mercaptans or thioalcohols condensed with ethylene oxide are suitable in the present invention also. The water-soluble polyoxyethylene condensates with hydrophobic polyoxypropylene glycols may be employed also.

Further suitable non-ionic detergents are the higher fatty acid alkanolamides, such as the monoethanolamides, diethanolamides and isopropanolamides wherein the acyl radical has about 10 to 14 carbon atoms. Examples are coconut (or equivalent lauric), capric and myristic diethanolamide, mono-ethanolamide and isopropanolamide. As part of their effects, the alkanolamide materials function to improve the foaming power and detergency of the compositions and aid also in the obtention of the desired liquids in a more stable form. These materials are employed preferably in an amount from about 1 to 15% by weight in the suspension.

The proportion of organic detergent material in the final composition is variable to some extent but it has been found that amounts from about 5 to about 30%, preferably about 10-25%, by weight are highly satisfactory with respect to both the physical appearance and performance of the product.

Any water-soluble alkaline builder salts may be used but it is preferred to employ the inorganic polyphosphate salts. Such polyphosphate materials have the property of inhibiting precipitation of calcium and magnesium material in aqueous solution and may be considered as derived from orthophosphoric acid or the like by the removal of water. These complex or molecularly dehydrated polyphosphate salts may be used in the form of the normal or completely neutralized salt, e.g. sodium tripolyphosphate, or the partially neutralized salt, e.g. sodium acid tripolyphosphate. It is preferred to employ the alkali metal polyphosphate, and particularly a sodium tripolyphosphate or a sodium pyrophosphate for optimum effects. Other suitable polyphosphate materials are potassium tripolyphosphate, tetrapotassium pyrophosphate, sodium hexametaphosphate, hexasodium hexametaphosphate, hexasodium tetrakisphosphate and tetrasodium pyrophosphate. Examples of other alkaline builder salts which may be employed are sodium orthophosphate, e.g. trisodium phosphate, soda ash, borax, and the like.

The alkaline builder salts should be employed in substantial amount such that the addition of a small portion of the liquid product to a washing bath will result in effective detergency and washing power. It has been found that it is possible to maintain in homogeneous suspension amounts of builder salts from about 15 to 45%, and preferably about 20 to 40%, by weight of the composition as formulated. In the present invention, such materials are present in amounts in excess of their solubility in the amount of water present in the product but, nevertheless, the excess is maintained in the form of dispersed or undissolved particles in substantially homogeneous suspension. For example, anhydrous sodium tripolyphosphate has a solubility at room temperature of the order of about 15% in water. In the liquid product, sodium tripolyphosphate or pyrophosphate may be incorporated in amounts as much as about fifty times, preferably about 10 to about 25 times its normal solubility in the amount of water present, even though the product contains alcohol as part of the solvent medium which tends to depress the solubility of the polyphosphate material.

For the obtention of a product having the desired physical properties, it is essential to incorporate minor proportions of a wax which is substantially insoluble in water and in the aqueous-alcoholic solvent of the compositions; a substantially water-insoluble colloidal material; and urea or thiourea. The quantities of these essential ingredients may be varied to some extent, depending upon the specific material used, and upon the viscosity desired for the finished composition.

The wax or wax-like substance, preferably hydrogenated castor oil, is employed usually in proportions from about 0.10% to about 1% by weight. Other suitable wax (including wax-like) substances are the naturally occurring waxes which consist essentially of esters of high molecular weight monohydric alcohols and higher fatty acids. Of the naturally occurring waxes, carnauba is particularly effective, although others including candelilla, montan and beeswax may also be used. Waxes from the class including ozokerite, ceresin and microcrystalline waxes also are suitable, as are synthetic wax-like substances including the esters of the higher fatty acid alkanolamides, e.g. the stearyl ester of stearic monoethanolamide and the lauryl ester of the monoethanolamide of hydrogenated castor oil. Higher fatty acids, fatty alcohols and fatty acid amides having more than 18 carbon atoms which are wax-like materials may be used also. In general, these materials may be used in-

dividually or in any suitable mixture. It has been found that particularly effective products are obtained using 0.4% hydrogenated castor oil or 0.5% carnauba wax by weight.

Suitable examples of the substantially water-insoluble colloidal materials are the substances forming colloidal suspensions in water selected from the group consisting of inorganic colloidal siliceous materials and polyvalent metal soaps. In general, they may be used in amounts from about 0.1 to about 10% by weight. Of the inorganic siliceous materials which are colloiddally dispersible in water, it is preferred to use bentonite in amounts of 1-5% but other colloidal clays and the like may be used also. Other suitable materials are colloidal silica, magnesium silicate, aluminum-magnesium silica gel (e.g. "Veegum") and the like. These materials may be used individually or in any suitable mixture. If desired, the siliceous material may be substituted in whole or part by polyvalent metal soaps, such as the heavy metal and alkaline earth metal salts of higher fatty acids, e.g. zinc, calcium or magnesium soaps of coconut, tallow or stearic fatty acids which are colloiddally dispersible also. The polyvalent metal soaps may be used to advantage with the inorganic siliceous materials in preferred amounts from about 0.1 to about 4% of the total compositions.

The inclusion of urea or thiourea as indicated aids vitally in the production of suspensions having thixotropic properties and easily pourable viscosity. In the absence of the ureas, the compositions tend to form stiff, unpourable, irreversible gels. Any suitable amount of urea or thiourea may be employed, but it is usual to employ at least about 2% and preferably about 5 to 20% by weight of the formulation.

The aqueous alcoholic solvent is an essential consideration also. In general, the alcohol is water-miscible such as the saturated lower aliphatic monohydric alcohols. Suitable examples are ethyl, propyl and isopropyl alcohol. The proportions of water and alcohol may be varied for optimum viscosity and stability for each preparation. It has been found that superior products may be formed having a solids content from about 60 to 90% and an aqueous alcohol content from about 10 to 40%, preferably 15-25%, by weight of the formulation. Suitable proportions of water and alcohol may be selected from the range of about 5-20%, preferably 5-15% water and 5-20%, preferably 5-15% alcohol by weight. In an excessive amount of alcohol is used the thixotropy of the compositions is impaired and the phosphate materials tend to settle and form a cake which is not readily redispersible in the liquid. Upon proportioning of the essential ingredients, the suspension is fairly viscous and stable without any apparent or significant tendency to separation. Upon shaking in a bottle, it does not foam but drains evenly, quickly permitting pouring of uniform portions of the product. The agitation of the viscous product by shaking converts the system to a highly fluid mixture which flows freely. It dissolves readily upon addition of small portions to a laundering bath and exhibits a high degree of washing power.

Various other ingredients may be added as desired including compatible perfumes, coloring materials, corrosion or anti-tarnishing inhibitors, germicides, hydrotropes, bleaching agents, optical bleaches or fluorescent brighteners, and the like. It is preferred to add a minor amount, such as 1/4-5% by weight, of a soil-anti-redeposition agent, e.g. cellulose ethers. Suitable examples are methyl-, ethyl-, and hydroxyethylcellulose, alkali metal carboxymethylcellulose.

The following examples are additionally illustrative of the nature of the invention and it will be understood that the invention is not limited thereto. All parts are by weight unless otherwise specified.

Example I

The following formulation results in a satisfactory

heavy-duty liquid detergent composition in homogeneous suspension:

Ingredient:	Percent
Sodium tripolyphosphate	35.0
Sodium dodecyl benzene sulfonate	15.0
Nonyl phenol ethylene oxide condensate (Antarox A400)	5.0
Coconut diethanolamide	5.0
Hydrogenated castor oil	0.4
Urea	14.0
Bentonite	4.0
Sodium carboxymethylcellulose	1.5
Ethyl alcohol	10.0
Water	9.1
	99.0

the balance being minor amounts of perfume, coloring material, optical bleach and corrosion inhibitor.

This suspension is prepared by the preferred method whereby sodium dodecyl benzene sulfonate which is substantially free of inorganic salts, the Antarox A400 and the coconut diethanolamide are mixed in the water and ethanol. The castor wax is melted and added to the detergent solution with mixing. The remaining ingredients are added individually with stirring to form a substantially uniform and homogeneous mixture. The final product has a viscosity of about 1400 centipoises.

A similar product having about 10.4% water and 9.9% alcohol has a viscosity of about 700 centipoises.

Example II

	Percent
Sodium lauryl sulfate	25.00
Ethyl alcohol	12.00
Water	10.00
Fully hydrogenated castor oil	0.40
Sodium tripolyphosphate	35.00
Bentonite	4.00
Urea	13.60
	100.00

Example III

	Percent
Sodium dodecyl benzene sulfonate	20.00
Ethyl alcohol	15.00
Water	10.00
Fully hydrogenated castor oil	0.40
Sodium tripolyphosphate	35.00
Bentonite	4.00
Sodium carboxymethylcellulose	1.50
Urea	13.89
	99.79

the balance being minor amounts of perfume and optical bleach.

Example IV

	Percent
Nonyl phenol ethylene oxide condensate (Antarox A400)	20.00
Ethyl alcohol	15.00
Water	10.00
Fully hydrogenated castor oil	0.40
Sodium tripolyphosphate	35.00
Bentonite	4.00
Sodium carboxymethylcellulose	1.50
Urea	13.34
	99.24

the balance being minor amounts of perfume, coloring material and optical bleach.

Example V

	Percent
Sodium dodecyl benzene sulfonate -----	15.00
Nonyl phenol ethylene oxide condensate (Antarox (A400)) -----	5.00
Coconut diethanolamide -----	5.00
Ethyl alcohol -----	15.00
Water -----	10.00
Carnauba wax -----	0.50
Tetrasodium pyrophosphate -----	35.00
Bentonite -----	3.00
Zinc stearate -----	1.00
Sodium carboxymethylcellulose -----	1.50
Urea -----	8.24
	99.24

the balance being minor amounts of perfume, coloring material and optical bleach.

Example VI

	Percent
Sodium dodecyl benzene sulfonate -----	15.00
Nonyl phenol ethylene oxide condensate (Antarox A400) -----	5.00
Coconut diethanolamide -----	5.00
Ethyl alcohol -----	15.00
Water -----	10.00
Fully hydrogenated castor oil -----	0.40
Soda ash -----	35.00
Bentonite -----	4.00
Sodium carboxymethylcellulose -----	1.50
Urea -----	8.34
	99.24

the balance being minor amounts of perfume, coloring material and optical bleach.

Although the present invention has been described and illustrated with a reference to specific examples, it is understood that modifications and variations of composition and procedure are contemplated within the scope of the appended claims.

Having thus described the invention, what is claimed is:

1. A liquid detergent composition in the form of a stable, free-flowing suspension having thixotropic properties which consists essentially of about 5 to 30% by weight of a water-soluble detergent selected from the group consisting of the water-soluble anionic organic sulfate and sulfonate, and non-ionic organic detergents; and about 15 to 45% by weight of a water-soluble inorganic alkaline builder salt in an aqueous alcoholic medium containing about 5 to 20% by weight of a water-miscible saturated lower aliphatic monohydric alcohol, the amount of said inorganic salt being in excess of its normal solubility in the amount of water present and maintained in a permanently non-caking suspension in the presence of about 0.1 to 1% by weight of a substantially water-insoluble wax, about 0.1 to 10% by weight of a substantially water-insoluble material selected from the group consisting of inorganic colloidal silicates, colloidal silica, and polyvalent metal soaps of higher fatty acids; and about 2 to 20% by weight of a water-soluble nitrogen compound selected from the group consisting of urea and thiourea.

2. A liquid detergent composition in accordance with claim 1 wherein the polyvalent metal soap is polyvalent metal stearate.

3. A liquid detergent composition in the form of a stable, free-flowing suspension having thixotropic properties which consists essentially of about 5 to 30% by weight of a water-soluble detergent selected from the group consisting of a water-soluble anionic organic sulfate and sulfonate, and non-ionic organic detergents; and about 15 to 45% by weight of a water-soluble inorganic polyphos-

phate salt in an aqueous alcoholic medium containing about 5 to 20% by weight of a water-miscible saturated lower aliphatic monohydric alcohol, the amount of said polyphosphate salt being in excess of its normal solubility in the amount of water present and maintained in a permanently non-caking suspension in the presence of about 0.1 to 1% by weight of a substantially water-insoluble wax, about 0.1 to 10% by weight of a substantially water-insoluble inorganic colloidal silicate, and about 2 to 20% by weight of a water-soluble nitrogen compound selected from the group consisting of urea and thiourea.

4. A liquid detergent composition in accordance with claim 3 wherein the polyphosphate salt is sodium tripolyphosphate.

5. A liquid detergent composition in accordance with claim 3 wherein the polyphosphate salt is sodium pyrophosphate.

6. A liquid detergent composition in accordance with claim 3 wherein the detergent is a water-soluble higher alkyl benzene sulfonate detergent.

7. A liquid detergent composition in accordance with claim 3 wherein the detergent is a water-soluble higher alkyl sulfate detergent.

8. A liquid detergent composition in accordance with claim 3 wherein the detergent is a water-soluble higher alkyl phenol condensate with ethylene oxide.

9. A liquid detergent composition in accordance with claim 3 which contains hydrogenated castor oil.

10. A liquid detergent composition in accordance with claim 3 wherein the wax is carnauba wax.

11. A liquid detergent composition in accordance with claim 3 wherein the inorganic colloidal silicate is bentonite.

12. A liquid detergent composition in accordance with claim 3 wherein the nitrogen compound is urea.

13. A liquid detergent composition in the form of a stable, free-flowing, substantially homogeneous suspension having thixotropic properties which consists essentially of about 5 to 30% by weight of a water-soluble detergent selected from the group consisting of the water-soluble anionic organic sulfate and sulfonate, and non-ionic organic detergents; about 15 to 45% by weight of water-soluble inorganic polyphosphate salt in an aqueous ethanol medium containing about 5 to 20% by weight of ethanol, the amount of said polyphosphate being in excess of its normal solubility in the amount of water present and maintained in a permanently non-caking suspension in the presence of about 0.1 to 1% by weight of hydrogenated castor oil, about 1 to 5% by weight of bentonite and about 5 to 20% by weight of urea.

14. A liquid detergent composition in the form of a stable, free-flowing suspension in accordance with claim 13 which contains about 1 to 15% by weight of a higher fatty acid alkanolamide.

15. A liquid detergent composition in the form of a stable, free-flowing, substantially homogeneous suspension having thixotropic properties which consists essentially of about 5 to 30% by weight of a detergent selected from the group consisting of water-soluble anionic organic sulfate and sulfonate, and non-ionic organic detergents; and about 15 to 45% by weight of sodium tripolyphosphate in about 10 to 40% by weight of an aqueous ethanol medium containing about 5 to 20% ethanol, the amount of tripolyphosphate being from about 10 to about 25 times its normal solubility in the amount of water present and maintained in a permanently non-caking suspension in the presence of about 0.1 to 1% by weight of a substantially water-insoluble wax, about 1 to 5% by weight of bentonite and about 5 to 20% by weight of urea.

16. A liquid detergent composition in the form of a stable, free-flowing suspension in accordance with claim 15 wherein the wax is hydrogenated castor oil.

17. A liquid detergent composition in the form of a

stable, free-flowing suspension in accordance with claim 15 wherein the wax is carnauba wax.

18. A liquid detergent composition in the form of a substantially homogeneous suspension having thixotropic properties consisting essentially of the following approximate formulation:

Ingredients:	Percent	
Higher alkyl benzene sulfonate detergent	10-25	
Sodium tripolyphosphate	20-40	5
Wax	0.1-1	
Bentonite	1-5	10
Urea	2-20	
Ethyl alcohol	5-20	
Water	5-20	15

19. A liquid detergent composition in the form of a substantially homogeneous suspension in accordance with claim 18 which contains about 1-15% by weight of a higher fatty acid diethanolamide.

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