

1

2

3,254,028

LIQUID DETERGENT COMPOSITION

Harold Eugene Wixon, Jersey City, N.J., assignor to Colgate-Palmolive Company, New York, N.Y., a corporation of Delaware

No Drawing. Filed Feb. 6, 1961, Ser. No. 87,113

The portion of the term of the patent subsequent to Aug. 20, 1980, has been disclaimed and dedicated to the Public

10 Claims. (Cl. 252—137)

The present application is a continuation-in-part of abandoned application Serial No. 861,192, filed December 22, 1959, which was a continuation-in-part of Serial Nos. 532,734 and 532,735, filed September 6, 1955.

The present invention relates to a substantially homogeneous heavy-duty liquid detergent composition comprising a water-soluble organic detergent, a water-soluble alkaline inorganic builder salt, a water soluble cellulosic compound and a water-soluble vinyl polymer, as hereinafter described and claimed.

In the detergent art, it is known to prepare detergent compositions in powdered form, such as obtained by the spray-drying of a slurry of the detergent composition. Such powdered products may comprise an organic detergent and inorganic builders, such as phosphates and silicates, and a soil-suspending or anti-redeposition agent such as carboxymethylcellulose. Many soil-anti-redeposition agents are known, including various cellulosic compounds, natural gums, carbohydrates, vinyl polymers, protein materials, etc.

The incorporation of sodium carboxymethylcellulose or the like in a heavy-duty liquid detergent solution comprising substantial amounts of an organic detergent, e.g., alkyl benzene sulfonate, and water-soluble inorganic builder salts, e.g., polyphosphate salts, results in a tendency towards phase separation, or formation of a plurality of distinct layers, one of which has the carboxymethylcellulose concentrated therein. The use of other soil-suspending agents such as polyvinyl alcohol or polyvinylpyrrolidone or the like results also in a tendency for phase separation and non-uniformity of the product.

In accordance with the present invention, it has been found that the separation of such soil-suspending agents in a heavy-duty liquid detergent composition may be inhibited by the simultaneous presence of a suitable mixture of soil-suspending agents which act as mutual or reciprocal stabilizing agents, said mixture comprising a water-soluble cellulose compound and a water-soluble vinyl polymer.

More particularly, the present invention relates to a substantially homogeneous, heavy-duty liquid detergent composition which comprises essentially of a water-soluble non-cationic organic detergent in an amount from the range of about 5 to 30% by weight, a water-soluble alkaline inorganic builder salt in an amount from the range of about 5 to 30% by weight, about 0.1 to 5% by weight of a mixture of said vinyl polymer and cellulosic material in a suitable ratio from the range of about 20:1 to 1:20 by weight, and an aqueous solubilizing medium in admixture therewith sufficient to form a pourable, homogeneous liquid. An embodiment thereof relates to the mixture of a carboxymethylcellulose and vinyl polymer in a ratio from about 10:1 to 1:10 by weight in a liquid containing 5 to 20% by weight of an alkali metal

anionic sulfonated detergent such as a higher alkyl benzene sulfonate, a potassium polyphosphate selected from the group consisting of pyrophosphates and tripolyphosphates, a water-soluble sulfonated hydrotropic salt, and a higher fatty acid alkylolamide in proportions to form a substantially homogeneous product.

Such product exhibits many desirable characteristics including, particularly, the improved stability against separation of the soil-suspending agents. The product is maintained in substantially homogeneous condition upon aging. This improved stability is exhibited upon storage for long periods of time at normal room temperature and upon testing at elevated temperatures and upon cooling and permitting the product to return to room temperature, as compared to similar products which contain only one of said suspending agents. The composition is pourable and free-flowing from the container at room temperature. The product may be utilized conveniently by the consumer by the addition of small portions to a laundering bath or the like and, by reason of the substantial homogeneity of the liquid each such small portion, will have practically the same composition. The liquid 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.

The composition exhibits a high level of washing power during the laundering in washing baths of a wide variety of natural and synthetic materials. It is particularly effective for the laundering of resin-treated cottons known as "wash-and-wear" materials, and for synthetic fabrics such as nylon and Dacron in addition to cotton. In general, the over-all deterative properties of the liquid results in a superior whiteness in the laundering of a variety of white materials as compared to the effects obtained using an equivalent amount of either of the soil-suspending agents alone.

The cellulose compound is a hydrophilic colloid which is soluble or dispersible in water. In general, these materials are classified as water-soluble and act as soil anti-redeposition agents during washing of soiled articles. It is preferred to use the alkali metal salts of a carboxy lower alkyl cellulose having up to 3 carbons in the alkyl group, such as the sodium and potassium salts of carboxymethylcellulose. Sodium carboxymethylcellulose and the like are available usually in the form of powders in various grades of purity and viscosity in solution. The commercial grades of sodium carboxymethylcellulose having a purity from about 60 to 100% on a dry basis and which are of low, medium or high viscosity may be employed. The degree of substitution of the carboxymethyl group per anhydroglucose unit in the cellulose molecule is variable, but is within the range from about 0.5 to 2, and usually up to about 1.25 substitution. It is preferred to employ carboxylated cellulose having about 0.5 to 0.9 substitution, particularly about 0.5 to 0.7, for highly effective soil-suspending properties. Another known water soluble carboxyalkylcellulose salt is sodium carboxyethylcellulose. Other cellulose compounds are the lower alkyl and hydroxyalkyl ethers such as methyl-, ethyl-, and hydroxyethylcellulose. The cellulose sulfates may be used also.

A water-soluble vinyl polymer is used in admixture with the cellulosic material. The specific or exact degree of polymerization of the vinyl polymer is not criti-

cal provided the material has the desired water-solubility or dispersibility and soil-suspending power to produce the desired effects. It is usually a mixture of specific polymers containing a different number of monomer units, depending upon the manner and degree of polymerization. In general, these polymers are linear in structure and have an average molecular weight of less than about one million and preferably up to 100,000 depending upon the type of polymer. It is usually within the range of about 5,000 to about 500,000. The term "vinyl polymer" includes both homo-polymers and copolymers of vinyl type compounds. Examples are polymers derived from unsaturated compounds having the typical vinyl structure $\text{CH}_2=\text{CHX}$ wherein X is hydroxyl, alkylol, nitrile, carboxylic, amide, pyrrolidone or the like.

It is preferred to employ the water-soluble polyvinyl alcohol. These materials may be considered as polymers of vinyl alcohol, though they are prepared from polyvinyl acetate or similar polyvinyl esters by replacement of acetate groups by hydroxyl groups and this chemical reaction is commonly known as hydrolysis in the art. The polyvinyl alcohol is often identified by its viscosity, and percent hydrolysis or percent ester content. The polyvinyl alcohol may be of low, medium or high viscosity and may be selected from the range of about 1.8 to 65, and preferably up to 6 centipoises. Reference to centipoises herein refers to determinations made in a 4% aqueous solution at 20° C. The product may contain minor amounts of polyvinyl acetate such as up to about 30% by weight and preferably from about 10 to 30% ester content. The degree of hydrolysis is thus usually within the range from about 70 to 100%. Suitable examples are polyvinyl alcohol which has a viscosity of 4 to 6 cps. with about 12% ester (88-89% hydrolysis); and polyvinyl alcohols having a viscosity of 21-25 cps. or 35-45 cps. with about 12% ester.

It is preferred to employ polyvinyl alcohol having a viscosity of 1.8 to 3 centipoises and a polyvinyl acetate content of about 10 to 30% by weight. This material exhibits maximum stability upon storage of the composition at elevated temperature resulting in maximum soil-suspending power for the composition. It may be prepared by any suitable manner such as by control of the degree of polymerization and alcoholysis of the polyvinyl acetate to produce a product of the above characteristics. The above viscosity range corresponds to an approximate weight average degree of polymerization of about 35 to 100. Examples thereof are polyvinyl alcohols having a viscosity of 2.34 cps. and 22.3% polyvinyl acetate; 1.88 cps. and 19.6% ester; 1.98 cps. and 29.4% ester; 2.38 cps. and 12.8% ester; and the like.

The water-soluble vinyl polymeric amides such as polyvinylpyrrolidone may be employed also. This material is a polymer of N-vinyl pyrrolidone and is soluble in water colloiddally. Examples of specific suitable vinyl pyrrolidone polymers are those having an average molecular weight of about 15,000; 20,000; 30,000; 40,000; 80,000; and 100,000.

Another type of polymeric vinyl soil-suspending agent known in the art which may be used is a copolymer of a lower N-alkyl acrylamide and vinyl alcohol. In such copolymers, the lower N-alkyl group has up to 3 carbon atoms usually, and preferably is a methyl group. The molar ratio of the N-alkyl acrylamide to the vinyl alcohol in each repeating unit of the copolymer is from about 1:1 to 10:1 with about 50 to 1000 repeating units. Specific examples of these polymers are the copolymers of N-methylacrylamide and vinyl alcohol wherein the ratio of the acrylamide component to vinyl alcohol component in each repeating unit is 66:34 with about 500 repeating units. Another example is a similar copolymer having an acrylamide to vinyl alcohol ratio of 80:20 with about 500 and 600 repeating units.

Other known polymeric amide soil-suspending agents are copolymers of acrylonitrile with acrylamide or lower alkyl acrylamide. The molar ratio of the acrylamide moiety to the acrylonitrile portion is from 1:1 to 20:1 with about 50 to 1000 repeating units. Examples are copolymers of N-methyl methacrylamide and acrylonitrile in a molar ratio of 85:15, 90:10 and 70:30 with about 500 repeating units.

The amount of the combined soil-suspending agents should be a minor proportion of the liquid such as from about 0.1 to about 5% by weight. It has been found that amounts within this range can be used in the preparation of substantially homogeneous products and exhibit a high level of soil suspension during washing. In general, such products containing carboxymethylcellulose or the like in the absence of the vinyl polymer or a suitable suspending agent usually tend to form a lower layer or precipitate upon aging. A similar product containing a vinyl polymer free of the cellulose and in the absence of a suspending agent usually tends to separate also such as forming an upper layer from the bulk of the liquid upon aging. The combination of these materials inhibits such separation. For example, the addition of increasing amounts of vinyl polymer to a liquid containing carboxymethylcellulose results in improved stability and lesser separation. It is within the scope of this invention to employ in the product other materials such as castor wax which tends to suspend these soil anti-redeposition agents and maintain the product substantially homogeneous. The amount and ratio of vinyl polymer and cellulose will be influenced in part by the presence of additional ingredients. They should be selected and integrated with the other ingredients so as to achieve a substantially homogeneous product having the desired anti-redeposition properties. In general, the ratio of said cellulose to vinyl polymer is within the range 20:1 to 1:20 by weight and usually about 10:1 to about 1:10 by weight. It is preferred that the ratio be from about 5:1 to 1:5 by weight and total about 0.1 to 2% in the product.

The water-soluble alkaline inorganic builder salts are preferably the polyphosphate salts which have the property of inhibiting precipitation of calcium and magnesium material in aqueous solution and of contributing to the heavy-duty performance of the liquid detergent product. They may be considered as derived from orthophosphoric acid or the like by the removal of molecularly-bound water, though any suitable means of manufacture may be employed if desired. Such complex or molecularly dehydrated polyphosphate salts may be used in the form of the normal or completely neutralized salt, e.g., pentapotassium tripolyphosphate, or partially neutralized salt, e.g. potassium tripolyphosphate. It is preferred to use the pentapotassium tripolyphosphate or tetrapotassium pyrophosphate salts including any desired combination of the same. The alkali metal salts of tetraphosphoric acid may be used also. Other suitable materials which may be employed are sodium tripolyphosphate and its hexahydrate, and tetrasodium pyrophosphate in suitable proportions so as to form a substantially homogeneous product.

Other alkaline builder salts may be employed also such as the soluble alkali metal silicates. These silicates may be employed as the sole builder salt if desired or in suitable combination with the polyphosphates. Suitable silicates are those having an alkali oxide to silica ratio within the range of about 1:1 to 1:4, and preferably from about 1:2 to 1:3. Examples are sodium silicates having an Na_2O to SiO_2 ratio of 1:2.35, 1:2.5, 1:3.2, 1:2.0, 1:1.6 and 1:1. The potassium silicates having a ratio of 1:2 to 1:2.5 may be used also. In general, the silicates are commonly prepared in solution form.

These inorganic 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

5

detergency and washing powder. These salts are present preferably in amounts which are soluble in the amount of water present in the product. In general, the amount of the builder salts will be within the range of about 5 to 30% by weight and preferably about 10 to 25%.

The liquid composition should contain a water-soluble non-cationic organic detergent, such as the anionic sulfonated detergent. The term "sulfonated" used in the specification and claims refers to the materials having a sulfonate or sulfate group, and is not limited to a sulfonation procedure since any method of preparation may be employed. These detergent materials are known and have sufficient water-solubility or dispersibility to form detergent aqueous solutions in the concentrations which are suitable for use such as in the washing of laundry and other soiled articles. The detergents may be used individually or in any desired combination. It is preferred that the detergent content be at least in part an anionic detergent such as the sulfonates and sulfates.

Among suitable synthetic detergents with which the combination of soil-suspending agents in particularly effective are water-soluble higher alkyl aryl sulfonates, 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 mono-nuclear aryl group, 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 substituents being nonyl, dodecyl and pentadecyl groups derived from polymers of lower mono-olefins which are branched-chain, and decyl, keryl and the like which are straight chain.

Another type of suitable detergent is the sulfated higher alkyl phenol-ethylene oxide condensates having an average of about 2 to 18 moles of ethylene oxide per phenol group and about 6 to 18 carbons in the alkyl group. It is preferred to employ the product having about 4 to 6 moles of ethylene oxide and 8 to 10 carbons in the alkyl group.

Examples of suitable aliphatic sulfonated synthetic 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; higher alkyl glyceryl ether sulfonate, e.g., dodecyl glyceryl ether sulfonate; and the like. The sulfated products of higher fatty alcohols of 6 to 18 carbons condensed with about 2 to 18 moles ethylene oxide may be used also.

These sulfate and sulfonate detergents are used preferably in the form of their alkali metal salts, such as the sodium and potassium salts. Other water-soluble salts such as the nitrogen-containing salts, e.g., lower alkylolamine salts, may be used also, examples being the ammonium, isopropanolamine, mono-, di-, and tri-ethanolamine salts of said detergents. It is preferred that the amount of detergent be from 5 to 20% by weight, usually at least about 10%, with at least about 5% sulfonated detergent.

If desired, suitable amounts of various water-soluble non-ionic organic detergents may be employed also, provided the proportions employed maintain the product in substantially homogeneous form. In general, the non-ionic detergents are used in relatively small amounts such as about 5% by weight since they are ordinarily less compatible with builder salts than the sulfonated detergents.

6

Examples of 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. The polyoxyethylene condensates are derived from ethylene oxide, although other lower alkylene oxides such as propylene oxide, butylene oxide and the like may be substituted therefore.

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 6, 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 C₆-C₇ olefin, and the like.

Other non-ionic 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.

It is preferred to incorporate a higher fatty acid alkylolamide, the acyl radical being within the range of 8 to 18 carbons and each alkylol group having up to 3 carbons. It is preferred to use the monoethanolamides, diethanolamides and isopropanolamides having about 10 to 14 carbon atoms in the acyl radical. Examples are the coconut or equivalent lauric, capric and myristic diethanolamides, monoethanolamides and isopropanolamides. There may be employed also the alkylolamides which are substituted by additional alkylol groups, suitable examples being the above monoethanolamides, diethanolamides and isopropanolamides condensed with one or two moles of ethylene oxide. These materials will be used so as to be compatible in the system with suitable amounts being within the range from about 1 to 15%, preferably about 3 to 12%, by weight of the compositions. The alkylolamides function primarily to improve the detergency and modify the foaming power, e.g., as a suds builder, of the composition. In certain formulations, it provides an additional solubilizing effect. It should not be employed in an amount sufficient to destroy the de-

sired properties since it is considered part of the solids content.

The detergent and builder salt should be formulated so as to form a substantially homogeneous liquid. In the formulation of the product, these ingredients should be suitably selected and proportioned so that they are compatible in the composition using, as required, a suitable solubilizing or coupling agent. Various suitable solubilizing materials are known in the art, such as hydrotropic salts, aliphatic alcohol of 2-3 carbons, and other solvents, emulsifiers, and the like. These materials may be employed in minor amount to form a homogeneous clear or opaque liquid at room temperature with the detergent and builder in the absence of the soil-suspending agents. It is preferred that the liquid be formulated so as to be clear without the soil-suspending agents. The addition of the soil-suspending agents will render the product translucent or opaque.

The inclusion of a suitable water-soluble hydrotropic substance is effective in promoting the compatibility of the ingredients so as to form a homogeneous liquid product. Suitable materials are the alkali metal organic sulfonate (including sulfated) salts having a lower alkyl group up to about 6 carbons. It is preferred to employ an alkyl aryl sulfonate having up to 3 carbons in the alkyl group such as the sodium and potassium toluene and xylene sulfonate salts. Sulfonates made from xylene include orthoxylene sulfonate, metaxylene sulfonate, paraxylene sulfonate and ethylbenzene sulfonate. Commercial xylene sulfonates usually contain metaxylene sulfonate as the main ingredient. Analyses of typical commercial products show about 40-50% metaxylene sulfonate, 10-35% orthoxylene sulfonate and 15-30% paraxylene sulfonate with 0-20% ethylbenzene sulfonate. Any suitable isomeric mixture may be employed, however. Suitable lower alkyl sulfate salts having 5 to 6 carbons in the alkyl group may be employed also such as the alkali metal n-amyl and n-hexyl sulfates. The hydrotrope is employed in a variable amount depending upon the other ingredients but will be used usually in a suitable amount from about 4% to about 12%, preferably about 4 to 10%, by weight of the composition.

The solids content is variable but generally within the range of about 15 to 65% by weight, and preferably about 30 to 60% by weight of the formulation. It is preferred to have a maximum of about 60% solids for liquids which are normally opaque and a maximum of 50% solids for liquids which are normally clear solutions in the absence of the soil-suspending agents. The balance of the composition is primarily water with the liquid medium or solvent being about 35 to 85%, preferably about 40 to 70% by weight. If desired, and particularly where a relatively high solids content is desired, it may be advantageous to reduce or modify the viscosity of a given formula by adding to the water a minor amount of a compatible organic solvent or solubilizer. Examples of suitable water-miscible solvent materials are lower aliphatic monohydric alcohol, e.g., ethanol, propanol or isopropanol; urea, diethylene glycol monobutyl ether, and an alkylolamine such as triethanolamine, which may be employed in a minor amount such as less than about 15% by weight, and preferably not in excess of about 5% by weight of the product.

The liquid detergent product is prepared in any suitable manner. The cellulosic and vinyl polymer may be added in the form of aqueous solutions at any stage during the mixing operations and the order of addition of the other ingredients may be varied as desired. In general, it is preferred to use the major amount of water initially. The cellulosic material and vinyl polymer are added in the form of an aqueous gel or powder with sufficient stirring to insure that a uniform product is obtained. The hydrotrope, the builder salt and the detergents are added successively as powders, aqueous solution or slurries. The alkylolamide and any waxy material are preferably added

in liquid or molten form with agitation to form a homogeneous product. The temperature of admixture should be sufficient to dissolve or melt the ingredients and reasonably elevated temperature conditions such as up to about 200° F. may be employed as desired.

Various other ingredients may be added as desired including compatible perfumes, added suspending or stabilizing materials, coloring materials, corrosion or tarnish inhibitors, germicides, bleaching agents, optical bleaches or fluorescent dyes, viscosity modifiers and the like.

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

Example I

A heavy-duty liquid detergent composition is prepared according to the following formulation:

Ingredients:	Percent
Sodium dodecyl benzene sulfonate	9.7
Sodium xylene sulfonate (commercial)	8.0
Potassium pyrophosphate	20.0
Coconut isopropanolamide	2.7
Sodium carboxymethylcellulose	0.5
Polyvinylpyrrolidone	0.5
Water	Balance

In the above formulation, the alkyl aryl sulfonate is a propylene tetramer having about 10% sodium sulfate as a by-product resulting from the manufacture and purification of the sulfonated detergent. The carboxymethylcellulose has a purity of about 66% (0.7 sub.) with the balance being soluble inorganic salt and the pyrrolidone has an average molecular weight of approximately 20,000.

This product remains substantially homogeneous upon standing. A similar composition containing only the pyrrolidone polymer forms an upper layer containing the polymer concentrated therein upon aging and a similar composition containing only the cellulose compound forms a lower layer containing the cellulose material concentrated therein over the same period of time.

Example II-VI

Ingredients	II	III	IV	V	VI
Sodium higher alkyl benzene sulfonate	10.0	10.0	9.0	9.0	9.0
Sodium nonyl phenol-ethylene oxide sulfate			6.0	6.0	
Sodium lauryl alcohol sulfate					6.0
Lauric-myristic (70:30) isopropanolamide	2.5	2.5	3.0	3.0	3.0
Lauric-myristic (70:30) diethanolamide	2.5	2.5	3.0	3.0	3.0
Sodium xylene sulfonate (comm.)	8.0	6.0	6.0	7.0	6.8
Potassium toluene sulfonate		2.0	2.0	2.0	2.3
Potassium pyrophosphate	20.0	20.0	15.0	15.0	15.0
Polyvinylpyrrolidone	0.5	0.5	0.5	0.25	0.25
Sodium carboxymethylcellulose	0.2	0.2	0.1	0.25	0.25
Castor wax				0.3	0.3
Water	Bal.	Bal.	Bal.	Bal.	Bal.
Stability: Examined at end of	7 mo.	6 mo.	5 mo.	3 mo.	1 mo.
Amount of separation	<5%	<5%	<5%		

In the above formulations, the higher alkyl group of the alkyl benzene sulfonate is derived from propylene polymer containing mixtures of propylene tetramer and pentamer corresponding on the average to a tridecyl group. The nonyl phenol-ethylene oxide sulfate has an average number of about 5 ethylene oxide groups per nonyl phenol. The carboxymethylcellulose has about 0.7 carboxy groups per glucose unit and the pyrrolidone has a molecular weight of about 40,000. The specified proportions are on an active ingredient basis. It is understood that these products may contain small amounts of

perfume, color and fluorescent dye as desired. The specified period of stability refers only to the number of months after which each composition was examined and does not mean that the compositions did not remain substantially homogeneous afterwards.

Examples VII-XI

Other suitable compositions are:

Ingredients	VII	VIII	IX	X	XI
Sodium higher alkyl benzene sulfonate.....	9.0	9.0	10.0	9.0	10.0
Sodium nonyl phenol-ethylene oxide sulfate.....	6.0	6.0	6.0	6.0	6.0
Sodium lauryl ether sulfate.....	3.0	3.0	2.5	3.0	5.0
Lauric-myristic (70:30) isopropanolamide.....	3.0	3.0	2.5	3.0	3.0
Lauric-myristic (70:30) diethanolamide.....	6.5	6.0	6.0	6.5	8.0
Sodium xylene sulfonate (comm.).....	2.0	2.0	2.0	2.0	2.0
Potassium toluene sulfonate.....	15.0	15.0	20.0	15.0	20.0
Potassium pyrophosphate.....	0.3	0.3	0.3	0.3	0.2
Sodium silicate.....	0.25	0.25	0.25	0.25	0.25
Castor wax.....	0.25	0.25	0.5	0.25	0.25
Sodium carboxymethyl-cellulose.....	Bal.	Bal.	Bal.	Bal.	Bal.
Polyvinyl alcohol.....					
Water.....					

In the above formulations, the higher alkyl benzene sulfonate has alkyl chains corresponding on the average to a tridecyl group, as described. The sulfated nonyl phenol has on the average about 5 ethylene oxide groups and the lauryl ether sulfate has about 3 ethylene oxide groups on the average condensed to lauryl alcohol. The sodium silicate has a sodium oxide to silica ratio of 1:2.35 and is given on a solids basis. The polyvinyl alcohol has a viscosity of about 4-6 cps. and about 88% hydrolysis.

Examples XII-XIII

The formulations of Examples VII and X above are prepared using polyvinyl alcohol having a viscosity of 1.8-3 centipoises and a polyvinyl acetate content of 10-30%, e.g., 2.34 cps. and 22.3% acetate.

Examples XIV-XV

Ingredients	XIV	XV
	<i>Percent</i>	<i>Percent</i>
Sodium tridecyl benzene sulfonate.....	10	20
Coconut diethanolamide.....	3	3
Sodium xylene sulfonate (comm.).....	7	7
Potassium pyrophosphate.....	15	15
Sodium silicate.....	0.3	0.3
Castor wax.....	0.25	0.25
Sodium carboxymethylcellulose.....	0.25	0.25
Polyvinyl alcohol.....	4	2.5
Ethanol.....	Bal.	Bal.
Water.....		

In these examples, the same ingredients are employed as described with the silicate having an alkali oxide to silica ratio of 1:2, and the polyvinyl alcohol having a viscosity of 1.8-3 and an acetate content of 10-30% as described above.

Example XVI

Ingredients:	Percent
Nonyl phenol ethylene oxide (9 moles) ----	5
Sodium tridecyl benzene sulfonate -----	2
Sodium di-lauryl di-phenyl oxide di-sulfonate -	10
Sodium xylene sulfonate (comm.) -----	5
Potassium pyrophosphate -----	20
Castor wax -----	0.3
Sodium carboxymethylcellulose -----	0.25
Polyvinyl alcohol (1.8-3 cps., 10-30% ester) -	0.25
Water -----	Bal.

In addition to maintaining a substantially homogeneous appearance, such formulations exhibit a high degree of washing power, particularly in soil-suspension ability, in the laundering of fabrics, particularly resin-treated cottons and synthetic materials, e.g., nylon and Dacron.

In general, the compositions containing the cellulose compound and polyvinyl alcohol are preferred since they exhibit markedly better soil-suspension properties upon aging for prolonged periods of time compared to similar compositions containing the cellulose compound and polyvinylpyrrolidone.

Although the present invention has been described with reference to particular embodiments and examples, it will be apparent to those skilled in the art that variations and modifications can be substituted therefor without departing from the principles and true spirit of the invention.

Having described the invention, what is desired to be claimed by Letters Patent is:

1. An aqueous liquid detergent composition which consists essentially of about 5 to 30% by weight of a water-soluble anionic organic sulfonated detergent, about 10 to 30% by weight of a water-soluble alkaline inorganic builder salt selected from the group consisting of alkali metal polyphosphates and alkali metal silicates, about 4 to 12% by weight of water-soluble organic hydrotropic salt selected from the group consisting of alkali metal alkyl substituted benzene sulfonates having up to 3 carbon atoms in said alkyl substituent and alkyl sulfates having 5 to 6 carbon atoms in the alkyl group, about 0.1 to 5% by weight of a mixture of (a) water-soluble alkali metal carboxymethylcellulose salt normally tending to separate from an aqueous mixture of said detergent salt and said builder salt in said proportions, and (b) a water-soluble polyvinyl compound selected from the group consisting of polyvinyl alcohol having a viscosity from the range of about 1.8 to 65 centipoises in a 4% aqueous solution with a polyvinyl acetate content from about 10 to about 30% and polyvinylpyrrolidone having an average molecular weight in the range of 15,000 to 100,000, said polyvinyl compound normally tending to separate from an aqueous mixture of said detergent and said builder salt in said proportions, the ratio of said carboxymethylcellulose to said polyvinyl compound being from about 20:1 to about 1:20 by weight and effective to inhibit the separation of one another from said aqueous mixture, and the balance being water sufficient to form a pourable, substantially homogeneous liquid, the total solids content being less than about 65% by weight of the composition.

2. A liquid detergent composition in accordance with claim 1 wherein said builder comprises a potassium polyphosphate selected from the group consisting of potassium pyrophosphate and tripolyphosphate.

3. A liquid detergent composition in accordance with claim 1, wherein said builder comprises sodium silicate.

4. A liquid detergent composition in accordance with claim 1 which contains about 1-15% by weight of higher fatty acyl alkylolamide selected from the group consisting of diethanolamides, monoethanolamides and isopropanolamides having about 10 to 14 carbon atoms in said fatty acyl group.

5. An aqueous liquid detergent composition in accordance with claim 1 which contains polyvinyl alcohol having a viscosity of about 1.8 to 6 centipoises.

6. An aqueous liquid detergent composition in accordance with claim 1 which contains polyvinylpyrrolidone having an average molecular weight of about 15,000 to 40,000.

7. An aqueous liquid detergent composition in accordance with claim 1 wherein the ratio of said carboxymethylcellulose to said polyvinyl compound is from about 5:1 to 1:5 by weight.

8. A detergent composition in the form of a substantially homogeneous, pourable aqueous liquid which consists essentially of about 5 to 30% by weight of a water-soluble anionic organic sulfonated detergent, said detergent comprising an alkali metal alkyl benzene sulfonate having about 8 to 15 carbons in the alkyl group, about 10 to 25% by weight of a potassium polyphosphate salt selected from the group consisting of potassium pyro-

11

phosphate and tripolyphosphate, about 4 to 12% by weight of an alkali metal lower alkyl aryl sulfonate selected from the group consisting of xylene and toluene sulfonates, about 0.1 to 5% of a mixture of sodium carboxymethylcellulose and water-soluble polyvinyl alcohol having a viscosity in the range of about 1.8 to 6 centipoises in a ratio from about 10:1 to about 1:10 by weight, and the balance being water sufficient to form a pourable substantially homogeneous liquid, the total solids content being less than about 65% by weight of the composition.

9. A detergent composition in the form of a substantially homogeneous, pourable aqueous liquid which consists essentially of about 5 to 30% by weight of a water-soluble anionic organic sulfonated detergent, said detergent comprising an alkali metal alkyl benzene sulfonate having about 8 to 15 carbons in the alkyl group, about 10 to 25% by weight of a potassium polyphosphate salt selected from the group consisting of potassium pyrophosphate and tripolyphosphate, about 4 to 12% by weight of an alkali metal lower alkyl aryl sulfonate selected from the group consisting of xylene and toluene sulfonates, about 0.1 to 5% of a mixture of sodium carboxymethylcellulose and water-soluble polyvinylpyrrolidone having an average molecular weight from about 15,000 to 100,000 in a ratio from about 10:1 to about 1:10 by weight, and the balance being water sufficient to form a pourable substantially homogeneous liquid, the total solids content being less than about 65% by weight of the composition.

10. An aqueous liquid detergent composition which consists essentially of about 5 to 30% by weight of alkali metal higher alkyl benzene sulfonate detergent having 12 to 15 carbons in the alkyl group, about 10 to 30% by weight of potassium pyrophosphate, about 4 to 12% by weight of an alkali metal organic hydrotropic salt selected from the group consisting of alkali metal toluene and xylene sulfonates, about 3 to 12% by weight of a higher fatty acyl alkylolamide having about 10 to 14 carbons in

12

said acyl group and up to 3 carbons in each alkylol group, and about 0.1 to 2% by weight of a mixture of (a) sodium carboxymethylcellulose salt normally tending to separate from an aqueous mixture of said detergent salt and said pyrophosphate in said proportions and (b) water-soluble polyvinyl alcohol having a viscosity from the range of about 1.8 to 3 centipoises in a 4% aqueous solution with a polyvinyl acetate content from about 10 to about 30% by weight normally tending to separate from an aqueous mixture of said detergent and said pyrophosphate in said proportions, the ratio of said carboxymethylcellulose to said polyvinyl alcohol being from about 10:1 to about 1:10 by weight and effective to inhibit the separation of one another from said aqueous mixture, and the balance being water sufficient to form a pourable, substantially homogeneous liquid, said ingredients forming a clear solution at room temperature in the absence of said carboxymethylcellulose and polyvinyl alcohol, the total solids content being a maximum of about 50% by weight of the composition.

References Cited by the Examiner

UNITED STATES PATENTS

2,798,047	7/1957	Touey et al.	252—152
2,805,205	9/1957	Touey et al.	252—152
2,859,182	11/1958	Carroll	252—137
2,877,187	3/1959	Henderson et al. .	252—137 XR
2,981,692	4/1961	Stillo et al.	252—161 XR
2,994,665	8/1961	Reich et al.	252—137
2,999,068	9/1961	Pilcher et al.	252—137
3,000,830	9/1961	Fong et al.	252—117
3,060,124	10/1962	Ginn	252—135
3,101,324	8/1963	Wixon	252—137

35 JULIUS GREENWALD, *Primary Examiner.*ALBERT T. MEYERS, *Examiner.*