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HEAVY DUTY LIQUID DETERGENT

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This invention relates to heavy duty liquid detergent compositions and more particularly to heavy duty liquid detergent compositions containing sodium carboxymethylcellulose.

The development of heavy duty detergent compositions for cleaning heavily soiled cotton cloth materials has been marked by a number of successive improvements. One of the first and most important developments was the use of a class of surface active agents comprising the water soluble salts of the alkylated benzene sulfonic acids wherein the alkyl group contains from 9 to 15 carbon atoms and in particular the highly soluble triethanolamine salt of these sulfonic acids.

It was discovered subsequently that certain inorganic salts when combined with such synthetic detergents would improve their detergency properties and also effect savings in material costs. Some of the most important salts found suitable for this purpose were the alkali metal tripolyphosphates. The combination of the synthetic detergent and inorganic salts in the form of solid powders or flakes, termed "built" formulations, were found to be objectionable by the consumer, however, primarily for two reasons—one reason being that they were not readily soluble either in cold or hot water and required an appreciable time to go into solution, and the second reason being that the dust which arose from these flakes or powders was often times extremely irritating and caused violent sneezing by anyone standing nearby. In order to solve these problems aqueous solutions or suspensions of these built formulations were developed.

With the development of more accurate means of measuring detergency it was found that built detergent formulations were subject to another disadvantage—namely that after the dirt had been removed from the cloth by the detergent, frequently a portion of this dirt was redeposited in the cloth thus giving a gray appearance to the "washed" cloth. It was found that when certain suspending agents were added to built detergent compositions that this redeposition of soil could be prevented in large measure thus eliminating the grayish appearance of the washed cloth.

A composition now has been found whereby a heavy duty built detergent formulation may be contained in an aqueous medium to avoid the disadvantages of the solid powdered formulations and which aqueous formulation also contains a suspending agent to provide the means of preventing redeposition of soil on the washing cloth.

It is an object of this invention to provide an improved heavy duty liquid detergent composition.

It is a further object of this invention to provide an improved heavy duty liquid detergent composition containing a built formulation of inorganic salts and a synthetic detergent together with a suspending agent.

Further objects of this invention will be apparent from the description and claims that follow.

In accordance with this invention it has been found that an improved heavy duty liquid detergent composition can be produced if the triethanolamine salt of alkyl benzene sulfonic acids in which the alkyl group contains from 9 to 15 carbon atoms are combined with alkali metal tripolyphosphates in certain specific ratios and amounts and with sodium carboxymethylcellulose as a suspending agent. The improved heavy duty liquid detergent composition of this invention contains the following active ingredients in an aqueous medium with the range of amounts of each ingredient being expressed as weight percent based on the total weight of the composition including the water:

Potassium tripolyphosphate	7.5–25.0
Sodium tripolyphosphate	0–10.0
Triethanolamine C_9–C_{15} alkyl benzene sulfonate	10.0–25.0
Laurylethanolamide	0– 5.0
Sodium carboxymethylcellulose	0.2– 1.0

It has also been found, however, that the total quantity of potassium and sodium tripolyphosphate cannot exceed 25 weight percent of the total composition and that the sum of the quantities of triethanolamine alkyl benzene sulfonate and the laurylethanolamide cannot exceed 25 weight percent of the composition. Moreover, it has been found necessary to maintain the ratio of the total quantity of sodium and potassium tripolyphosphates to the sum of the quantities of sulfonate and amide within rather narrow limits in order to provide a stable homogeneous composition. The ratio of the total quantity of the tripolyphosphate salts to the sum of the quantities of triethanolamine alkyl benzene sulfonate and laurylethanolamide should range between 0.8 to 1.0 and 1.25 to 1.0.

The compositions of this invention are suspensions instead of true solutions and thus have a cloudy appearance; however, when the concentrations and ratios of the ingredients are maintained within the limits set forth, these formulations are completely homogeneous and stable, i.e. the ingredients do not settle and separate upon standing.

It will be noted from the ranges which have been set forth that all of the tripolyphosphate may be the potassium salt because of the inherently greater solubility of this salt as compared with the sodium salt. In such compositions the potassium tripolyphosphate may range from 10 to 25 weight percent. These tripolyphosphates have the general formula $M_5P_3O_{10}$ wherein the M represents either sodium or potassium.

The alkylated benzene sulfonic acids which are neutralized to produce the surface active agent of this composition contain from 9 to 15 carbon atoms in the alkyl group and may be produced by any one of a number of well known methods; for example, the alkylation may be accomplished by treating an excess of the benzene with a halogenated aliphatic hydrocarbon of 9 to 15 carbon atoms in the presence of a suitable alkylation catalyst of the Friedel-Crafts type, i.e. $AlCl_3$, to obtain substantial yields of mono-alkylated benzenes. These mono-alkylated benzenes may also be produced by alkylating benzene with an alcohol or mono-olefin of 9 to 15 carbon atoms using either sulfuric acid or a Friedel-Crafts catalyst.

A further method for producing the alkylated benzene or mixture of alkylated benzenes having 9 to 15 carbon atoms in the alkyl group is to polymerize an olefin such as propylene, or a gas stream containing propylene, with an acid catalyst such as a supported phosphoric acid catalyst or boron trifluoride catalyst at elevated temperatures and pressures according to well known methods thereby obtaining a mixture of propylene polymers which are fractionated to produce polymers of from 9 to 15 carbon atoms or intermediate fractions of a narrower molecular weight range. The benzene is then alkylated with the propylene polymer fraction in the presence of a Friedel-Crafts catalyst or with a sulfuric acid catalyst to produce the alkylated benzene or mixture of alkylated benzenes.

The alkylated benzene having an alkyl group of from 9 to 15 carbon atoms or a mixture of alkylated benzenes within this range is subjected to sulfonation with sulfuric

acid of 98 to 100 percent concentration at temperatures of 150° F. to 160° F. using about one volume of acid to one volume of the alkylated benzene mixture or more preferably it is subjected to sulfonation with 20 percent fuming sulfuric acid at somewhat lower temperatures, i.e. 135° F. with about the same ratio of acid to hydrocarbon. When the sulfonation reaction is completed the reaction mixture is diluted with a solvent such as benzene or hexane or mixtures thereof and the spent sulfuric acid is settled out leaving the alkylated benzene sulfonic acids in solution in the immiscible benzene layer. The benzene solution of the sulfonic acids is then extracted with a mixture of water and methanol or other lower alcohol to dissolve and remove the sulfonic acids from the benzene. The aqueous alcohol solution, after separation from the benzene, is neutralized with triethanolamine and the resulting sulfonate solution evaporated to remove water and alcohol to produce a finished solution containing approximately 60 percent by weight of the triethanolamine alkyl benzene sulfonate. It is to be noted that in the foregoing composition the quantities of the triethanolamine alkyl benzene sulfonate are based on the anhydrous salt and not on the 60 percent solution which is produced commercially. A particularly preferred triethanolamine C_9–C_{15} alkyl benzene sulfonate has a major portion of the alkyl groups in the C_{10}–C_{12} range. Moreover, it has been found that only the triethanolamine salt is suitable for preparing the compositions of this invention. The alkali metal salts for example cannot be used since they are not sufficiently soluble to give a homogeneous composition.

The function of the laurylethanolamide is that of a sudsing agent. Its use is not always required in certain applications of heavy duty detergents and accordingly it may be omitted entirely and replaced by an equal quantity of the triethanolamine alkyl benzene sulfonate. Laurylethanolamide is a commercially available material and it is this commercial material that is contemplated for use in this invention.

The sodium carboxymethylcellulose suspending agent is the sodium salt of carboxymethylcellulose formed by the reaction of alkali cellulose with monochloroacetic acid. Sodium carboxymethylcellulose is available commercially in several viscosity types of the technical grade product and is generally a cream colored powder which dissolves readily in either hot or cold water to give a viscous colloidal solution. The viscosity types most suitable for use as suspending agents in the instant detergent formulation are the medium to high viscosity types particularly those which in 2 percent aqueous solution have a viscosity ranging between 50 and 2000 centipoises at 25° C. Sodium carboxymethylcellulose viscosity types below the 50 centipoise lower limit do not produce suitable suspensions when combined with the other ingredients of the instant formulation since upon standing such formulations will stratify and settle. Viscosity types above the 2000 centipoise upper limit produce formulations which are too viscous for detergent formulations and hence are not desirable. The commercial sodium carboxymethylcellulose product is from 65 to 70 percent pure. The remaining 30 to 35 percent of the product being various residual salts, principally sodium chloride with small amounts of sodium glycolate and sodium carbonate. The sodium carboxymethylcellulose to be used in this invention is the commercial product and the quantities set forth are based on the total commercial product containing the aforesaid impurities. Although quantities of the commercial sodium carboxymethylcellulose to be used in the compositions of this invention may range between 0.2 and 1.0 percent by weight based on the total weight of the composition, it has been found preferable to use about 0.5 weight percent since amounts in excess of this give very little added suspending action.

In addition to the ingredients which have been set forth for this formulation, naphtha or pine oils may be added to the formulation in amounts ranging up to 5 percent of the total solid content of the formulation. These materials are useful because of their solvent action.

The novel formulations of this invention may be prepared by a number of conventional methods; however, the preferred method is to add the tripolyphosphate salts to water and then heat the water to approximately 180° F. to 190° F. until they are dissolved. The solution is cooled to approximately 100° F. and the triethanolamine alkyl benzene sulfonate and laurylethanolamide are added. The powdered sodium carboxymethylcellulose is then added to the solution and put into colloidal suspension by means of high speed stirring with a propeller type mixer. If desired the sodium carboxymethylcellulose may be dissolved by adding the dry powder slowly to water heated to 120° F. to 175° F. and the resulting solution added to the aqueous polyphosphate-sulfonate-amide components. This method is not preferred, however, since the quantity of water required for solution may be too great to permit producing a finished formulation having the desired concentrations. Accordingly, therefore, the preferred method is to add the dry powder by means of high speed mixing to the aqueous suspension of the other components of the formulation.

The following examples will serve to illustrate certain specific embodiments of the invention and to demonstrate the usefulness of the formulations of the invention as heavy duty detergents.

EXAMPLE I

Two separate formulations were prepared having the composition shown in weight percent based on the total weight of the composition:

Formulation	A	B
Potassium tripolyphosphate	20.0	19.5
Sodium tripolyphosphate	5.0	5.0
Triethanolamine alkyl benzene sulfonate [1]	20.0	20.0
Laurylethanolamide	5.0	5.0
Sodium carboxymethylcellulose (vis. 50–100 cp. in 2 percent aqueous solution at 25° C.)	0.0	0.5
Water	50.0	50.0

[1] The triethanolamine salt of the mono-alkyl benzene sulfonic acids wherein the alkyl group contains between 9 and 15 carbon atoms with the major portion contalning from 10 to 12 carbon atoms.

The detergency and foam of these compositions were measured by the use of the Atlas Launderometer, in the manner described in "Soap and Sanitary Chemicals," September 1948, page 42. This test procedure as described by S. Machlis and E. B. Michaels was modified by using cotton cloth in place of the glass fiber and maintaining a temperature of 120° F. during the washing cycle. Aqueous detergent concentrations of 0.2 percent, 0.3 percent and 0.5 percent of the total solids were employed in the test comparisons. A detailed description of the testing device is found in the "Technical Manual and Yearbook" of the American Association of Textile Chemists and Colorists for 1947–48 on page 98. In these tests detergencies are compared by means of the reflectance of washed cotton cloth, with a high reflectance (indicated by a large number of reflectometer units) corresponding to a high detergency value. The results are set forth in Table I below:

Table I

Formulation	A		B	
Detergent concentration in weight percent solids	Reflectometer units	Foam height in ⅛" units	Reflectometer units	Foam height in ⅛" units
0.2	69	22	76	21
0.3	66	22	76	23
0.5	67	22	77	25

These data demonstrate the marked superiority of the sodium carboxymethylcellulose containing compositions of this invention as compared with the same detergent composition without the suspending agent.

EXAMPLE II

A portion of formulation B of Example I was compared with a commercial standard alcohol sulfonate type built detergent composition by the same test methods as employed in Example I. The results of these tests are shown in Table II.

Table II

Formulation	Commercial standard		B	
Detergent concentration in weight percent solids	Reflectometer units	Foam height in 1/8" units	Reflectometer units	Foam height in 1/8" units
0.3	70	24	73	21

It will be seen from these data that the liquid detergent compositions of this invention are superior to commercial standard high detergency powdered formulations.

EXAMPLE III

Another detergent composition was prepared in accordance with the teachings of this invention to have the following composition in weight percent based on the total weight of the composition:

Formulation, C:

Potassium tripolyphosphate	14.5
Sodium tripolyphosphate	10.0
Triethanolamine alkyl benzene sulfonate [1]	20.0
Laurylethanolamide	5.0
Sodium carboxymethylcellulose	0.5

[1] The same material as employed in Example I.

Duplicate tests were made by the method of Example I to compare this formulation with the commercial standard of Example II. The results of these tests are set forth in Table III.

Table III

Formulation	Commercial Standard		C	
Detergent concentration in weight percent solids	Reflectometer units	Foam height in 1/8" units	Reflectometer units	Foam height in 1/8" units
1st test	70	24	80	22
2nd test	70	24	78	20

This example demonstrates that by following the teachings of this invention, formulations may be prepared which are far superior to commercial standard high detergency solid formulations.

I claim:

1. An improved heavy duty liquid detergent composition consisting essentially of a stable aqueous suspension of the following ingredients in weight percent based on the total weight of the composition:

Potassium tripolyphosphate	7.5–25.0
Sodium tripolyphosphate	0–10.0
Triethanolamine C_9–C_{15} alkyl benzene sulfonate	10.0–25.0
Laurylethanolamide	0–5.0
Sodium carboxymethylcellulose	0.2–1.0

wherein the total quantity of the tripolyphosphate salts does not exceed 25.0 weight percent, the sum of the quantities of the triethanolamine alkyl benzene sulfonate and the laurylethanolamide does not exceed 25.0 weight percent and the ratio of the total quantity of tripolyphosphate salts to the sum of the quantities of the triethanolamine alkyl benzene sulfonate and the laurylethanolamide ranges between 0.8 to 1.0 and 1.25 to 1.0.

2. An improved heavy duty liquid detergent composition consisting essentially of a stable aqueous suspension of the following ingredients in weight percent based on the total weight of the composition:

Potassium tripolyphosphate	10.0–25.0
Triethanolamine C_9–C_{15} alkyl benzene sulfonate	10.0–25.0
Laurylethanolamide	0–5.0
Sodium carboxyethylcellulose	0.2–1.0

wherein the sum of the quantities of the triethanolamine C_9–C_{15} alkyl benzene sulfonate and the laurylethanolamide does not exceed 25.0 weight percent and the ratio of the quantity of potassium tripolyphosphate to the sum of the quantities of the triethanolamine alkyl benzene sulfonate and the laurylethanolamide ranges between 0.8 to 1.0 and 1.25 to 1.0.

3. An improved heavy duty liquid detergent composition consisting essentially of a stable aqueous suspension of the following ingredients in weight percent based on the total weight of the composition:

Potassium tripolyphosphate	7.5–25.0
Sodium tripolyphosphate	0–10.0
Triethanolamine C_9–C_{15} alkyl benzene sulfonate	10.0–25.0
Laurylethanolamide	0–5.0
Sodium carboxymethylcellulose	0.5

wherein the total quantity of the tripolyphosphate salts does not exceed 25.0 weight percent, the sum of the quantities of the triethanolamine alkyl benzene sulfonate and the laurylethanolamide does not exceed 25.0 weight percent and the ratio of the total quantity of tripolyphosphate salts to the sum of the quantities of the triethanolamine alkyl benzene sulfonate and the laurylethanolamide ranges between 0.8 to 1.0 and 1.25 to 1.0.

4. An improved heavy duty liquid detergent composition consisting essentially of a stable aqueous suspension of the following ingredients in weight percent based on the total weight of the composition:

Potassium tripolyphosphate	19.5
Sodium tripolyphosphate	5.0
Triethanolamine C_9–C_{15} alkyl benzene sulfonate	20.0
Laurylethanolamide	5.0
Sodium carboxymethylcellulose	0.5

5. An improved heavy duty liquid detergent composition consisting essentially of a stable aqueous suspension of the following ingredients in weight percent based on the total weight of the composition:

Potassium tripolyphosphate	14.5
Sodium tripolyphosphate	10.0
Triethanolamine C_9–C_{15} alkyl benzene sulfonate	20.0
Laurylethanolamide	5.0
Sodium carboxymethylcellulose	0.5

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,023,168 February 27, 1962

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 12, for "carboxyethylcellulose" read -- carboxymethylcellulose --.

Signed and sealed this 12th day of June 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents