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DETERGENT COMPOSITION

Coleman R. Caryl, Riverside, Conn., assignor to American Cyanamid Company, New York, N. Y., a corporation of Maine

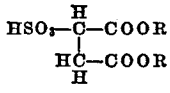
No Drawing. Application September 27, 1940, Serial No. 358,658

17 Claims. (Cl. 252—138)

This invention relates to a new detergent composition which is particularly valuable in the laundering of silks, woolens and rayons, in the washing of glassware, silverware, dishes and woodwork, and in the cleaning of rugs and upholstery and the like. The composition is also suitable for wider uses in those commercial operations which require a washing agent of low alkalinity and good detergency and sudsing qualities in both soft and hard water.

Objects of my invention are therefore to produce a detergent composition which possesses all of the good qualities of soap, but without its inherent disadvantages in hard water. More specific objects of my invention are to produce a detergent of low alkalinity, good solubility, sudsing and detergent qualities in both hard and soft water, which is entirely harmless to the hands or fabrics, and which is stable and non-caking upon storage.

In the U. S. Patent No. 2,028,091, dated January 14, 1936, of A. O. Jaeger, there is described a class of esters of sulfodicarboxylic acids which have excellent wetting and detergent properties in aqueous solutions when used in the form of their water-soluble salts. These compounds have the following structural formula:

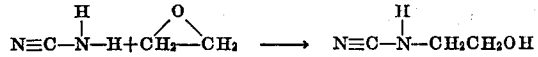


in which R is an alkyl group and the hydrogen atom of the sulfosuccinic acid group is preferably replaced by an alkali-metal salt such as sodium, potassium or ammonium or by an organic base such as ethanolamine, etc. Compounds of this kind in which R is an alkyl group having 6 to 10 carbon atoms have been found particularly desirable for use in the compositions of my invention.

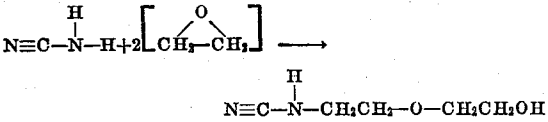
It has been found that although these esters produce a normal amount of foam in aqueous solution this foam is not stable and breaks down within a short time. It has also been found that while esters of this class have good detergent power on fatty soils, that is grease spots and the like, their detergent power on non-fatty soils is not as high as might be desired. These difficulties are overcome by the present invention.

In my copending application, Serial No. 289,525, filed August 12, 1939, now Patent No. 2,295,831, dated September 15, 1942, I have disclosed that an increase in the amount and stability of the foam produced by the above-mentioned sulfosuccinic acid esters can be obtained by the use therewith of water-soluble salts of pyrophosphoric acid such as tetrasodium pyrophosphate. I have now discovered that the sudsing qualities of the compositions of my above-mentioned application may be further enhanced and the non-fatty soil detergent qualities greatly improved by the use of small amounts of the material produced by the reaction of a monocarboxylic acid with a member of the group consisting of monoalkylol cyanamides and polymerized monoalkylol cyanamides.

These condensation products and method of manufacture are described in detail in the U. S. application of W. P. Ericks, Serial No. 278,456, filed June 10, 1939, now Patent No. 2,258,320 dated October 7, 1941. In general, these condensation products are prepared by heating an alkylol cyanamide or its polymer with an organic monocarboxylic acid. Monoalkylol cyanamides may be prepared for use in the condensation reaction by reacting a suitable cyanamide compound such as sodium cyanamide with an alkylene oxide such as ethylene oxide, propylene oxide, methyl, ethyl or propyl ether of ethylene glycol and the like or with compounds containing such groups or 5.6 anhydro-monoacetone glucose. When equimolecular ratios of the cyanamide salt and an alkylene oxide are used a simple alkylol derivative is obtained such as, for example:



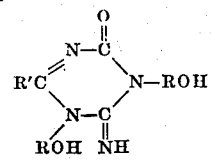
When two or more moles of the alkylene oxide are reacted with each mole of the cyanamide derivative there are obtained ether-alcohol derivatives which may be designated as alkoxyalkyl cyanamides.



For convenience, however, these derivatives are also broadly termed alkylol cyanamides hereinafter in the specification and claims.

These alkylol cyanamides are all extremely reactive and polymerize readily upon heating. However, in the present specification and claims both the monomers and their polymers will be described as monoalkylol cyanamides. Upon heating the alkylol cyanamide or its polymer with an organic monocarboxylic acid to temperatures of 110–160° C. a condensation takes place with evolution of water. The product is a surface-active agent that is resistant to acids and only slowly attacked by alkalies.

The structural formula of the condensation products has not as yet been definitely established. However, the following structural formula has been suggested



in which R is a member of the group consisting

of alkyl and alkoxy-alkyl radicals and R' is an alkyl radical. It is to be understood that I am not limited in my invention to this exact formula since it is subject to further verification.

Condensation products of the above type which have been found especially useful in my new detergent composition are those resulting from the condensation of an aliphatic monocarboxylic acid having 10 to 18 carbon atoms with alkylol cyanamides. When a higher molecular weight acid is used it is sometimes found desirable to employ alkylol cyanamides obtained by reacting two or more moles of alkylene oxide with one mole of cyanamide. The lauric acid derivative of monoethylol cyanamide or its polymer is of particular value and is defined hereinafter and in the claims as cyanamino ethyl laurate. The myristic acid and palmitic acid derivatives are also particularly well suited for use in my new detergent composition.

I have found that the sudsing and detergent properties of the dialkyl sulfodicarboxylic acid esters of aliphatic alcohols of 6 to 10 carbon atoms may be greatly improved by the incorporation therewith of small amounts of the above-described condensation products of aliphatic monocarboxylic acids with monoalkylol cyanamide and polymerized monoalkylol cyanamide. In the preferred compositions of my invention I therefore include 0.5 to 3 parts of the condensation product for each 5 to 10 parts of the sulfosuccinic ester, as smaller amounts do not usually give the improvement desired, whereas larger amounts are unnecessary. In fact, I have noted in some cases that with larger amounts of the condensation product there may be an actual reduction in the amount of foam.

Further increases in the stability of the foam and detergency of the mixture may be obtained by addition thereto of a water-soluble salt of pyrophosphoric acid such as the sodium, potassium or ammonium and the like salts. For the reasons pointed out in my application referred to above, I prefer to use tetrasodium pyrophosphate in amounts ranging from 10 to 50 parts. In some cases materials such as sodium carbonate and sodium bicarbonate, di- and trisodium phosphates, etc. may be substituted in whole or in part for the tetrasodium pyrophosphate of my composition. However, I have found that the tetrasodium pyrophosphate gives much superior results in my composition.

In my preferred detergents a bulking agent is used so that a composition of less concentrated form may be marketed. The bulking agents should preferably be water-soluble although this is not absolutely necessary. The bulking agent should also be stable and non-hygroscopic in order to prevent caking of the detergent composition upon standing. Of the various bulking agents found suitable sodium sulfate is most preferable since it is neutral, inexpensive, dissolves readily in hot and cold water and actually appears to improve the detergent action of my composition. Other materials such as dextrose, sugars, urea, salts of organic acids such as tartrates, succinates, disodium phthalates, sodium bisulfate, boric acid, borax, sodium chloride and the like may also be used for this purpose in greater or lesser amounts. It is of course possible to omit entirely the bulking agent from the mixture if a very concentrated detergent is desired. In addition to the above components the compositions may also contain soaps, saponin, abrasives or other substances designed to improve its scouring, foaming and cleansing properties.

My detergent compositions may be prepared by simply mixing the various ingredients or, preferably, by spray-drying in known spray-drying equipment. Excellent results have been obtained with a standard type of spray-drier now on the market in which the material to be dried is atomized into a vertical chamber containing a descending vortex of hot air or hot products of combustion. Air temperatures of 400–700° F. are preferably used in this equipment.

In addition to the powdered or spray-dried form my compositions are well-suited for manufacture and sale in the form of cakes, bars, chips, granules, or flakes. In this form of my invention it is preferable to employ bulking agents having greater mechanical strength than sodium sulfate; boric acid, for example, may be used as a binding material in these forms of my product.

The following specific examples are given by way of illustration and not of limitation. The relative proportion of tetrasodium pyrophosphate and sodium sulfate is not varied in these examples in order that the effect of the condensation product may be shown more clearly. In these examples the parts are indicated by weight.

Example 1

61 parts of sodium sulfate and 30 parts of tetrasodium pyrophosphate ($Na_4P_2O_7$) were dry mixed and fed at the rate of 5 lbs. per minute, by means of a vibrating feeder, to a kettle to which water heated to 150° F. was supplied at the rate of 5 lbs. per minute. The slurry was agitated and allowed to flow by gravity to the funnel of the distributor system of a spray-drier. An alcoholic solution of 1.0 part of cyanamino ethyl laurate, 5 parts sodium di-n-octyl sulfosuccinate, and 3 parts of sodium di(2-ethylhexyl) sulfosuccinate was also fed to the funnel at the same time. The resulting mixture was spray-dried in the drying chamber by a current of hot air according to conventional spray-drier practice.

The dried product is obtained in the form of a light, fluffy white powder, which dissolves instantly in water. The apparent density of the material is of the order of 30–35 grams per 100 cc. but may be increased or decreased by modifying the operating conditions of the spray-drier.

The non-fatty soil detergent power of the product was determined by means of an empirical washing test which gives good comparative results. A clean white 80 x 80 cotton cloth was impregnated with a non-fatty soil such as carbon black. The soiled cloth was then washed in a 0.1% solution of the detergent for ½ hour at 60° C. in a standard washing machine. The washed cloth was rinsed thoroughly and dried. The detergent power of the washing solution was then expressed as the difference in percent light reflection between soiled and washed pieces. The light reflectance was measured in an electrophotometer. The greater the difference in light reflection between the washed and unwashed pieces, the greater has been the detergent action of the washing solution.

It was found that the product of Example 1 has a detergency in soft water of 11.0% and in hard water (300 p. p. m. $CaCO_3$) of 12.4%. The foaming quality was excellent in both hard and soft water. A composition consisting of 30 parts tetrasodium pyrophosphate, 62 parts sodium sulfate, 4 parts sodium di-n-octyl sulfosuccinate and 4 parts sodium di(2-ethylhexyl) sulfosuccinate had a detergent power of only 8.0 in soft water by the same test and the foaming quality

was not as good as in the product of Example 1. A popular commercial alkali-metal fatty acid soap gave good detergency and foaming in soft water but in hard water the detergent power was only 6.4 and the foam was practically non-existent.

Example 2

A composition containing 1 part cyanamino ethyl laurate, 5 parts sodium di-n-octyl sulfosuccinate, 2 parts sodium di(2-ethylhexyl) sulfosuccinate, 1 part disodium mono-oleyl-sulfosuccinate, 30 parts tetrasodium pyrophosphate and 61 parts of sodium sulfate, was prepared by a spray-drying process described in Example 1. This composition had excellent foaming qualities in both hard and soft water. The detergent power was found to be 10.8 in soft water and 12.2 in hard water.

Example 3

A composition consisting of 4 parts cyanamino ethyl laurate, 4 parts sodium di-n-octyl sulfosuccinate, 30 parts tetrasodium pyrophosphate and 62 parts sodium sulfate gave a detergency of 11.6 in soft water by the standard detergency test, but had less foaming qualities than Example 1, due probably to the larger proportion of cyanamino ethyl laurate employed in the composition. It was observed, however, in tests made on the product of Example 1 that smaller amounts of cyanamino ethyl laurate improved the foaming quality of compositions containing sodium dioctyl sulfosuccinate, tetrasodium pyrophosphate and sodium sulfate.

Example 4

A composition consisting of 2 parts cyanamino ethyl laurate, 4 parts sodium di(2-ethylhexyl) sulfosuccinate, 4 parts sodium di-n-octyl sulfosuccinate, 30 parts tetrasodium pyrophosphate and 60 parts sodium sulfate, prepared as described above, had good foaming properties in both hard and soft water and had a detergent power of 10.9 in soft water and 12.8 in hard water.

What I claim is:

1. A detergent composition comprising 0.5 to 3 parts of the condensation product of an aliphatic monocarboxylic acid having 10 to 18 carbon atoms with a monoalkylol cyanamide, 5 to 10 parts of the sulfosuccinic ester of at least one aliphatic alcohol having 6 to 10 carbon atoms, and 10 to 50 parts of a water-soluble salt of pyrophosphoric acid, the parts being by weight.

2. A detergent composition comprising 0.5 to 3 parts of the condensation product of an aliphatic monocarboxylic acid having 10 to 18 carbon atoms with monoethylol cyanamide, 5 to 10 parts of the sulfosuccinic ester of at least one aliphatic alcohol having 6 to 10 carbon atoms, and 10 to 50 parts of a water-soluble salt of pyrophosphoric acid, the parts being by weight.

3. A detergent composition comprising 0.5 to 3 parts of the condensation product of lauric acid with monoethylol cyanamide, 5 to 10 parts of an alkali-metal dioctyl sulfosuccinate and 10–50 parts of an alkali-metal pyrophosphate, the parts being by weight.

4. A detergent composition comprising 0.5 to 3 parts of the condensation product of lauric acid with monoethylol cyanamide, 5 to 10 parts of sodium dioctyl sulfosuccinate and 10 to 50 parts of tetrasodium pyrophosphate, the parts being by weight.

5. The product of claim 2 containing a water-soluble, non-hygroscopic bulking agent.

6. The product of claim 2 containing sodium sulfate as a bulking agent.

7. A detergent composition comprising 0.5 to 3 parts of cyanamino ethyl laurate, 5 to 10 parts of an alkali-metal salt of the sulfosuccinic acid ester of an aliphatic alcohol of 6 to 10 carbon atoms and 10 to 50 parts of an alkali-metal salt of pyrophosphoric acid, the parts being by weight.

8. A detergent composition comprising 0.5 to 3 parts of cyanamino ethyl myristate, 5 to 10 parts of an alkali-metal salt of the sulfosuccinic acid ester of an aliphatic alcohol having 6 to 10 carbon atoms and 10 to 50 parts of an alkali-metal salt of pyrophosphoric acid, the parts being by weight.

9. A detergent composition comprising 0.5 to 3 parts of cyanamino ethyl palmitate, 5 to 10 parts of an alkali-metal salt of the sulfosuccinic acid ester of an aliphatic alcohol having 6 to 10 carbon atoms and 10 to 50 parts of an alkali-metal salt of pyrophosphoric acid, the parts being by weight.

10. A detergent composition comprising by weight

	Parts
Cyanamino ethyl laurate	1
Sodium dioctyl sulfosuccinate	8
Tetrasodium pyrophosphate	30
Sodium sulfate	61

11. A detergent composition comprising 5 to 10 parts by weight of a sulfosuccinic di-ester of an aliphatic alcohol having 6 to 10 carbon atoms together with 0.5 to 3 parts by weight of the condensation product of an aliphatic monocarboxylic acid having 10 to 18 carbon atoms with a monoalkylol cyanamide.

12. A detergent composition comprising 5 to 10 parts by weight of a sulfosuccinic di-ester of an aliphatic alcohol having 6 to 10 carbon atoms together with 0.5 to 3 parts by weight of the condensation product of an aliphatic monocarboxylic acid having 10 to 18 carbon atoms with monoethylol cyanamide.

13. A detergent composition comprising 5 to 10 parts by weight of dioctyl sulfosuccinate together with 0.5 to 3 parts by weight of the condensation product of an aliphatic monocarboxylic acid having 10 to 18 carbon atoms with a monoalkylol cyanamide.

14. A detergent composition comprising 5 to 10 parts by weight of a dioctyl sulfosuccinate together with 0.5 to 3 parts by weight of the condensation product of an aliphatic monocarboxylic acid having 10 to 18 carbon atoms with monoethylol cyanamide.

15. A detergent composition comprising 5 to 10 parts by weight of a mixture of sodium di-n-octyl sulfosuccinate and sodium di-(2-ethylhexyl) sulfosuccinate and 0.5 to 3 parts by weight of the condensation product of an aliphatic monocarboxylic acid having 10 to 18 carbon atoms with monoethylol cyanamide.

16. A detergent composition comprising 5 to 10 parts by weight of sodium dioctyl sulfosuccinate, 10 to 50 parts by weight of tetrasodium pyrophosphate and 0.5 to 3 parts by weight of the condensation product of lauric acid with a monoalkylol cyanamide.

17. A detergent composition comprising 5 to 10 parts by weight of sodium dioctyl sulfosuccinate, 10 to 50 parts by weight of tetrasodium pyrophosphate and 0.5 to 3 parts by weight of the condensation product of lauric acid with monoethylol cyanamide.

COLEMAN R. CARYL.