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HEAVY DUTY DETERGENT COMPOSITION CONTAINING A QUATERNARY AMMONIUM SALT

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This invention has to do with detergent compositions and to processes for forming the same. More specifically, the invention relates to detergents of controlled foam or sudsing capability and to a process by which such detergents can be prepared.

The development of a universally acceptable heavy duty laundry composition satisfactory for use in any washing machine has been complicated by the housewife's acceptance of laundering machines having different mechanical characteristics. At present, mechanical characteristics determine to a large extent the nature of a detergent product that may satisfactorily be used in a particular machine. For example, highly effective heavy duty detergent products containing anionic detergents may be satisfactorily used in top-loading machines in which agitation of the wash solution is provided by a reciprocating agitator or a pulsating agitator mounted in a vertical position. Such products produce a high stable foam which persists throughout the laundering cycle. However, this same high stable foam tends to interfere with use of such products at concentration levels consistent with satisfactory detergency in front-loading washing machines in which agitation is provided by a horizontally mounted rotating drum having internal ridges thereon. It has been found that high foam levels in the latter type machines adversely affect detergency action by impeding agitation of the soiled laundry such that the laundered articles still exhibit high residual soil levels. This foam also increases mechanical wear which, in turn, leads to higher maintenance costs. Further, excessive foam levels often cause a front-loading machine to "foam over," resulting in puddles of detergent solution in the floor area around the machine which must be mopped up by the housewife or laundry operator. Thus, this type of machine has created a need for controlled sudsing detergents.

Not only is there a need for controlling the quantity of suds formed in automatic or semi-automatic washing equipment, but there is a need to provide for rapid collapse of the suds or foam preparatory to rinsing of the materials being laundered therein. Rapid foam collapse at this stage of the washing operation is advantageous to facilitate rinsing of the materials, and to prevent or reduce entrapment or inclusion of solids from the foam in the materials. Such entrapped or occluded solids can cause yellowing and objectionable stiffness in the laundered materials.

In attempting to solve the problem of excessive foam levels, detergent compositions containing nonionic synthetic detergents have been developed. Such compositions are based on alkylene oxide condensation products and these condensates generally possess cleansing ability with a minimum of suds. However, indications are that in the laundering of normally soiled clothes such compositions are not equal in cleansing action to the high sudsing anionic detergents.

It is also known in the art that certain cationic agents are useful in detergent compositions, particularly to

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render textiles soft. However, such cationic agents generally react with anionic detergents to form precipitates which are deposited upon articles being washed, thereby giving the washed articles an undesirable appearance. This reaction or interaction has effectively depleted the concentration of an anionic detergent in a washing bath to the detriment of detergency action and, therefore, should be avoided.

Additionally, it has been known that certain quaternary ammonium compounds, among the class of cationic agents, are generally unstable when heated and when in contact with alkaline builders. This instability has been characterized by development of strong amine odors and undesirable color.

Despite difficulties hitherto encountered in the preparation and use of detergent compositions containing anionic and cationic agents, I have found that outstanding compositions substantially free from such difficulties can be formed readily by control of certain salient relationships.

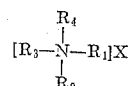
It is an object of the present invention, therefore, to provide detergent compositions of controlled sudsing capability. Another object is to provide such a composition characterized by rapid suds or foam collapse. Still another object is to provide a controlled sudsing, rapid-suds, collapsing, heavy-duty detergent composition. A further object is to provide a composition of the last-mentioned character suitable for use in laundering machines of diverse types. Still another object is to provide a process for forming the said compositions. Other objects of the invention will become apparent from the following description.

Broadly stated, according to the present invention, the foregoing objects are realized with compositions comprising:

- (a) A water-soluble, anionic, non-soap, organic detergent,
- (b) A water-soluble, higher fatty acid salt, and
- (c) A quaternary ammonium halide having one higher alkyl group.

Another embodiment of the invention serving to meet the foregoing objects comprises heavy-duty, detergent compositions containing (a), (b) and (c) and a water-soluble, builder salt, with or without other ingredients identified hereinafter.

One component of the compositions of this invention is a cationic material, namely, a quaternary ammonium compound having the general formula:



wherein R_1 is a higher alkyl group containing from about 10 to about 20 carbon atoms, R_2 and R_3 are lower alkyl groups each having from 1 to 3 carbon atoms, and R_4 is selected from the group consisting of lower alkyl groups having from 1 to 3 carbon atoms and aralkyl groups, and X is a halogen. Such compounds are characterized by some solubility in water. A wide variety of suitable cationic surface active agents can be employed herein, typical of which are:

Stearyl dimethyl benzyl ammonium chloride,
Cetyl trimethyl ammonium bromide,
Lauryl trimethyl ammonium chloride,
Lauryl dimethyl benzyl ammonium chloride,
Myristyl diethyl benzyl ammonium bromide,

Decyl trimethyl ammonium bromide,
 Arachidyl diethyl benzyl ammonium chloride,
 Oleyl triethyl ammonium chloride,
 n-Alkyl dimethyl ethylbenzyl ammonium chloride where-
 in the n-alkyl comprises a mixture of normal C₁₂ to
 C₁₈ groups, etc.

It is to be understood that mixtures of two or more of
 the cationic agents can be employed if desired.

Suitable quaternary ammonium compounds are avail-
 able as 95 percent active powders, 57 percent active
 aqueous pastes and in 25-50 percent aqueous alcoholic
 solutions. It is preferred to use the 95 percent active
 powder material, but choice of particular physical form
 is dependent upon storage and production facilities.

As indicated above, one component of compositions
 contemplated herein is a water-soluble, non-soap anionic,
 organic detergent. It is to be understood that one or
 several of such non-soap detergents can be used in com-
 positions of this invention. The said detergents may be
 designated as water-soluble salts of organic reaction prod-
 ucts having in their molecular structure an anionic solu-
 bilizing group such as SO₃H, SO₃Na, COOH and PO₃H
 and an alkyl or aralkyl radical having about 8 to 22 car-
 bon atoms in the alkyl group. Suitable detergents are
 anionic detergent salts having alkyl substituents of 8 to
 22 carbon atoms, such as: water-soluble sulfated and
 sulfonated anionic alkali metal and alkaline earth metal
 detergent salts containing a hydrophobic higher alkyl
 moiety, such as salts of higher alkyl-mono- or poly-
 nuclear aryl sulfonates having from about 8 to 18 carbon
 atoms in the alkyl group which may have a straight or
 branched structure, e.g. sodium dodecylbenzene sulfo-
 nate, magnesium tridecylbenzene sulfonate, lithium or
 potassium pentapropylene benzene sulfonate; alkali metal
 salts of sulfated condensation products of ethylene oxide
 (e.g., 3 to 20 and preferably 3-10 mols of ethylene oxide
 per mol of other compound) with aliphatic alcohols con-
 taining 8 to 18 carbon atoms, or with alkyl phenols hav-
 ing alkyl groups containing 6 to 18 carbon atoms, e.g.
 sodium nonyl phenol pentaethoxamer sulfate and sodium
 lauryl alcohol triethoxamer sulfate; alkali metal salts of
 sulfated alcohols containing from about 8 to 18 carbon
 atoms, e.g. sodium lauryl sulfate and sodium stearyl sul-
 fate; alkali metal salts of higher fatty acid esters of low
 molecular weight alkylol sulfonic acid, e.g. fatty acid
 esters of the sodium salt of isethionic acid; fatty etha-
 nolamide sulfates; fatty acid amides of amino alkyl sul-
 fonic acids, e.g. lauric acid amide of taurine; alkali metal
 salts of hydroxy alkane sulfonic acids having 8 to 18
 carbon atoms in the alkyl group, e.g. hexadecyl alpha-
 hydroxy sodium sulfonate. In general these organic sur-
 face active agents are employed in the form of their
 alkali metal salts or alkaline earth metal salts because
 such salts possess the requisite stability, water solubility,
 and low cost essential to practical utility.

Suitable water-soluble, higher fatty acid salts which
 are used in conjunction with the foregoing anionic deter-
 gents include alkali metal salts of saturated, unsaturated,
 or mixtures of unsaturated and saturated, fatty acids con-
 taining from about 8 to about 18 carbon atoms in the
 molecule such as: sodium caprate, sodium laurate,
 sodium myristate, sodium palmitate, potassium oleate,
 sodium stearate, sodium and potassium salts of tallow
 fatty acids, sodium and potassium salts of coconut oil
 fatty acids, and the like.

Generally, a water-soluble higher fatty acid salt will
 be added to compositions of the invention as a salt. How-
 ever, a water-soluble higher fatty acid salt can also be
 formed in situ by adding stoichiometric amounts of the
 desired fatty acid and the desired alkaline hydroxide
 directly to a composition; or, alternatively, by adding a
 desired fatty acid or fatty acid mixture directly to a
 heavy-duty detergent composition where the normal alka-
 linity desirable in such compositions is sufficient to form
 the water-soluble, higher fatty acid salt.

Another component of heavy-duty, detergent composi-
 tions of this invention is a water-soluble builder salt. The
 salt can be inorganic or organic, illustrative of which are:

- Trisodium phosphate,
- 5 Tetrasodium pyrophosphate,
- Sodium acid pyrophosphate,
- Sodium tripolyphosphate,
- Sodium monobasic phosphate,
- Sodium dibasic phosphate,
- 10 Sodium hexametaphosphate,
- Sodium metasilicate,
- Sodium silicates, Na₂O/SiO₂ of 1.6/1 to 3.2/1,
- Sodium carbonate,
- Sodium sulfate,
- 15 Borax,
- Nitriloacetic acid trisodium salt,
- Ethylene diamine tetraacetic acid tetrasodium salts, etc.

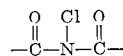
Mixtures of two or more inorganic or organic salts can
 be used, as can mixtures of inorganic and organic salts.

Particularly preferred herein are water-soluble, alkali
 alkali metal polyphosphate builder salts. These salts form
 water-soluble complexes with calcium and magnesium
 ions found in hard water and thereby prevent the forma-
 25 tion of insoluble salts which tend to deposit upon textiles
 during a washing cycle. Further, such phosphates enhance
 the deterative efficiency of anionic detergents, aid in con-
 trolling sudsing powers and aid in keeping soil suspended
 in the washing bath after its removal from the soiled tex-
 30 tiles.

Various other materials may be included in composi-
 tions of the invention, whether in solid or liquid form,
 by addition in a known manner to the aqueous mixtures
 or to the solidified product. Examples thereof are the
 35 higher fatty acid amides such as coconut or lauric mono-
 ethanolamide, isopropanolamide and the like; hydro-
 tropic solubilizing agents such as xylene or toluene sul-
 fonates; organic solubilizing agents such as ethanol,
 ethylene glycol and hexylene glycol; sodium carboxy-
 40 methylcellulose and polyvinyl alcohol antiredeposition
 agents; optical and fluorescent brightener materials;
 coloring agents; corrosion inhibiting agents; germicides;
 perfumes; bluing agents; and the like.

Preferred compositions advantageously contain a
 45 hydrophobic colloidal cellulosic soil-suspending agent
 which is soluble or dispersible in water also. The joint
 use of the combination of the cellulosic compound and
 polyvinyl alcohol is particularly effective for soil-suspen-
 sion properties during the washing of a variety of fabrics,
 including both cotton and synthetic fibers such as nylon,
 50 Dacon and resin-treated cottons. The mixtures is used pref-
 erably in a total amount of 0.1 to 2 percent by weight
 of the solids. Preferred cellulosic compounds are the
 alkali metal salts of a carboxy lower alkyl cellulose hav-
 ing up to 3 carbons in the alkyl group, such as the
 55 sodium and potassium salt of carboxymethylcellulose.
 Suitable salts are sodium carboxyethylcellulose, the cel-
 lulose sulfates and lower alkyl and hydroxyalkylcellulose
 ethers such as methyl-, ethyl- and hydroxyethylcellulose.

Another ingredient which can be present in the heavy-
 duty detergent compositions of this invention is a dry
 bleach. Chlorine bleaches are typified by sodium hy-
 pochlorite (NaOCl·5H₂O), potassium dichloroisocyanu-
 65 rate, trichloroisocyanuric acid, etc. Oxygen bleaches are
 represented by sodium and potassium perborates, potas-
 sium monopersulfate, etc. Bleaches particularly suitable
 for use herein are those water-soluble, organic, dry, solid
 heterocyclic N-chloro imides or alkali metal salts thereof.
 Such cyclic amides have from 4 to about 6 members
 70 in the ring, and are characterized by the following
 structure:



75 in which the electron donating nitrogen is doubly activat-

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ed to a highly acidic state by virtue of its proximity to two electro-positive carbonyl groups. Such N-chloro imides are known to the prior art, usually being prepared by passing chlorine gas into an alkaline aqueous solution of the parent imide. Compounds suitable for use in the present compositions include the N-chloro derivatives of cyanuric acid (e.g. mono-, di- and trichloro-cyanuric acid) and hydantoin as well as N-chloro succinimide, N-chloro malonimide, N-chloro phthalimide and N-chloro naphthalimide. In general it is preferred to employ those imides containing a plurality of chlorine-containing nitrogen atoms, e.g. trichlorocyanuric acid, dichlorocyanuric acid, sodium and potassium dichloroisocyanurates, etc. Suitable N-chloro hydantoins include: 1,3-dichloro-5,5-dimethyl hydantoin; N-monochloro-C,C-dimethyl hydantoin; methylene - bis - (N-chloro-C,C-dimethyl hydantoin); 1,3-dichloro-5-methyl - 5 - isobutyl hydantoin; 1,3-dichloro-5-methyl-5-ethyl hydantoin; 1,3-dichloro-5,5-diisobutyl hydantoin; 1,3-dichloro-5-methyl-5-n-amyl hydantoin, and the like.

Such imide bleaches are compatible with anionic-detergent-containing compositions contemplated herein. They are effective at normal washing temperatures. Normally, the bleaching agents are employed in a proportion in the mixture such that about 20 to about 200 parts per million (p.p.m.) of available chlorine will be present in a washing bath. However, other proportions of the bleach can be used if desired.

Proportions of the components of the new compositions are properly related in order to achieve the desired objects. The proportion of the quaternary ammonium halide can vary from about 0.1 to about 5 percent by weight of total solids, preferably 0.3 to 3 percent. The proportion of the quaternary ammonium halide is affected particularly by the proportions of the non-soap, anionic detergent, fatty acid salt, builder (e.g., a phosphate), the nature of the said halide, and the ultimate foam level desired in the washing bath containing soiled textiles. Therefore, the amount of the said halide is suitably proportioned in each composition that the desired suds characteristics are attained. More particularly, the proportions of the non-soap, anionic detergent, the fatty acid salt and the said quaternary compound are related and cooperate to provide for control of foam volume; and proportions of the fatty acid salt and said quaternary compound are related and cooperate to provide for rapid suds collapse.

A non-soap, anionic detergent—or a plurality thereof—is used in an amount in excess of the amount of the quaternary ammonium compound. Generally, in the heavy-duty detergent compositions, the non-soap detergent will be used in amounts from about 5 to about 50, and preferably about 7.5 to about 40, percent by weight. The weight ratio of non-soap to fatty salt will vary from about 50/1 to about 1/1, preferably 6/1 to 2/1.

In general, for laundering compositions, the balance of a formulation is primarily a water-soluble, builder salt or salts. The latter is generally used in an amount ranging from about 5 to about 90 percent by weight, particularly the phosphate, and preferably from about 25 to about 60 percent. When a bleach is used, amounts ranging from about 2 to about 30, preferably from about 5 to about 20, percent by weight, are needed.

In the process of this invention, a fluid aqueous slurry comprising water and an anionic organic detergent with a fatty acid salt, is formed. The slurry flows or is pumped into a conventional soap crutcher or any other suitable mixing apparatus such as a ribbon blender. The anionic detergent should desirably be added to the crutcher prior to addition of the quaternary compound in order to avoid formation of any significant amount of insoluble, anionic-cationic complex. The other ingredients are then added in any suitable order and form. The cationic quaternary ammonium compound is added, usually as a fine white powder with stirring. The resulting slurry should be suffi-

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ciently fluid at the elevated temperatures to insure adequate mixing and formation of a uniform product, and is subjected to a heat treatment at an elevated temperature such as with the range of about 100° to about 200° F., and usually from about 130° to 155° F. The slurry is heated by external means or even by the exothermic heat of reaction of certain ingredients. For example, the addition of hydratable inorganic salts such as the anhydrous forms of sodium triphosphate and sodium pyrophosphate results in exothermic reactions as hydration occurs. It is desirable generally to add the polyphosphate and/or other builder salt or salts in the final stages of the crutching operation. A fatty acid salt can be added at any suitable stage of the crutching operation, preferably before addition of polyphosphate. Mixing time is sufficient to insure adequate mixing and will usually be at least a few minutes, e.g., 5 minutes. To facilitate density control of the desired products, effective agitation is maintained throughout the crutching operation. Such agitation provides a vortex such that a substantial amount of air is incorporated into the mixture present in the crutcher. Aerated mixtures have lower specific gravities and the resulting spray dried products have lower densities. The aqueous mixture prior to drying can be aged at the elevated temperature for a time sufficient to insure adequate solubilization or hydration of certain ingredients. Such aging period can be a number of hours, such as up to about 8 hours. In general, it is preferred to employ time intervals of less than three hours and preferably less than one hour. It is understood that excessively high temperatures or unduly long aging periods are to be avoided to prevent any possible decomposition and insure efficient processing.

The solids content of the aqueous slurry is usually within the range from about 20 percent to 90 percent of total solids. In the manufacture of heat-dried products involving vaporization of the water, the solids content is usually within the range of about 40 to 65 percent by weight, the remainder being substantially free water content. The slurry is usually maintained at a temperature from about 160° to 180° F. This slurry is subjected to known spray-drying operations utilizing temperatures above about 212° F. to produce the detergent composition in particulate form, generally in the form of hollow, thin-walled spherical particles. The detergent composition can be transformed into beads, granules, flakes, chips, powders or the like as desired by use of conventional techniques.

In spray-drying the aqueous slurry, it is atomized or forced through spray nozzles into towers, with small liquid particles discharged from the nozzles becoming solidified and drying as they contact or fall through a stream or vortex of heated air or other inert gas which is at about 600° F. The composition is produced thereby in the form of hollow thin-walled spheres or beads having a small residual moisture content usually of about 3 to 15 percent by weight.

It has been found that, in the aqueous slurry present in the crutcher, the quaternary compound does not react with the non-soap, anionic detergent to form any insoluble precipitate to any significant extent. Even though there is considerable water present in the slurry present in the crutcher, thus allowing for interaction of the non-soap anionic detergent and the cationic quaternary compound, it has been found, surprisingly, that an insoluble precipitate is not formed in the crutcher. Furthermore, when the final product is dissolved in water, a substantially clear solution is obtained, thereby indicating the substantial absence of insoluble anionic-cationic complex or precipitate.

The present invention is more fully described and exemplified in the following examples. It is to be understood, however, that the invention is not to be limited to any specific form of materials or conditions set forth in the examples, but is limited solely by the description

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in the specification and the appended claims. All quantities are expressed in parts by weight unless otherwise indicated.

EXAMPLE 1

A heat-treated detergent composition in particulate form—Product 1—is prepared according to the following approximate formulation:

Components:	Percent by weight
Sodium tridecyl benzene sulfonate	12
Sodium tallow soap	3.2
Stearyl dimethyl benzyl ammonium chloride	0.8
Sodium tripolyphosphate	50
Sodium silicate ($1\text{Na}_2\text{O}:2.35\text{SiO}_2$)	3
Sodium carboxymethylcellulose	0.5
Polyvinyl alcohol	0.2
Water	8.5
Sodium sulfate	Balance

Product 1 is prepared by adding water to a crutcher followed by the addition of a 60 percent solids aqueous solution of the sulfonate detergent admixed with some sodium sulfate formed in its manufacture. The alkyl group of the detergent is derived from a mixture containing propylene tetramer and pentamer corresponding on the average to a tridecyl group. The sodium silicate solids in the form of an aqueous solution is added at a temperature of about 140° F. with stirring, followed by the addition of the remainder of sodium sulfate in powder form. The carboxymethylcellulose powder which is a commercial grade of about 67 percent purity and the polyvinyl alcohol having a viscosity of 2.34 centipoises and 22.3 percent polyvinyl acetate content are added with stirring at a temperature of about 140° F. to form a uniform slurry. Then, the stearyl dimethyl benzyl ammonium chloride in the form of a 95 percent active amber powder is added with stirring followed by the tripolyphosphate in powder form. The final ingredient added is the sodium tallow soap. The temperature of the crutcher slurry is maintained at 140–155° F. for one hour with agitation and there is formed a smooth, pumpable mixture having a total solids content of about 55–60 percent. It is then pumped into a spray tower where it is spray-dried with air heated to about 600° F. to yield a product in the forms of beads.

Samples of Product 1 were tested in a laboratory Tergotometer apparatus and in tumbler-type automatic washing machines. All testing was done in the presence of soil and Product 1 exhibited a low foam level and good detergency in all tests. Further, normal washing concentrations of 0.1–0.5 percent were completely soluble in 120° F. water and failed to exhibit cloudiness or a precipitate.

Elimination of the fatty acid salt from the composition of Example 1 yielded the same approximate foam volume in the Tergotometer test under the same conditions, but the foam volume was observed to be relatively stable and persistent under static conditions.

EXAMPLE 2

The following spray dried composition is prepared using the ingredients and procedure of Example 1 except as otherwise described:

Components:	Percent, by weight
Sodium tridecylbenzene sulfonate	22.6
Sodium tallow soap	6.6
Stearyl dimethyl benzyl ammonium chloride	1.5
Sodium tripolyphosphate	28.3
Sodium silicate	5.7
Sodium carboxymethyl cellulose	1.5
Polyvinyl alcohol	0.4
Water	2.0
Sodium sulfate	31.4

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The ingredients are mixed in the form of an aqueous slurry in a crutcher for 90 minutes at a temperature between 170° and 180° F. The resultant slurry of 50–60 percent solids is then pumped into a spray tower where it is spray-dried with air heated to about 550° F. to yield a product in the form of hollow beads. Samples of this product—Product 2—yielded clear solutions at 0.2 percent concentration in hot water.

EXAMPLE 3

Product 3 was prepared in spray-dried form as described in example.

Components:	Percent, by weight
Sodium tridecyl benzene sulfonate	6
Sodium tallow soap	1.5
Stearyl dimethyl benzyl ammonium chloride	0.4
Sodium tripolyphosphate	20
Sodium silicate	3
Water	8.5
Sodium sulfate	60.6

Product 3 is satisfactory for use in tumbler-type automatic washing machines, and produced a clear solution at a 0.15 percent concentration in water. The cellulose is a commercial detergent grade.

EXAMPLE 4

In the illustrations included in this example the effect of a water-soluble, higher fatty acid salt in the control of foaming, heavy duty anionic detergent compositions is demonstrated by practical laundering operations in agitator-type (the predominant type) and tumbler-type automatic washing machines. Results obtained demonstrate that the presence of a water-soluble, higher fatty acid salt in the detergent compositions does not have a significant effect on the suds level during the period the clothes are being agitated, but does have a significant effect on the rate at which the foam collapses when the agitation is stopped to empty the wash water prior to the initiation of the rinsing operation. Rapid foam collapse during this latter period is desirable to facilitate rinsing operations and to prevent entrapment or inclusion of solids from the foam in the textile fabrics whence it can cause yellowing and objectionable stiffness in the laundered textiles.

Foam behaviour was evaluated under dynamic and static conditions in the presence of terry cloth switches containing sebum soil. Testing was carried out using a Tergotometer apparatus. Testing procedure consisted of making up 300 cc. of detergent solution at a predetermined concentration level at 120° C., adding the solution to the Tergotometer along with three 1½ inch x 1 inch terry cloth swatches containing 40 mgs. of sebum soil each (120 mgs. total) and agitating the system for five minutes. Dynamic foam volume was measured at the end of the five minute agitation period and the static foam volume was determined at one minute intervals following the agitation period.

Dynamic foam volume in the presence of swatches containing 120 mgs. of sebum soil was found to be equivalent to the foam volume noted in the practical laundering of 8 pound loads of normally soiled textiles in automatic, tumbler-type washing machines; and with this correlation, it is possible to determine which detergent compositions can be classed as controlled foam products. Similarly, the rate of foam collapse noted under static conditions correlates closely with the observations noted under the foregoing practical laundering conditions following the agitation period in both types of washing machines.

The sebum soil was a mixture formed of:

	Percent, wt.
Palmitic acid	10
Stearic acid	5
Oleic acid	15

	Percent, wt.
Coconut oil -----	20
Olive oil -----	20
Squalene -----	5
Paraffin (M.P. 48° C.) -----	10
Spermaceti -----	15

As indicated, the inclusion of a water-soluble, higher fatty acid salt in the controlled suds, heavy-duty detergent compositions is an important consideration. The following three products, A, B and C, were evaluated in the foregoing laboratory test at 0.15 percent concentration of the detergent composition. Product A was formed by preparing an aqueous solution of the sulfonate, and adding thereto dry builders, polyphosphate and sulfate. Sufficient water was then added to the resulting solution to provide a composition of 100 parts by weight. Product B was prepared in much the same manner, except that an aqueous solution of the cationic agent was mixed with the aqueous sulfonate solution prior to addition of the builders. Product C was prepared in the same manner as Product B, except that an aqueous cocoate solution was mixed with the aqueous sulfonate and aqueous cationic agent solutions prior to addition of the builders.

Product A

	Parts
Sodium tridecylbenzene sulfonate -----	12
Sodium tripolyphosphate -----	40
Sodium sulfate -----	39.5

Product B

	Parts
Sodium tridecylbenzene sulfonate -----	12
Stearyl dimethyl benzyl ammonium chloride -----	0.8
Sodium tripolyphosphate -----	40
Sodium sulfate -----	38.7

Product C

	Parts
Sodium tridecylbenzene sulfonate -----	12
Stearyl dimethyl benzyl ammonium chloride -----	0.8
Sodium cocoate -----	3.5
Sodium tripolyphosphate -----	40
Sodium sulfate -----	35.2

The term "cocoate" refers to salts of fatty acid groups found in coconut oil fatty acids. Such acids contain from about 8 to about 18 carbon atoms per molecule, predominating in C₁₂-C₁₄ acids.

The sudsing characteristics of the three products were observed during the testing cycle and results so obtained are recorded in Table I following.

TABLE I

Composition	Dynamic Foam Volume (inches)	Change in Residual Static Foam Volume With Time (Percent of Dynamic Foam Volume)					
		1'	2'	3'	5'	7'	10'
A.-----	1¼	100	100	90	70	50	30
B.-----	1	88	75	75	63	50	38
C.-----	1½	78	56	44	22	0	

The above data show that the water-soluble fatty acid salt cooperates with the other ingredients to provide the desired rapid foam collapse required for good rinsing characteristics in compositions of the invention. However, initial foam volume values indicate that the same compositions are not satisfactory for use in automatic, tumbler-type washing machines because other experimental work indicates that satisfactory foam volumes in these machines correspond to dynamic foam values of ½-1½ inch in the laboratory test.

Thus, it is to be noted that suitable adjustments in the proportion of the cationic quaternary ammonium salt together with proportions of the non-soap anionic deter-

gent and fatty acid salt, are made to achieve satisfactory dynamic foam values equivalent to controlled foam products suitable for use in tumbler-type, automatic washing machines. The effect of this relationship is demonstrated by evaluating Products D, E and F in the Tergotometer test. Test conditions were: 120° F. washing temperature; 120 mgs. sebum soil introduced on 1½ inch x 1 inch terry cloth swatches each of three swatches containing 40 mgs. of sebum soil; 0.15% detergent composition concentration. Products D through F were prepared in a manner similar to the procedures described above for Products B and C.

Product D

	Parts
Sodium tridecylbenzene sulfonate -----	12
Sodium salt of mixed fatty acids (85% tallow-15% coconut) -----	3
Sodium tripolyphosphate -----	50
Sodium sulfate -----	26.5

Product E

	Parts
Sodium tridecylbenzene sulfonate -----	12
Sodium salt of mixed fatty acids (85% tallow-15% coconut) -----	3
Stearyl dimethyl benzyl ammonium chloride -----	1
Sodium tripolyphosphate -----	50
Sodium sulfate -----	25.5

Product F

	Parts
Sodium tridecylbenzene sulfonate -----	12
Sodium salt of mixed fatty acids (85%-15% coconut) -----	3
Stearyl dimethylbenzene ammonium chloride -----	2
Sodium tripolyphosphate -----	50
Sodium sulfate -----	24.5

The dynamic foam volumes of the three products were observed in the foregoing test and the results are recorded in Table II, below.

TABLE II

Composition	Cationic Quaternary Ammonium Compound (parts)	Dynamic Foam Volume (inches)
D.-----	0	1½
E.-----	1	¾
F.-----	2	1/16

The foregoing results clearly indicate that the desired dynamic foam volume corresponding to a satisfactory foam level in the automatic, tumbler-type washing machines is achieved with from about 1 to about 2 parts (or percent) of quaternary ammonium compound.

To recapitulate, Table I demonstrates that water-soluble, fatty acid salt cooperates with the quaternary compound to provide rapid foam collapse consistent with satisfactory rinsing characteristics; and Table II illustrates that the proportion of quaternary ammonium compound is suitably adjusted with the proportions of the non-soap anionic detergent and the fatty acid salt, to achieve the desired foam volume commensurate with satisfactory performance in the automatic, tumbler-type washing machines.

EXAMPLE 5

Another effective composition, prepared by the dry blending procedure mentioned in EXAMPLE 4 above, is identified below:

Components:	Percent, weight
Sodium tridecylbenzene sulfonate -----	12
Sodium salt of mixed fatty acids (85% tallow/15% coconut) -----	3
Stearyl dimethylbenzyl ammonium chloride-----	1
Sodium tripolyphosphate -----	38
Sodium sulfate -----	37.5

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The resulting product—Product 5—was dissolved in water and the resultant solution was used to wash naturally soiled textiles in an automatic, Westinghouse tumbler-type washing machine under normal laundering conditions. The foam volume during the washing cycle was approximately four inches and foam collapse was very rapid during the period in which the used wash solution was being removed from the machine. The appearance of the laundered textiles indicated the composition possessed excellent heavy duty detergency properties.

This same composition was observed to produce $\frac{3}{8}$ inch of dynamic foam at 0.15% product concentration in the presence of 120 mgs. of sebum soil in the Tergotometer test. Rapid foam collapse was also observed under static conditions following the foregoing agitation period indicating good rinsing characteristics.

EXAMPLE 6

Another effective composition, prepared by dry blending as in Example 4 above, is as follows:

Components:	Percent by weight
Sodium tridecyl benzene sulfonate	12
Sodium tallow soap	3
Stearyl dimethyl benzyl ammonium chloride	3
Sodium tripolyphosphate	50
Sodium carboxymethyl cellulose	0.5
Sodium sulfate	23
Water	8.5

EXAMPLE 7

Components:	Parts
Sodium tridecylbenzene sulfonate	6
Sodium salt of mixed fatty acids (85% tallow/15% coconut)	2
Stearyl dimethylbenzyl ammonium chloride	0.6
Sodium tripolyphosphate	20
Sodium silicate (ratio of $\text{Na}_2\text{O}/\text{SiO}_2=1:2.35$)	3
Sodium sulfate	59.9

The product of this example—Product 7—was prepared by the spray drying technique described in Example 1, above. It was evaluated at 0.3% concentration in the Tergotometer test in the presence of 120 mgs. of sebum soil and yielded $\frac{9}{16}$ inch of foam volume under agitated conditions and rapid foam collapse in the absence of agitation. Satisfactory foam characteristics were observed when this product was used in the automatic, Westinghouse tumbler-type washing machine.

EXAMPLES 8-11

Other compositions serving to illustrate the invention are given below:

Components	Parts			
	8	9	10	11
Sodium alpha-hydroxy hexadecyl sulfonate	12			
Sodium lauryl alcohol sulfate		12	12	
Sodium sulfate of tetraethoxylated nonyl phenol				15
Sodium tallow-coco (85/15) soap	2	3.2		3.5
High titer soda tallow soap			3	
Stearyl dimethyl benzyl ammonium chloride	0.8	1.2		1
Mixed C_{12} — C_{18} alkyl dimethyl benzyl ammonium chloride			0.8	
Sodium silicate solids	3	3		3
Sodium tripolyphosphate	45	40	50	40
Sodium sulfate	22.2	25.6	5.2	22.5
Sodium carboxymethyl cellulose			0.5	
Water	5	5	8.5	5

EXAMPLE 12

A particularly outstanding composition containing a bleach is that shown below. The composition was formed in accordance with the spray drying technique described above.

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Components:	Parts
Sodium tridecyl benzene sulfonate	12
High titer soda tallow soap	3.2
Stearyl dimethyl benzyl ammonium chloride	0.8
Sodium tripolyphosphate	50
Sodium silicate solids	3
Sodium sulfate	16.9
Sodium carboxymethyl cellulose	0.5
Polyvinyl alcohol	0.2
Brighteners, perfume, etc.	0.4
Potassium dichloroisocyanurate	10
Water	3

Performance of the compositions of this invention is excellent. Advantages realized therewith include: soft, fluffy towels, diapers, etc.; smooth, silky sheets, pillow cases, etc.; easy-to-iron shirts, sheets, etc.; reduced cling on nylon and other synthetics; long garment life; less wrinkling.

The new compositions can be used to launder a variety of fabrics, which can be made from natural animal fibers, natural vegetable fibers, mineral fibers and synthetic fibers. These include wool, silk, cotton, linen, glass, acetate, rayon, nylon, Orlon, Dacron, and others. The fabrics can be those classified as outer garments, under garments, diapers, etc.

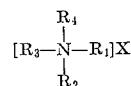
The new compositions can be packaged in paper, plastic or any other suitable packaging medium.

It is to be understood, in keeping with the illustrations given above, that the additive compositions, etc. of this invention can be in solid form in the character of free-flowing powders, granules, tablets, etc. By the term "solids" used herein, it is intended to include sizes and shapes of material having at least one dimension of relatively low order, such as grains, chips, flakes and other forms having proportionally large surface areas, and in any other suitable form.

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 may be made by those skilled in the art within the principle and scope of the invention as expressed in the appended claims.

I claim:

1. A controlled sudsing, rapid-suds-collapsing, heavy-duty detergent composition consisting essentially of: (a) from about 7.5 to 40% by weight of a water-soluble, anionic, non-soap, organic detergent salt selected from the group consisting of sulfated and sulfonated salts having an alkyl group of about 8 to 22 carbon atoms in their molecular structure; (b) a water-soluble, higher fatty acid salt selected from the group consisting of sodium and potassium salts of fatty acids containing from about 8 to about 18 carbon atoms in the molecule, the weight ratio of said non-soap organic detergent to said fatty acid salt being in the range of about 6/1 to about 2/1; (c) from about 0.3 to about 3% by weight of a quaternary ammonium salt having the formula



wherein R_1 is an alkyl group of about 10 to 20 carbon atoms, R_2 and R_3 are alkyl groups of 1 to 3 carbon atoms each, R_4 is selected from the group consisting of alkyl groups of 1 to 3 carbon atoms and benzyl groups and X is a halogen selected from the group consisting of chlorine and bromine; and (d) from about 5 to about 90% by weight of a water-soluble, inorganic, builder salt selected from the group consisting of phosphates, silicates, carbonates, sulfates, borates and mixtures thereof.

2. A composition defined by claim 1 wherein said detergent (a) is a water-soluble alkali metal higher alkyl benzene sulfonate salt having about 8 to 18 carbon atoms in the alkyl group.

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3. A composition defined by claim 1 wherein said detergent (a) is sodium tridecyl benzene sulfonate.

4. A composition defined by claim 1 wherein said salt (b) is a water-soluble salt of a fatty acid selected from the group consisting of sodium and potassium salts of fatty acids having from about 12 to about 18 carbon atoms per molecule.

5. A composition defined by claim 1 wherein said quaternary ammonium salt (c) is stearyl dimethyl benzyl ammonium chloride.

6. A composition defined by claim 1 containing a water-soluble, inorganic, alkali metal polyphosphate.

7. A detergent composition in accordance with claim 1 wherein the composition is in the form of spray-dried particles.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,325,414

June 13, 1967

Jack Thomas Inamorato

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 10, line 47, "116" should read -- 1/16 --.

Signed and sealed this 19th day of August 1969.

(SEAL)

Attest:

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Attesting Officer

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Commissioner of Patents