Title: PROCESSES FOR MAKING A GRANULAR DETERGENT COMPOSITION CONTAINING MID-CHAIN BRANCHED SURFACTANTS

Abstract

Processes for preparing high density detergent composition containing a mid-chain branched surfactant are provided. The processes involve spray drying, agglomerating, mixing, blending or a combination thereof and produce a granular and/or agglomerated detergent composition directly from mid-chain branched surfactants and other starting detergent ingredients. The mid-chain branched surfactants are mid-chain branched primary alkyl sulfate surfactants and mid-chain branched primary alkyl alkoxyxylated sulfate surfactants having an average of greater than 14.5 carbon atoms.
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PROCESSES FOR MAKING A GRANULAR DETERGENT COMPOSITION CONTAINING MID-CHAIN BRANCHED SURFACTANTS

FIELD OF THE INVENTION

The present invention generally relates to processes for producing a granular detergent composition. More particularly, the invention is directed to processes during which detergent granules or agglomerates are produced from starting detergent materials, one of which is a mid-chain branched surfactant. The mid-chain branched surfactants are mid-chain branched primary alkyl sulfate surfactants and mid-chain branched primary alkyl alkoxylated sulfate surfactants having an average of greater than 14.5 carbon atoms. The process produces a free flowing, granular detergent composition which can be commercially sold as a modern compact detergent product.

BACKGROUND OF THE INVENTION

Recently, there has been considerable interest within the detergent industry for laundry detergents which are "compact" and therefore, have low dosage volumes. To facilitate production of these so-called low dosage detergents, many attempts have been made to produce high bulk density detergents, for example with a density of 600 g/l or higher. The low dosage detergents are currently in high demand as they conserve resources and can be sold in small packages which are more convenient for consumers.

Generally, there are two primary types of processes by which detergent granules or powders can be prepared. The first type of process involves spray-drying an aqueous detergent slurry in a spray-drying tower to produce highly porous detergent granules. In the second type of process, the various detergent components are dry mixed after which they are agglomerated with a binder such as a nonionic or anionic surfactant. In both processes, the most important factors which govern the density of the resulting detergent granules are the density, porosity and surface area of the various starting materials and their respective chemical composition.

There has been interest in the art for providing processes which increase the density of detergent granules or powders. Particular attention has been given to densification of spray-dried granules by post tower treatment. For example, one attempt involves a batch process in which spray-dried or granulated detergent powders containing sodium tripolyphosphate and sodium sulfate are densified and spheronized in a Marumerizer®. This apparatus comprises a substantially horizontal, roughened, rotatable table positioned within and at the base of a substantially vertical, smooth walled cylinder. This process,
however, is essentially a batch process and is therefore less suitable for the large scale production of detergent powders. More recently, other processes have developed for increasing the density of "post-tower" or spray dried detergent granules. Typically, such processes require a first apparatus which pulverizes or grinds the granules and a second apparatus which increases the density of the pulverized granules by agglomeration. These processes achieve the desired increase in density by treating or densifying "post tower" or spray dried granules. The art is also replete with disclosures of processes which entail agglomerating detergent compositions. For example, attempts have been made to agglomerate detergent builders by mixing zeolite and/or layered silicates in a mixer to form free flowing agglomerates.

Furthermore, it has been long-established practice for detergent formulators to use surfactants and combinations thereof in detergent compositions. By way of example, various anionic surfactants, especially the alkyl benzene sulfonates, alkyl sulfates, alkyl alkoxy sulfates and various nonionic surfactants, such as alkyl ethoxylates and alkylphenol ethoxylates are commonly used in detergent formulations. Surfactants have found use as detergent components capable of the removal of a wide variety of soils and stains. A consistent effort, however, is made by detergent manufacturers to improve detergents properties of detergent compositions by providing new and improved surfactants. A problem commonly associated with anionic surfactants is their sensitivity to cold water and/or hard water. Improved cleaning performance above and beyond current standards, especially for granular detergent compositions to be used under colder wash water conditions and/or in hard water, has been difficult to attain. Therefore, it would be desirable to have a process for making a detergent composition which exhibits improved cleaning performance over a wide variety of soils and stains.

Accordingly, there remains a need in the art for a process which produces a granular and/or agglomerated detergent composition from starting detergent ingredients including a surfactant which exhibits improved cleaning performance over a wide variety of soils and stains. Also, there remains a need for such a process which is more efficient and economical to facilitate large-scale production of low dosage or compact detergents.

**BACKGROUND ART**

U.S. 3,480,556 to deWitt, et al., November 25, 1969, EP 439,316, published by Lever July 31, 1991, and EP 684,300, published by Lever November 29, 1995, describe beta-branched alkyl sulfates. EP 439,316 describes certain laundry detergents containing a specific commercial C14/C15 branched primary alkyl sulfate, namely LIAL 145 sulfate. This is believed to have 61% branching in the 2-position; 30% of this involves branching with a hydrocarbon chain having four or more carbon atoms. U.S. 3,480,556 describes mixtures of from 10 to 90 parts of a straight chain primary alkyl sulfate and from 90 to 10 parts of a beta branched (2-position branched) primary alcohol sulfate of formula:

\[ R^1 \text{CH}_2 \text{OSO}_3 \text{X} \]

wherein the total number of carbon atoms ranges from 12 to 20 and R1 is a straight chain alkyl radical containing 9 to 17 carbon atoms and R2 is a straight chain alkyl radical containing 1 to 9 carbon atoms (67% 2-methyl and 33% 2-ethyl branching is exemplified).


EP 342,917 A, Unilever, published Nov. 23, 1989 describes laundry detergents containing a surfactant system in which the major anionic surfactant is an alkyl sulfate having an assertedly "wide range" of alkyl chain lengths (the experimental appears to involve mixing coconut and tallow chain length surfactants).

U.S. Patent 4,102,823 and GB 1,399,966 describe other laundry compositions containing conventional alkyl sulfates.

G.B. Patent 1,299,966, Matheson et al., published July 2, 1975, discloses a detergent composition in which the surfactant system is comprised of a mixture of sodium tallow alkyl sulfate and nonionic surfactants.

Methyl-substituted sulfates include the known "isostearyl" sulfates; these are typically mixtures of isomeric sulfates having a total of 18 carbon atoms. For example, EP 401,462 A, assigned to Henkel, published December 12, 1990, describes certain isostearyl alcohols and ethoxylated isostearyl alcohols and their sulfation to produce the corresponding alkyl sulfates such as sodium isostearyl sulfate. See also K.R. Wormuth and S. Zushma, Langmuir, Vol. 7, (1991), pp 2048-2053 (technical studies on a number of branched alkyl sulfates, especially the "branched Guerbet" type); R. Varadaraj et al., J. Phys. Chem., Vol. 95, (1991), pp 1671-1676 (which describes the surface tensions of a
variety of "linear Guerbet" and "branched Guerbet"-class surfactants including alkyl sulfates); Varadaraj et al., J. Colloid and Interface Sci., Vol. 140, (1990), pp 31-34 (relating to foaming data for surfactants which include C12 and C13 alkyl sulfates containing 3 and 4 methyl branches, respectively); and Varadaraj et al., Langmuir, Vol. 6 (1990), pp 1376-1378 (which describes the micropolarity of aqueous micellar solutions of surfactants including branched alkyl sulfates).

"Linear Guerbet" alcohols are available from Henkel, e.g., EUTANOL G-16.

Primary alkyl sulfates derived from alcohols made by Oxo reaction on propylene or n-butylene oligomers are described in U.S. Patent 5,245,072 assigned to Mobil Corp. See also: U.S. Patent 5,284,989, assigned to Mobil Oil Corp. (a method for producing substantially linear hydrocarbons by oligomerizing a lower olefin at elevated temperatures with constrained intermediate pore siliceous acidic zeolite), and U.S. Patents 5,026,933 and 4,870,038, both to Mobil Oil Corp. (a process for producing substantially linear hydrocarbons by oligomerizing a lower olefin at elevated temperatures with siliceous acidic ZSM-23 zeolite).


SUMMARY OF THE INVENTION

The present invention meets the aforementioned needs in the art by providing a process which produces a granular and/or agglomerated detergent composition directly from mid-chain branched surfactants and other starting detergent ingredients. The processes include a variety of embodiments including spray drying, agglomerating, mixing, blending, and combinations thereof. The mid-chain branched surfactants are mid-chain branched primary alkyl sulfate surfactants and mid-chain branched primary alkyl alkoxoxygenated sulfate surfactants having an average of greater than 14.5 carbon atoms. The detergent compositions resulting from the processes of the invention exhibit improved cleaning performance over a wide variety of stains and/or soils, even under relatively high water hardness and low temperature wash water conditions.
As used herein, the term "agglomerates" refers to particles formed by build-up agglomeration of starting detergent ingredients (particles) which typically have a smaller median particle size than the formed agglomerates. All percentages and ratios used herein are expressed as percentages by weight (anhydrous basis) unless otherwise indicated. All documents are incorporated herein by reference. All viscosities referenced herein are measured at 70°C (±5°C) and at shear rates of about 10 to 100 sec⁻¹.

In accordance with one aspect of the invention, a process for preparing a crisp, free flowing, high density detergent composition is provided. The process comprises the steps of: A process for continuously preparing a high density detergent composition comprising the steps of: (A) continuously mixing a detergent surfactant paste and dry starting detergent material into a high speed mixer/densifier to obtain detergent agglomerates, wherein the ratio of the surfactant paste to the dry detergent material is from about 1:10 to about 10:1, the surfactant paste containing mid-chain branched surfactant compounds of the formula:

\[ A^b - X - B \]

wherein:

(a) \( A^b \) is a hydrophobic C9 to C22, total carbons in the moiety, preferably from about C12 to about C18, mid-chain branched alkyl moiety having: (1) a longest linear carbon chain attached to the - X - B moiety in the range of from 8 to 21 carbon atoms; (2) one or more \( C_1 - C_3 \) alkyl moieties branching from this longest linear carbon chain; (3) at least one of the branching alkyl moieties is attached directly to a carbon of the longest linear carbon chain at a position within the range of position 2 carbon, counting from carbon #1 which is attached to the - X - B moiety, to position 8 - 2 carbon, the terminal carbon minus 2 carbons; and (4) the surfactant composition has an average total number of carbon atoms in the \( A^b \)-X moiety in the above formula within the range of greater than 14.5 to about 18, preferably from about 15 to about 17; (b) \( B \) is a hydrophilic moiety selected from sulfates, sulfonates, amine oxides, polyoxyalkylene, alkoxyated sulfates, polyhydroxy moieties, phosphate esters, glycerol sulfonates, polygluconates, polyphosphate esters, phosphonates, sulfosuccinates, sulfosuccaminates, polyalkoxylated carboxylates, glucamides, taurinates, sarcosinates, glycinites, isethionates, dialkanolamides, monoalkanolamides, monoalkanolamide sulfates, diglycomides, diglycomide sulfates, glycerol esters, glycerol ester sulfates, glycerol ethers, glycerol ether sulfates, polyglycerol ethers, polyglycerol ether sulfates, sorbitan esters, polyalkoxylated sorbitan esters, ammonioalkanesulfonates, amidopropyl betaines, alkylated quats, alkylated/polyhydroxyalkylated quats, alkylated quats, alkylated/polyhydroxyolated oxypropyl quats, imidazolines, 2-yl-succinates, sulfonated alkyl esters, and sulfonated fatty acids; and (c) \( X \) is \(-\text{CH}_2\)-; (B) mixing the detergent agglomerates in a moderate speed
miller/densifier to densify further and agglomerate the detergent agglomerates; and (C) 
drying the detergent agglomerates so as to form the high density detergent composition. 
Another aspect of the invention involves similar steps, wherein step (A) entails 
continuously mixing an acid precursor of an anionic surfactant and dry starting detergent 
material containing an alkaline inorganic material capable of neutralizing the acid precursor 
into a high speed mixer/densifier to obtain detergent agglomerates. 
In another aspect of the invention, a process involving spray drying and 
agglomeration of detergent ingredients to provide a high density detergent composition is 
provided. More particularly, the process comprises the steps of: (A) spray drying an 
aqueous slurry containing a mid-chain branched surfactant and adjunct detergent 
ingredients to form spray dried granules, wherein the mid-chain branched surfactant has the 
formula, as described above; (B) continuously mixing a detergent surfactant paste and dry 
starting detergent material into a high speed mixer/densifier to obtain detergent 
agglomerates, wherein the ratio of the surfactant paste to the dry detergent material is from 
about 1:10 to about 10:1; (C) mixing the detergent agglomerates in a moderate speed 
mixer/densifier to densify further and agglomerate the detergent agglomerates; and (D) 
blending the granules and the detergent agglomerates together so as to form the high 
density detergent composition. 
Accordingly, it is an object of the present invention to provide a process for 
producing a granular and/or agglomerated detergent composition directly from starting 
detergent ingredients which includes a surfactant having improved cleaning performance. 
It is also an object of the invention to provide such a process which is not limited by 
unnecessary process parameters so that large-scale production of low dosage or compact 
detergents is more economical and efficient. These and other objects, features and 
attendant advantages of the present invention will become apparent to those skilled in the 
art from a reading of the following drawing, detailed description of the preferred 
embodiment and the appended claims. 

BRIEF DESCRIPTION OF THE DRAWING 
FIG. 1 is a flow chart illustrating a preferred process in which two agglomerating 
mixer/densifiers, fluid bed dryer, fluid bed cooler and screening apparatus are serially 
positioned in accordance with one process of the invention. 

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT 
The present process is used in the production of detergent compositions by way of 
agglomeration of starting detergent ingredients including a mid-chain branched surfactant 
or by way of spray drying techniques which can include further processing of the "post-
tower" detergent granules. By "post-tower" detergent granules, it is meant those detergent 
granules which have been processed through a conventional spray-
drying tower or similar apparatus.

**Agglomeration Process**

Reference is now made to Fig. 1 which presents a flow chart illustrating the agglomeration process and various embodiments thereof. In the first step of the process, the invention entails continuously mixing into a high speed mixer/densifier 10 several streams of starting detergent ingredients including a surfactant paste stream 12 which includes the mid-chain branched surfactant and a dry starting detergent material stream 14. Based on the finished agglomerate weight basis, the surfactant paste 12 preferably comprises water and from about 25% to about 75%, preferably from about 35% to about 65% and, most preferably from about 38% to about 55%, of the mid-chain branched surfactant or combinations of such a surfactant and adjunct surfactants, all of which is described in detail hereinafter. Preferably, the dry starting detergent material 14 comprises from about 10% to about 50%, preferably from about 15% to about 45% and, most preferably from about 20% to about 40% of an aluminosilicate or zeolite builder and from about 10% to about 40%, preferably from about 15% to about 30% and, most preferably from about 15% to about 25% of a sodium carbonate. It should be understood that additional starting detergent ingredients several of which are described hereinafter may be mixed into high speed mixer/densifier 10 without departing from the scope of the invention.

However, it has been found that the surfactant paste 12 and the dry starting detergent material 14 are continuously mixed within the ratio ranges described herein so as to ensure production of the desired free flowing, crisp, high density detergent composition. Preferably, the ratio of the surfactant paste 12 to the dry starting detergent material 14 is from about 1:10 to about 10:1, more preferably from about 1:4 to about 4:1 and, most preferably from about 2:1 to about 2:3.

Also, it has been found that the first processing step can be successfully completed, under the process parameters described herein, in a high speed mixer/densifier 10 which preferably is a Lödige CB mixer or similar brand mixer. These types of mixers essentially consist of a horizontal, hollow static cylinder having a centrally mounted rotating shaft around which several plough-shaped blades are attached. Preferably, the shaft rotates at a speed of from about 300 rpm to about 2500 rpm, more preferably from about 400 rpm to about 1600 rpm. Preferably, the mean residence time of the detergent ingredients in the high speed mixer/densifier 10 is preferably in range from about 2 seconds to about 45 seconds, and most preferably from about 5 seconds to about 15 seconds. The mean residence time can be conveniently and accurately measured by dividing the tear weight of the mixer/densifier by the throughput (e.g., kg/hr).

The resulting detergent agglomerates formed in the high speed mixer/densifier 10 are then fed into a lower or moderate speed mixer/densifier 16 during which further
agglomeration and densification is carried forth. This particular moderate speed mixer/densifier 16 used in the present process should include liquid distribution and agglomeration tools so that both techniques can be carried forth simultaneously. It is preferable to have the moderate speed mixer/densifier 16 to be, for example, a Lödige KM (Ploughshare) mixer, Drais® K-T 160 mixer or similar brand mixer. The main centrally rotating shaft speed is from about 30 to about 160 rpm, more preferably from about 50 to about 100 rpm. The mean residence time in the moderate speed mixer/densifier 16 is preferably from about 0.25 minutes to about 15 minutes, most preferably the residence time is about 0.5 to about 10 minutes. This mean residence time also can be conveniently and accurately measured by dividing the tear weight of the mixer/densifier at steady state by the throughput (e.g., kg/hr). The liquid distribution is accomplished by cutters, generally smaller in size than the rotating shaft, which preferably operate at about 3600 rpm.

In accordance with the present process, the high speed mixer/densifier 10 and moderate speed mixer/densifier 16 in combination preferably impart a requisite amount of energy to form the desired agglomerates. More particularly, the instant process imparts from about $5 \times 10^{10}$ erg/kg to about $2 \times 10^{12}$ erg/kg at a rate of from about $3 \times 10^8$ erg/kg-sec to about $3 \times 10^9$ erg/kg-sec to form free flowing high density detergent agglomerates. The energy input and rate of input can be determined by calculations from power readings to the moderate speed mixer/densifier with and without granules, residence time of the granules in the mixer/densifier, and the mass of the granules in the mixer/densifier. Such calculations are clearly within the scope of the skilled artisan.

The density of the resulting detergent agglomerates exiting the moderate speed mixer/densifier 16 is at least 600 g/l, more preferably from about 700 g/l to about 800 g/l. Thereafter, the detergent agglomerates are dried in a fluid bed dryer 18 or similar apparatus to obtain the high density granular detergent composition which is ready for packaging and sale as a low dosage, compact detergent product at this point. The particle porosity of the resulting detergent agglomerates of the composition is preferably in a range from about 5% to about 20%, more preferably at about 10%. As those skilled in the art will readily appreciate, a low porosity detergent agglomerate provides a dense or low dosage detergent product, to which the present process is primarily directed. In addition, an attribute of dense or densified detergent agglomerates is the relative particle size. The present process typically provides agglomerates having a median particle size of from about 400 microns to about 700 microns, and more preferably from about 475 microns to about 600 microns. As used herein, the phrase "median particle size" refers to individual agglomerates and not individual particles or detergent granules. The combination of the above-referenced porosity and particle size results in agglomerates having density values of 600 g/l and
higher. Such a feature is especially useful in the production of low dosage laundry detergents as well as other granular compositions such as dishwashing compositions.

Optional Process Steps

In an optional step of the present process, the detergent agglomerates exiting the fluid bed dryer 18 are further conditioned by cooling the agglomerates in a fluid bed cooler 20 or similar apparatus as are well known in the art. Another optional process step involves adding a coating agent to improve flowability and/or minimize over agglomeration of the detergent composition in one or more of the following locations of the instant process: (1) the coating agent can be added directly after the fluid bed cooler 20 as shown by coating agent stream 22 (preferred); (2) the coating agent may be added between the fluid bed dryer 18 and the fluid bed cooler 20 as shown by coating agent stream 24; (3) the coating agent may be added between the fluid bed dryer 18 and the moderate speed mixer/densifier 16 as shown by stream 26; and/or (4) the coating agent may be added directly to the moderate speed mixer/densifier 16 and the fluid bed dryer 18 as shown by stream 28. It should be understood that the coating agent can be added in any one or a combination of streams 22, 24, 26, and 28 as shown in Fig. 1. The coating agent stream 22 is the most preferred in the instant process. See Capeci et al, U.S. Patent 5,516,448, issued May 14, 1996 and Capeci et al, U.S. Patent 5,489,392, issued February 6, 1996.

The coating agent is preferably selected from the group consisting of aluminosilicates, silicates, carbonates and mixtures thereof. The coating agent can also be the improved builder material described in more detail hereinafter. However, the coating agent may be one or more combinations of the builder material, aluminosilicates, carbonates, silicates and the like. The coating agent not only enhances the free flowability of the resulting detergent composition which is desirable by consumers in that it permits easy scooping of detergent during use, but also serves to control agglomeration by preventing or minimizing over agglomeration, especially when added directly to the moderate speed mixer/densifier 16. As those skilled in the art are well aware, over agglomeration can lead to very undesirable flow properties and aesthetics of the final detergent product.

Optionally, the process comprises the step of spraying an additional binder in one or both of the mixer/densifiers 10 and 16. A binder is added for purposes of enhancing agglomeration by providing a "binding" or "sticking" agent for the detergent components. The binder is preferably selected from the group consisting of water, anionic surfactants, nonionic surfactants, polyethylene glycol, polyvinyl pyrrolidone polyacrylates, citric acid and mixtures thereof. Other suitable binder materials including those listed herein are described in Beerse et al, U.S. Patent No. 5,108,646 (Procter & Gamble Co.), the disclosure of which is incorporated herein by reference.
Other optional steps contemplated by the present process include screening the oversized detergent agglomerates in a screening apparatus 30 which can take a variety of forms including but not limited to conventional screens chosen for the desired particle size of the finished detergent product. Other optional steps include conditioning of the detergent agglomerates by subjecting the agglomerates to additional drying.

Another optional step of the instant process entails finishing the resulting detergent agglomerates by a variety of processes including spraying and/or admixing other conventional detergent ingredients, collectively referenced as the finishing step 32 in Fig. 1. For example, the finishing step encompasses spraying perfumes, brighteners and enzymes onto the finished agglomerates to provide a more complete detergent composition. Such techniques and ingredients are well known in the art.

Preferably, the resulting detergent agglomerates produced by the process embodiments described herein contain from about 20% to about 50% by weight of the mid-chain branched surfactant, from about 10% to about 65% of a detergent builder such as aluminosilicate, and optionally, up to about 40% by weight of sodium carbonate. The surfactant, builder, and carbonate levels can vary beyond those given here as described previously and hereinafter.

**Spray Drying Process**

One or more spray drying techniques can be used alone, or in combination with the aforementioned agglomeration processes, to make detergent compositions containing the mid-chain branched surfactants in accordance with the instant invention. One or more spray-drying towers may be employed to manufacture granular laundry detergents which often have a density of about 500 g/l or less. In this procedure, an aqueous slurry of various heat-stable ingredients in the final detergent composition are formed into homogeneous granules by passage through a spray-drying tower, using conventional techniques, at temperatures of about 175°C to about 225°C. If spray drying is used as part of the overall process herein, additional process steps as described herein can be optionally used to obtain the level of density (i.e., > 650 g/l) required by modern compact, low dosage detergent products.

For example, spray-dried granules from a tower can be densified further by loading a liquid such as water or a nonionic surfactant into the pores of the granules and/or subjecting them to one or more high speed mixer/densifiers. A suitable high speed mixer/densifier for this process is the aforementioned "Lödige CB 30" or "Lödige CB 30 Recycler" which comprises a static cylindrical mixing drum having a central rotating shaft with mixing/cutting blades mounted thereon. In use, the ingredients for the detergent composition are introduced into the drum and the shaft/blade assembly is rotated at speeds in the range of 100-2500 rpm to provide thorough mixing/densification. See Jacobs et al,
U.S. Patent 5,149,455, issued September 22, 1992. Other such apparatus includes the devices marketed under the trade name "Shugi Granulator" and under the tradename "Drais K-TTP 80).

Another process step which can be used to densify further spray-dried granules involves grinding and agglomerating or deforming the spray-dried granules in a moderate speed mixer/densifier so as to obtain particles having lower porosity. Equipment such as the aforementioned "Lödige KM" (Series 300 or 600) or "Lödige Ploughshare" mixer/densifiers are suitable for this process step. Other useful equipment includes the device which is available under the tradename "Drais K-T 160". This process step which employs a moderate speed mixer/densifier (e.g. Lödige KM) can be used by itself or sequentially with the aforementioned high speed mixer/densifier (e.g. Lödige CB) to achieve the desired density. Other types of granules manufacturing apparatus useful herein include the apparatus disclosed in U.S. Patent 2,306,898, to G. L. Heller, December 29, 1942.

While it may be more suitable to use the high speed mixer/densifier followed by the low speed mixer/densifier, the reverse sequential mixer/densifier configuration is also contemplated by the invention. One or a combination of various parameters including residence times in the mixer/densifiers, operating temperatures of the equipment, temperature and/or composition of the granules, the use of adjunct ingredients such as liquid binders and flow aids, can be used to optimize densification of the spray-dried granules in the process of the invention. By way of example, see the processes in Appel et al, U.S. Patent 5,133,924, issued July 28, 1992 (spray-dried granules are brought into a deformable state prior to densification); Delwel et al, U.S. Patent 4,637,891, issued January 20, 1987 (granulating spray-dried granules with a liquid binder and aluminosilicate); Kruse et al, U.S. Patent 4,726,908, issued February 23, 1988 (granulating spray-dried granules with a liquid binder and aluminosilicate); and, Bortolotti et al, U.S. Patent 5,160,657, issued November 3, 1992 (coating densified spray-dried granules with a liquid binder and aluminosilicate).

**Admixing Process**

Specifically, other aspects of the process invention include admixing the builder material with spray dried granules, agglomerates or combinations thereof. This admixing step may be enhanced by combining the granules, agglomerates, or combinations thereof with the builder material and a liquid binder as described previously in a mixing drum or other similar device. Optionally, the builder material may be coated with a nonionic surfactant or other liquid binder as described previously before the admixing step so as to preclude any deleterious interaction with the other detergent ingredients (e.g. anionic surfactants) prior to immersion in the washing solution (i.e. during processing and storage).
This liquid binder (e.g. nonionic surfactant) coating also improves the flow properties of
the detergent composition in which the builder material is included.

Other Processes

In yet another process embodiment, the high density detergent composition can be
produced by feeding a liquid acid precursor of an anionic surfactant, such as the mid-chain
branched surfactant described herein, an alkaline inorganic material (e.g. sodium carbonate)
and optionally other detergent ingredients into a high speed mixer/densifier (residence time
5-30 seconds) so as to form agglomerates containing a partially or totally neutralized
anionic surfactant salt and the other starting detergent ingredients. Subsequently, the
contents in the high speed mixer/densifier can be sent to a moderate speed mixer/densifier
(e.g. Lödige KM) for further agglomeration resulting in the finished high density detergent
composition. In another process embodiment, the surfactant paste is premixed or extruded
in a mixing or extruding apparatus such as a twin-screw extruder (e.g., Werner and
Pfleiderer, Continua Series) to structure the paste for easier agglomeration. Additionally,
structuring agents such as polymers, sodium hydroxide, sodium chloride, postassium
hydroxide silicates and the like can be used to render the paste more suitable for loading
higher amounts of surfactant. See Aouad et al, U.S. Patent 5,451,354, issued September 19,
1995.

Optionally, high density detergent compositions can be produced by blending
conventional or densified spray-dried detergent granules with detergent agglomerates in
various proportions (e.g. a 60:40 weight ratio of granules to agglomerates) produced by one
or a combination of the processes discussed herein. Additional adjunct ingredients such as
enzymes, perfumes, brighteners and the like can be sprayed or admixed with the
agglomerates, granules or mixtures thereof produced by the processes discussed herein.

Another process of the invention involves cooling a molten surfactant paste
containing the mid-chain branched surfactant and forming flakes on a chill roll, after which
the flakes are ground to the desired particle size. The cooled flakes can be dried further
using a rotary drum dryer.

Surfactant Paste

The viscoelastic surfactant paste used herein has viscoelastic fluid properties which can
be described by a commonly used mathematical model that accounts for the shear thinning nature
of the paste. The mathematical model is called the Power Law Model and is described by the
following relation:

$$\sigma = K\gamma^n$$

where $\sigma$ = Shear Stress (dyne/cm$^2$), $K$ = Consistency (Poise·sec$^{n-1}$), $\gamma$ = Shear Rate (sec$^{-1}$), and $n$
= Rate Index (dimensionless). The rate index $n$ varies from 0 to 1. The closer $n$ is to 0, the more
shear thinning the fluid. The closer \( n \) is to 1, the closer it is to simple Newtonian behavior, i.e. constant viscosity behavior. \( K \) can be interpreted as the apparent viscosity at a shear rate of 1 sec\(^{-1}\).

In this context, the viscoelastic surfactant paste used in the process has a consistency \( K \) at 70°C of from about 50,000 to about 450,000 cPoise•sec\(^{n-1}\) (500 to 2,500 Poise•sec\(^{n-1}\)), more preferably from about 100,000 to about 195,000 cPoise•sec\(^{n-1}\) (1,000 to 1,950 Poise•sec\(^{n-1}\)), and most preferably from about 120,000 to about 180,000 cPoise•sec\(^{n-1}\) (1,200 to 1,800 Poise•sec\(^{n-1}\)). Preferably, the surfactant paste has a shear index \( n \) of from about 0.05 to about 0.25, more preferably from about 0.08 to about 0.20 and most preferably from about 0.10 to about 0.15.

The surfactant paste includes surfactant mixtures comprising mid-chain branched surfactant compounds as described herein before. In such compositions, certain points of branching (e.g., the location along the chain of the \( R, R^1 \), and/or \( R^2 \) moieties in the above formula) are preferred over other points of branching along the backbone of the surfactant. The formula below illustrates the mid-chain branching range (i.e., where points of branching occur), preferred mid-chain branching range, and more preferred mid-chain branching range for mono-methyl branched alkyl A\(^b\) moieties useful according to the present invention.

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot
\]

more preferred range

preferred range

mid-chain branching range

It should be noted that for the mono-methyl substituted surfactants these ranges exclude the two terminal carbon atoms of the chain and the carbon atom immediately adjacent to the -X - B group.

The formula below illustrates the mid-chain branching range, preferred mid-chain branching range, and more preferred mid-chain branching range for di-methyl substituted alkyl A\(^b\) moieties useful according to the present invention.

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot
\]

more preferred range

preferred range

mid-chain branching range

The preferred branched surfactant compositions useful in cleaning compositions according to the present invention are described in more detail hereinafter.
(1) Mid-chain Branched Primary Alkyl Sulfate Surfactants

The present invention branched surfactant compositions may comprise two or more mid-chain branched primary alkyl sulfate surfactants having the formula

\[
\text{CH}_3\text{CH}_2(\text{CH}_2)_w\text{CH}(\text{CH}_2)_x\text{CH}(\text{CH}_2)_y\text{CH}(\text{CH}_2)_z\text{OSO}_3\text{M}
\]

The surfactant mixtures of the present invention comprise molecules having a linear primary alkyl sulfate chain backbone (i.e., the longest linear carbon chain which includes the sulfated carbon atom). These alkyl chain backbones comprise from 12 to 19 carbon atoms; and further the molecules comprise a branched primary alkyl moiety having at least a total of 14, but not more than 20, carbon atoms. In addition, the surfactant mixture has an average total number of carbon atoms for the branched primary alkyl moieties within the range of from greater than 14.5 to about 17.5. Thus, the present invention mixtures comprise at least one branched primary alkyl sulfate surfactant compound having a longest linear carbon chain of not less than 12 carbon atoms or more than 19 carbon atoms, and the total number of carbon atoms including branching must be at least 14, and further the average total number of carbon atoms for the branched primary alkyl chains is within the range of greater than 14.5 to about 17.5.

For example, a C16 total carbon primary alkyl sulfate surfactant having 13 carbon atoms in the backbone must have 1, 2, or 3 branching units (i.e., R, R\(^1\) and/or R\(^2\)) whereby total number of carbon atoms in the molecule is at least 16. In this example, the C16 total carbon requirement may be satisfied equally by having, for example, one propyl branching unit or three methyl branching units.

R, R\(^1\), and R\(^2\) are each independently selected from hydrogen and C\(_1\)-C\(_3\) alkyl (preferably hydrogen or C\(_1\)-C\(_2\) alkyl, more preferably hydrogen or methyl, and most preferably methyl), provided R, R\(^1\), and R\(^2\) are not all hydrogen. Further, when z is 1, at least R or R\(^1\) is not hydrogen.

Although for the purposes of the present invention surfactant compositions the above formula does not include molecules wherein the units R, R\(^1\), and R\(^2\) are all hydrogen (i.e., linear non-branched primary alkyl sulfates), it is to be recognized that the present invention compositions may still further comprise some amount of linear, non-branched primary alkyl sulfate. Further, this linear non-branched primary alkyl sulfate surfactant may be present as the result of the process used to manufacture the surfactant mixture having the requisite one or more mid-chain branched primary alkyl sulfates according to the present invention, or for purposes of formulating detergent compositions some amount
of linear non-branched primary alkyl sulfate may be admixed into the final product formulation.

Further it is to be similarly recognized that non-sulfated mid-chain branched alcohol may comprise some amount of the present invention compositions. Such materials may be present as the result of incomplete sulfation of the alcohol used to prepare the alkyl sulfate surfactant, or these alcohols may be separately added to the present invention detergent compositions along with a mid-chain branched alkyl sulfate surfactant according to the present invention.

M is hydrogen or a salt forming cation depending upon the method of synthesis. Examples of salt forming cations are lithium, sodium, potassium, calcium, magnesium, quaternary alkyl amines having the formula

\[
R^3 \quad \text{+} \quad R^6 \quad N \quad R^4 \quad \text{+} \quad R^5
\]

wherein R^3, R^4, R^5 and R^6 are independently hydrogen, C_1-C_{22} alkylene, C_{4-22} branched alkylene, C_{1-6} alkanol, C_{1-22} alkenylene, C_{4-22} branched alkenylene, and mixtures thereof. Preferred cations are ammonium (R^3, R^4, R^5 and R^6 equal hydrogen), sodium, potassium, mono-, di-, and trialkanol ammonium, and mixtures thereof. The monoalkanol ammonium compounds of the present invention have R^3 equal to C_{1-6} alkanol, R^4, R^5 and R^6 equal to hydrogen; dialkanol ammonium compounds of the present invention have R^3 and R^4 equal to C_{1-6} alkanol, R^5 and R^6 equal to hydrogen; trialkanol ammonium compounds of the present invention have R^3, R^4 and R^5 equal to C_{1-6} alkanol, R^6 equal to hydrogen. Preferred alkanol ammonium salts of the present invention are the mono-, di- and tri- quaternary ammonium compounds having the formulas:

\[
H_2N^+(CH_2CH_2OH), \quad H_2N^+(CH_2CH_2OH)_2, \quad HN^+(CH_2CH_2OH)_3.
\]

Preferred M is sodium, potassium and the C_2 alkanol ammonium salts listed above; most preferred is sodium.

Further regarding the above formula, w is an integer from 0 to 13; x is an integer from 0 to 13; y is an integer from 0 to 13; z is an integer of at least 1; and \( w + x + y + z \) is an integer from 8 to 14.

The preferred surfactant mixtures of the present invention have at least 0.001%, more preferably at least 5%, most preferably at least 20% by weight, of the mixture one or more branched primary alkyl sulfates having the formula

\[
\begin{align*}
R^1 & \quad R^2 \\
\text{CH}_3\text{CH}_2(\text{CH}_2)_x\text{CH}(\text{CH}_2)_y\text{CH}(\text{CH}_2)_z\text{OSO}_3M
\end{align*}
\]
wherein the total number of carbon atoms, including branching, is from 15 to 18, and wherein further for this surfactant mixture the average total number of carbon atoms in the branched primary alkyl moieties having the above formula is within the range of greater than 14.5 to about 17.5; R¹ and R² are each independently hydrogen or C₁-C₃ alkyl; M is a water soluble cation; x is from 0 to 11; y is from 0 to 11; z is at least 2; and x + y + z is from 9 to 13; provided R¹ and R² are not both hydrogen. More preferred are compositions having at least 5% of the mixture comprising one or more mid-chain branched primary alkyl sulfates wherein x + y is equal to 9 and z is at least 2.

Preferably, the mixtures of surfactant comprise at least 5% of a mid chain branched primary alkyl sulfate having R¹ and R² independently hydrogen, methyl, provided R¹ and R² are not both hydrogen; x + y is equal to 8, 9, or 10 and z is at least 2. More preferably the mixtures of surfactant comprise at least 20% of a mid chain branched primary alkyl sulfate having R¹ and R² independently hydrogen, methyl, provided R¹ and R² are not both hydrogen; x + y is equal to 8, 9, or 10 and z is at least 2.

Preferred detergent compositions according to the present invention, for example one useful for laundering fabrics, comprise from about 0.001% to about 99% of a mixture of mid-chain branched primary alkyl sulfate surfactants, said mixture comprising at least about 5% by weight of two or more mid-chain branched alkyl sulfates having the formula:

\[
\text{CH}_3
\]
\[
\text{CH}_3 \text{(CH}_2\text{)}_a \text{CH(} \text{CH}_2\text{)}_b \text{CH}_2 \text{OSO}_3\text{M}
\]

(I)

\[
\text{CH}_3 \quad \text{CH}_3
\]
\[
\text{CH}_3 \text{(CH}_2\text{)}_d \text{CH(} \text{CH}_2\text{)}_e \text{CHCH}_2 \text{OSO}_3\text{M}
\]

(II)

or mixtures thereof; wherein M represents one or more cations; a, b, d, and e are integers, a+b is from 10 to 16, d+e is from 8 to 14 and wherein further

when a + b = 10, a is an integer from 2 to 9 and b is an integer from 1 to 8;
when a + b = 11, a is an integer from 2 to 10 and b is an integer from 1 to 9;
when a + b = 12, a is an integer from 2 to 11 and b is an integer from 1 to 10;
when a + b = 13, a is an integer from 2 to 12 and b is an integer from 1 to 11;
when a + b = 14, a is an integer from 2 to 13 and b is an integer from 1 to 12;
when a + b = 15, a is an integer from 2 to 14 and b is an integer from 1 to 13;
when a + b = 16, a is an integer from 2 to 15 and b is an integer from 1 to 14;
when d + e = 8, d is an integer from 2 to 7 and e is an integer from 1 to 6;
when d + e = 9, d is an integer from 2 to 8 and e is an integer from 1 to 7;
when d + e = 10, d is an integer from 2 to 9 and e is an integer from 1 to 8;
when d + e = 11, d is an integer from 2 to 10 and e is an integer from 1 to 9;
when d + e = 12, d is an integer from 2 to 11 and e is an integer from 1 to 10;
when \( d + e = 13 \), \( d \) is an integer from 2 to 12 and \( e \) is an integer from 1 to 11;
when \( d + e = 14 \), \( d \) is an integer from 2 to 13 and \( e \) is an integer from 1 to 12;
wherein further for this surfactant mixture the average total number of carbon atoms in the branched primary alkyl moieties having the above formulas is within the range of greater than 14.5 to about 17.5.

Further, the present invention surfactant composition may comprise a mixture of branched primary alkyl sulfates having the formula

\[
\text{CH}_3\text{CH}_2(\text{CH}_2)_w\text{CH}(\text{CH}_2)_x\text{CH}(\text{CH}_2)_y\text{CH}(\text{CH}_2)_z\text{OSO}_3\text{M}
\]

wherein the total number of carbon atoms per molecule, including branching, is from 14 to 20, and wherein further for this surfactant mixture the average total number of carbon atoms in the branched primary alkyl moieties having the above formula is within the range of greater than 14.5 to about 17.5; \( R \), \( R^1 \), and \( R^2 \) are each independently selected from hydrogen and \( C_1-C_3 \) alkyl, provided \( R \), \( R^1 \), and \( R^2 \) are not all hydrogen; \( M \) is a water soluble cation; \( w \) is an integer from 0 to 13; \( x \) is an integer from 0 to 13; \( y \) is an integer from 0 to 13; \( z \) is an integer of at least 1; and \( w + x + y + z \) is from 8 to 14; provided that when \( R^2 \) is a \( C_1-C_3 \) alkyl the ratio of surfactants having \( z \) equal to 1 to surfactants having \( z \) of 2 or greater is at least about 1:1, preferably at least about 1:5, more preferably at least about 1:10, and most preferably at least about 1:100. Also preferred are surfactant compositions, when \( R^2 \) is a \( C_1-C_3 \) alkyl, comprising less than about 20%, preferably less than 10%, more preferably less than 5%, most preferably less than 1%, of branched primary alkyl sulfates having the above formula wherein \( z \) equals 1.

Preferred mono-methyl branched primary alkyl sulfates are selected from the group consisting of: 3-methyl pentadecanol sulfate, 4-methyl pentadecanol sulfate, 5-methyl pentadecanol sulfate, 6-methyl pentadecanol sulfate, 7-methyl pentadecanol sulfate, 8-methyl pentadecanol sulfate, 9-methyl pentadecanol sulfate, 10-methyl pentadecanol sulfate, 11-methyl pentadecanol sulfate, 12-methyl pentadecanol sulfate, 13-methyl pentadecanol sulfate, 3-methyl hexadecanol sulfate, 4-methyl hexadecanol sulfate, 5-methyl hexadecanol sulfate, 6-methyl hexadecanol sulfate, 7-methyl hexadecanol sulfate, 8-methyl hexadecanol sulfate, 9-methyl hexadecanol sulfate, 10-methyl hexadecanol sulfate, 11-methyl hexadecanol sulfate, 12-methyl hexadecanol sulfate, 13-methyl hexadecanol sulfate, 14-methyl hexadecanol sulfate, and mixtures thereof.

Preferred di-methyl branched primary alkyl sulfates are selected from the group consisting of: 2,3-methyl tetradecanol sulfate, 2,4-methyl tetradecanol sulfate, 2,5-methyl tetradecanol sulfate, 2,6-methyl tetradecanol sulfate, 2,7-methyl tetradecanol sulfate, 2,8-
methyl tetradecanol sulfate, 2,9-methyl tetradecanol sulfate, 2,10-methyl tetradecanol sulfate, 2,11-methyl tetradecanol sulfate, 2,12-methyl tetradecanol sulfate, 2,3-methyl pentadecanol sulfate, 2,4-methyl pentadecanol sulfate, 2,5-methyl pentadecanol sulfate, 2,6-methyl pentadecanol sulfate, 2,7-methyl pentadecanol sulfate, 2,8-methyl pentadecanol sulfate, 2,9-methyl pentadecanol sulfate, 2,10-methyl pentadecanol sulfate, 2,11-methyl pentadecanol sulfate, 2,12-methyl pentadecanol sulfate, 2,13-methyl pentadecanol sulfate, and mixtures thereof.

The following branched primary alkyl sulfates comprising 16 carbon atoms and having one branching unit are examples of preferred branched surfactants useful in the present invention compositions:

5-methylpentadecylsulfate having the formula:

\[
\text{CH}_3 \quad \begin{array}{c}
\text{OSO}_3\text{M} \\
\end{array}
\]

6-methylpentadecylsulfate having the formula

\[
\text{CH}_3 \quad \begin{array}{c}
\text{OSO}_3\text{M} \\
\end{array}
\]

7-methylpentadecylsulfate having the formula

\[
\begin{array}{c}
\text{OSO}_3\text{M} \\
\end{array}
\]

8-methylpentadecylsulfate having the formula

\[
\text{CH}_3 \quad \begin{array}{c}
\text{OSO}_3\text{M} \\
\end{array}
\]

9-methylpentadecylsulfate having the formula

\[
\begin{array}{c}
\text{OSO}_3\text{M} \\
\end{array}
\]

10-methylpentadecylsulfate having the formula

\[
\text{CH}_3 \quad \begin{array}{c}
\text{OSO}_3\text{M} \\
\end{array}
\]

wherein M is preferably sodium.

The following branched primary alkyl sulfates comprising 17 carbon atoms and having two branching units are examples of preferred branched surfactants according to the present invention:
2,5-dimethylpentadecylsulfate having the formula:

\[
\text{CH}_3 \quad \text{OSO}_3\text{M}
\]

2,6-dimethylpentadecylsulfate having the formula:

\[
\text{CH}_3 \quad \text{CH}_3 \quad \text{OSO}_3\text{M}
\]

2,7-dimethylpentadecylsulfate having the formula:

\[
\text{CH}_3 \quad \text{OSO}_3\text{M}
\]
2,8-dimethylpentadecylsulfate having the formula

\[
\text{CH}_3 \quad \text{CH}_3 \quad \text{OSO}_3M
\]

2,9-dimethylpentadecylsulfate having the formula

\[
\text{CH}_3 \quad \text{OSO}_3M
\]

2,10-dimethylpentadecylsulfate having the formula

\[
\text{CH}_3 \quad \text{CH}_3 \quad \text{OSO}_3M
\]

wherein \( M \) is preferably sodium.

(2) Mid-chain Branched Primary Alkyl Polyoxyalkylene Surfactants

The present invention branched surfactant compositions may comprise one or more mid-chain branched primary alkyl polyoxyalkylene surfactants having the formula

\[
R \quad R^1 \quad R^2 \quad \text{CH}_3\text{CH}_2\text{(CH}_2\text{)}_x\text{CH(CH}_2\text{)}_y\text{CH(CH}_2\text{)}_z\text{(EO/PO)mOH}
\]

The surfactant mixtures of the present invention comprise molecules having a linear primary polyoxyalkylene chain backbone (i.e., the longest linear carbon chain which includes the alkoxyated carbon atom). These alkyl chain backbones comprise from 12 to 19 carbon atoms; and further the molecules comprise a branched primary alkyl moiety having at least a total of 14, but not more than 20, carbon atoms. In addition, the surfactant mixture has an average total number of carbon atoms for the branched primary alkyl moieties within the range of from greater than 14.5 to about 17.5. Thus, the present invention mixtures comprise at least one polyoxyalkylene compound having a longest linear carbon chain of not less than 12 carbon atoms or more than 19 carbon atoms, and the total number of carbon atoms including branching must be at least 14, and further the average total number of carbon atoms for the branched primary alkyl chains is within the range of greater than 14.5 to about 17.5.

For example, a C16 total carbon (in the alkyl chain) primary polyoxyalkylene surfactant having 15 carbon atoms in the backbone must have a methyl branching unit
(either R, R\textsuperscript{1} or R\textsuperscript{2} is methyl) whereby the total number of carbon atoms in the molecule is 16.

R, R\textsuperscript{1}, and R\textsuperscript{2} are each independently selected from hydrogen and C\textsubscript{1}-C\textsubscript{3} alkyl (preferably hydrogen or C\textsubscript{1}-C\textsubscript{2} alkyl, more preferably hydrogen or methyl, and most preferably methyl), provided R, R\textsuperscript{1}, and R\textsuperscript{2} are not all hydrogen. Further, when z is 1, at least R or R\textsuperscript{1} is not hydrogen.

Although for the purposes of the present invention surfactant compositions the above formula does not include molecules wherein the units R, R\textsuperscript{1}, and R\textsuperscript{2} are all hydrogen (i.e., linear non-branched primary polyoxyalkylenes), it is to be recognized that the present invention compositions may still further comprise some amount of linear, non-branched primary polyoxyalkylene. Further, this linear non-branched primary polyoxyalkylene surfactant may be present as the result of the process used to manufacture the surfactant mixture having the requisite mid-chain branched primary polyoxyalkylenes according to the present invention, or for purposes of formulating detergent compositions some amount of linear non-branched primary polyoxyalkylene may be admixed into the final product formulation.

Further it is to be similarly recognized that non-alkoxylated mid-chain branched alcohol may comprise some amount of the present invention polyoxyalkylene-containing compositions. Such materials may be present as the result of incomplete alkoxylation of the alcohol used to prepare the polyoxyalkylene surfactant, or these alcohols may be separately added to the present invention detergent compositions along with a mid-chain branched polyoxyalkylene surfactant according to the present invention.

Further regarding the above formula, w is an integer from 0 to 13; x is an integer from 0 to 13; y is an integer from 0 to 13; z is an integer of at least 1; and w + x + y + z is an integer from 8 to 14.

EO/PO are alkoxy moieties, preferably selected from ethoxy, propoxy, and mixed ethoxy/proproxy groups, more preferably ethoxy, wherein m is at least about 1, preferably within the range of from about 3 to about 30, more preferably from about 5 to about 20, and most preferably from about 5 to about 15. The (EO/PO)	extsubscript{m} moiety may be either a distribution with average degree of alkoxylation (e.g., ethoxylation and/or propoxylation) corresponding to m, or it may be a single specific chain with alkoxylation (e.g., ethoxylation and/or propoxylation) of exactly the number of units corresponding to m.

The preferred surfactant mixtures of the present invention have at least 0.001%, more preferably at least 5%, most preferably at least 20% by weight, of the mixture one or more mid-chain branched primary alkyl polyoxyalkylenes having the formula
wherein the total number of carbon atoms, including branching, is from 15 to 18, and wherein further for this surfactant mixture the average total number of carbon atoms in the branched primary alkyl moieties having the above formula is within the range of greater than 14.5 to about 17.5; R1 and R2 are each independently hydrogen or C1-C3 alkyl; x is from 0 to 11; y is from 0 to 11; z is at least 2; and x + y + z is from 9 to 13; provided R1 and R2 are not both hydrogen; and EO/PO are alkoxy moieties selected from ethoxy, propoxy, and mixed ethoxy/propanoxy groups, more preferably ethoxy, wherein m is at least about 1, preferably within the range of from about 3 to about 30, more preferably from about 5 to about 20, and most preferably from about 5 to about 15. More preferred are compositions having at least 5% of the mixture comprising one or more mid-chain branched primary polyoxyalkylene wherein z is at least 2.

Preferably, the mixtures of surfactant comprise at least 5%, preferably at least about 20%, of a mid chain branched primary alkyl polyoxyalkylene having R1 and R2 independently hydrogen or methyl, provided R1 and R2 are not both hydrogen; x + y is equal to 8, 9 or 10 and z is at least 2.

Preferred detergent compositions according to the present invention, for example one useful for laundering fabrics, comprise from about 0.001% to about 99% of a mixture of mid-chain branched primary alkyl polyoxyalkylene surfactants, said mixture comprising at least about 5% by weight of one or more mid-chain branched alkyl polyoxyalkylenes having the formula:

\[
\begin{align*}
\text{CH}_3 \\
\text{CH}_3 (\text{CH}_2)_a \text{CH} (\text{CH}_2)_b \text{CH}_2 (\text{EO}/\text{PO}) \text{mOH}
\end{align*}
\]

(I)

\[
\begin{align*}
\text{CH}_3 \\
\text{CH}_3 (\text{CH}_2)_d \text{CH} (\text{CH}_2)_e \text{CH}_2 (\text{EO}/\text{PO}) \text{mOH}
\end{align*}
\]

(II)

or mixtures thereof; wherein a, b, d, and e are integers, a+b is from 10 to 16, d+e is from 8 to 14 and wherein further

when a + b = 10, a is an integer from 2 to 9 and b is an integer from 1 to 8;
when a + b = 11, a is an integer from 2 to 10 and b is an integer from 1 to 9;
when a + b = 12, a is an integer from 2 to 11 and b is an integer from 1 to 10;
when a + b = 13, a is an integer from 2 to 12 and b is an integer from 1 to 11;
when a + b = 14, a is an integer from 2 to 13 and b is an integer from 1 to 12;
when a + b = 15, a is an integer from 2 to 14 and b is an integer from 1 to 13;
when a + b = 16, a is an integer from 2 to 15 and b is an integer from 1 to 14;
when d + e = 8, d is an integer from 2 to 7 and e is an integer from 1 to 6;
when \( d + e = 9 \), \( d \) is an integer from 2 to 8 and \( e \) is an integer from 1 to 7;
when \( d + e = 10 \), \( d \) is an integer from 2 to 9 and \( e \) is an integer from 1 to 8;
when \( d + e = 11 \), \( d \) is an integer from 2 to 10 and \( e \) is an integer from 1 to 9;
when \( d + e = 12 \), \( d \) is an integer from 2 to 11 and \( e \) is an integer from 1 to 10;
when \( d + e = 13 \), \( d \) is an integer from 2 to 12 and \( e \) is an integer from 1 to 11;
when \( d + e = 14 \), \( d \) is an integer from 2 to 13 and \( e \) is an integer from 1 to 12;
and wherein further for this surfactant mixture the average total number of carbon atoms in
the branched primary alkyl moieties having the above formulas is within the range of
greater than 14.5 to about 17.5; and EO/PO are alkoxy moieties selected from ethoxy,
proproxy, and mixed ethoxy/proproxy groups, wherein \( m \) is at least about 1, preferably
within the range of from about 3 to about 30, more preferably from about 5 to about 20, and
most preferably from about 5 to about 15.

Further, the present invention surfactant composition may comprise a mixture of
branched primary alkyl polyoxyalkylenes having the formula

\[
\begin{align*}
R & \quad R^1 & \quad R^2 \\
CH_3CH_2(CH_2)_wCH(CH_2)_xCH(CH_2)_yCH(CH_2)_z(EO/PO)mOH
\end{align*}
\]

wherein the total number of carbon atoms per molecule, including branching, is from 14 to
20, and wherein further for this surfactant mixture the average total number of carbon
atoms in the branched primary alkyl moieties having the above formula is within the range of
greater than 14.5 to about 17.5; \( R, R^1, \) and \( R^2 \) are each independently selected from
hydrogen and \( C_1-C_3 \) alkyl, provided \( R, R^1, \) and \( R^2 \) are not all hydrogen; \( w \) is an integer
from 0 to 13; \( x \) is an integer from 0 to 13; \( y \) is an integer from 0 to 13; \( z \) is an integer of at
least 1; \( w + x + y + z \) is from 8 to 14; EO/PO are alkoxy moieties, preferably selected from
ethoxy, proproxy, and mixed ethoxy/proproxy groups, wherein \( m \) is at least about 1,
preferably within the range of from about 3 to about 30, more preferably from about 5 to
about 20, and most preferably from about 5 to about 15; provided that when \( R^2 \) is \( C_1-C_3 \)
alkyl the ratio of surfactants having \( z \) equal to 2 or greater to surfactants having \( z \) of 1 is at
least about 1:1, preferably at least about 1.5:1, more preferably at least about 3:1, and most
preferably at least about 4:1. Also preferred are surfactant compositions when \( R^2 \) is \( C_1-C_3 \)
alkyl comprising less than about 50%, preferably less than about 40%, more preferably less
than about 25%, most preferably less than about 20%, of branched primary alkyl
polyoxyalkylene having the above formula wherein \( z \) equals 1.

Preferred mono-methyl branched primary alkyl ethoxylates are selected from the
group consisting of: 3-methyl pentadecanol ethoxylate, 4-methyl pentadecanol ethoxylate,
5-methyl pentadecanol ethoxylate, 6-methyl pentadecanol ethoxylate, 7-methyl
pentadecanol ethoxylate, 8-methyl pentadecanol ethoxylate, 9-methyl pentadecanol
ethoxylate, 10-methyl pentadecanol ethoxylate, 11-methyl pentadecanol ethoxylate, 12-methyl pentadecanol ethoxylate, 13-methyl pentadecanol ethoxylate, 3-methyl hexadecanol ethoxylate, 4-methyl hexadecanol ethoxylate, 5-methyl hexadecanol ethoxylate, 6-methyl hexadecanol ethoxylate, 7-methyl hexadecanol ethoxylate, 8-methyl hexadecanol ethoxylate, 9-methyl hexadecanol ethoxylate, 10-methyl hexadecanol ethoxylate, 11-methyl hexadecanol ethoxylate, 12-methyl hexadecanol ethoxylate, 13-methyl hexadecanol ethoxylate, and mixtures thereof, wherein the compounds are ethoxylated with an average degree of ethoxylation of from about 5 to about 15.

Preferred di-methyl branched primary alkyl ethoxylates selected from the group consisting of: 2,3-methyl tetradecanol ethoxylate, 2,4-methyl tetradecanol ethoxylate, 2,5-methyl tetradecanol ethoxylate, 2,6-methyl tetradecanol ethoxylate, 2,7-methyl tetradecanol ethoxylate, 2,8-methyl tetradecanol ethoxylate, 2,9-methyl tetradecanol ethoxylate, 2,10-methyl tetradecanol ethoxylate, 2,11-methyl tetradecanol ethoxylate, 2,12-methyl tetradecanol ethoxylate, 2,3-methyl pentadecanol ethoxylate, 2,4-methyl pentadecanol ethoxylate, 2,5-methyl pentadecanol ethoxylate, 2,6-methyl pentadecanol ethoxylate, 2,7-methyl pentadecanol ethoxylate, 2,8-methyl pentadecanol ethoxylate, 2,9-methyl pentadecanol ethoxylate, 2,10-methyl pentadecanol ethoxylate, 2,11-methyl pentadecanol ethoxylate, 2,12-methyl pentadecanol ethoxylate, 2,13-methyl pentadecanol ethoxylate, and mixtures thereof, wherein the compounds are ethoxylated with an average degree of ethoxylation of from about 5 to about 15.

(3) Mid-chain Branched Primary Alkyl Alkoxylated Sulfate Surfactants

The present invention branched surfactant compositions may comprise one or more (preferably a mixture of two or more) mid-chain branched primary alkyl alkoxylated sulfates having the formula:

\[
\text{CH}_3\text{CH}_2(\text{CH}_2)_w\text{CH}(\text{CH}_2)_x\text{CH}(\text{CH}_2)_y\text{CH}(\text{CH}_2)_z(\text{EO/PO})_m\text{O SO}_3\text{M}
\]

The surfactant mixtures of the present invention comprise molecules having a linear primary alkoxylated sulfate chain backbone (i.e., the longest linear carbon chain which includes the alkoxy-sulfated carbon atom). These alkyl chain backbones comprise from 12 to 19 carbon atoms; and further the molecules comprise a branched primary alkyl moiety having at least a total of 14, but not more than 20, carbon atoms. In addition, the surfactant mixture has an average total number of carbon atoms for the branched primary alkyl moieties within the range of from greater than 14.5 to about 17.5. Thus, the present
invention mixtures comprise at least one alkoxylated sulfate compound having a longest linear carbon chain of not less than 12 carbon atoms or more than 19 carbon atoms, and the total number of carbon atoms including branching must be at least 14, and further the average total number of carbon atoms for the branched primary alkyl chains is within the range of greater than 14.5 to about 17.5.

For example, a C16 total carbon (in the alkyl chain) primary alkyl alkoxylated sulfate surfactant having 15 carbon atoms in the backbone must have a methyl branching unit (either R, R¹ or R² is methyl) whereby the total number of carbon atoms in the primary alkyl moiety of the molecule is 16.

R, R¹, and R² are each independently selected from hydrogen and C₁-C₃ alkyl (preferably hydrogen or C₁-C₂ alkyl, more preferably hydrogen or methyl, and most preferably methyl), provided R, R¹, and R² are not all hydrogen. Further, when z is 1, at least R or R¹ is not hydrogen.

Although for the purposes of the present invention surfactant compositions the above formula does not include molecules wherein the units R, R¹, and R² are all hydrogen (i.e., linear non-branched primary alkoxylated sulfates), it is to be recognized that the present invention compositions may still further comprise some amount of linear, non-branched primary alkoxylated sulfate. Further, this linear non-branched primary alkoxylated sulfate surfactant may be present as the result of the process used to manufacture the surfactant mixture having the requisite mid-chain branched primary alkoxylated sulfates according to the present invention, or for purposes of formulating detergent compositions some amount of linear non-branched primary alkoxylated sulfate may be admixed into the final product formulation.

It is also to be recognized that some amount of mid-chain branched alkyl sulfate may be present in the compositions. This is typically the result of sulfation of non-alkoxylated alcohol remaining following incomplete alkoylation of the mid-chain branched alcohol used to prepare the alkoxylated sulfate useful herein. It is to be recognized, however, that separate addition of such mid-chain branched alkyl sulfates is also contemplated by the present invention compositions.

Further it is to be similarly recognized that non-sulfated mid-chain branched alcohol (including polyoxyalkylene alcohols) may comprise some amount of the present invention alkoxylated sulfate-containing compositions. Such materials may be present as the result of incomplete sulfation of the alcohol (alkoxylated or non-alkoxylated) used to prepare the alkoxylated sulfate surfactant, or these alcohols may be separately added to the present invention detergent compositions along with a mid-chain branched alkoxylated sulfate surfactant according to the present invention.

M is as described hereinbefore.
Further regarding the above formula, \(w\) is an integer from 0 to 13; \(x\) is an integer from 0 to 13; \(y\) is an integer from 0 to 13; \(z\) is an integer of at least 1; and \(w + x + y + z\) is an integer from 8 to 14.

EO/PO are alkoxy moieties, preferably selected from ethoxy, propoxy, and mixed ethoxy/propoxy groups, wherein \(m\) is at least about 0.01, preferably within the range of from about 0.1 to about 30, more preferably from about 0.5 to about 10, and most preferably from about 1 to about 5. The (EO/PO)\(m\) moiety may be either a distribution with average degree of alkoxylation (e.g., ethoxylation and/or propoxylation) corresponding to \(m\), or it may be a single specific chain with alkoxylation (e.g., ethoxylation and/or propoxylation) of exactly the number of units corresponding to \(m\).

The preferred surfactant mixtures of the present invention have at least 0.001%, more preferably at least 5%, most preferably at least 20% by weight, of the mixture one or more mid-chain branched primary alkyl alkoxylated sulfates having the formula

\[
R^1 CH_3 CH_2(CH_2)_x CH(CH_2)_y CH(CH_2)_z(EO/PO)_m O SO_3 M
\]

wherein the total number of carbon atoms, including branching, is from 15 to 18, and wherein further for this surfactant mixture the average total number of carbon atoms in the branched primary alkyl moieties having the above formula is within the range of greater than 14.5 to about 17.5; \(R^1\) and \(R^2\) are each independently hydrogen or \(C_1-C_3\) alkyl; \(M\) is a water soluble cation; \(x\) is from 0 to 11; \(y\) is from 0 to 11; \(z\) is at least 2; and \(x + y + z\) is from 9 to 13; provided \(R^1\) and \(R^2\) are not both hydrogen; and EO/PO are alkoxy moieties selected from ethoxy, propoxy, and mixed ethoxy/propoxy groups, wherein \(m\) is at least about 0.01, preferably within the range of from about 0.1 to about 30, more preferably from about 0.5 to about 10, and most preferably from about 1 to about 5. More preferred are compositions having at least 5% of the mixture comprising one or more mid-chain branched primary alkoxylated sulfates wherein \(z\) is at least 2.

Preferably, the mixtures of surfactant comprise at least 5%, preferably at least about 20%, of a mid chain branched primary alkyl alkoxylated sulfate having \(R^1\) and \(R^2\) independently hydrogen or methyl, provided \(R^1\) and \(R^2\) are not both hydrogen; \(x + y\) is equal to 8, 9 or 10 and \(z\) is at least 2.

Preferred detergent compositions according to the present invention, for example one useful for laundering fabrics, comprise from about 0.001% to about 99% of a mixture of mid-chain branched primary alkyl alkoxylated sulfate surfactants, said mixture comprising at least about 5% by weight of one or more mid-chain branched alkyl alkoxylated sulfates having the formula:
or mixtures thereof; wherein M represents one or more cations; a, b, d, and e are integers, 
a+b is from 10 to 16, d+e is from 8 to 14 and wherein further 
when a + b = 10, a is an integer from 2 to 9 and b is an integer from 1 to 8; 
when a + b = 11, a is an integer from 2 to 10 and b is an integer from 1 to 9; 
when a + b = 12, a is an integer from 2 to 11 and b is an integer from 1 to 10; 
when a + b = 13, a is an integer from 2 to 12 and b is an integer from 1 to 11; 
when a + b = 14, a is an integer from 2 to 13 and b is an integer from 1 to 12; 
when a + b = 15, a is an integer from 2 to 14 and b is an integer from 1 to 13; 
when a + b = 16, a is an integer from 2 to 15 and b is an integer from 1 to 14; 
when d + e = 8, d is an integer from 2 to 7 and e is an integer from 1 to 6; 
when d + e = 9, d is an integer from 2 to 8 and e is an integer from 1 to 7; 
when d + e = 10, d is an integer from 2 to 9 and e is an integer from 1 to 8; 
when d + e = 11, d is an integer from 2 to 10 and e is an integer from 1 to 9; 
when d + e = 12, d is an integer from 2 to 11 and e is an integer from 1 to 10; 
when d + e = 13, d is an integer from 2 to 12 and e is an integer from 1 to 11; 
when d + e = 14, d is an integer from 2 to 13 and e is an integer from 1 to 12; 
and wherein further for this surfactant mixture the average total number of carbon atoms in 
the branched primary alkyl moieties having the above formulas is within the range of 
greater than 14.5 to about 17.5; and EO/PO are alkoxy moieties selected from ethoxy, 
propoxy, and mixed ethoxy/propoxy groups, wherein m is at least about 0.01, preferably 
within the range of from about 0.1 to about 30, more preferably from about 0.5 to about 10, 
and most preferably from about 1 to about 5.

Further, the present invention surfactant composition may comprise a mixture of 
 branched primary alkyl alkoxyalted sulfates having the formula 

$$CH_3CH_2(CH_2)_{x+y}CH(CH_2)xCH(CH_2)yCH(CH_2)z(EO/PO)mO SO_3M$$

wherein the total number of carbon atoms per molecule, including branching, is from 14 to 
20, and wherein further for this surfactant mixture the average total number of carbon 
atoms in the branched primary alkyl moieties having the above formula is within the range of 
greater than 14.5 to about 17.5; R, R¹, and R² are each independently selected from 
hydrogen and C₁-C₃ alkyl, provided R, R¹, and R² are not all hydrogen; M is a water
soluble cation; w is an integer from 0 to 13; x is an integer from 0 to 13; y is an integer from 0 to 13; z is an integer of at least 1; w + x + y + z is from 8 to 14; EO/PO are alkoxy moieties, preferably selected from ethoxy, propoxy, and mixed ethoxy/propoxy groups, wherein m is at least about 0.01, preferably within the range of from about 0.1 to about 30, more preferably from about 0.5 to about 10, and most preferably from about 1 to about 5; provided that when R² is C₁⁻C₃ alkyl the ratio of surfactants having z equal to 2 or greater to surfactants having z of 1 is at least about 1:1, preferably at least about 1.5:1, more preferably at least about 3:1, and most preferably at least about 4:1. Also preferred are surfactant compositions when R² is C₁⁻C₃ alkyl comprising less than about 50%, preferably less than about 40%, more preferably less than about 25%, most preferably less than about 20%, of branched primary alkyl alkoxyalted sulfate having the above formula wherein z equals 1.

Preferred mono-methyl branched primary alkyl ethoxylated sulfates are selected from the group consisting of: 3-methyl pentadecanol ethoxylated sulfate, 4-methyl pentadecanol ethoxylated sulfate, 5-methyl pentadecanol ethoxylated sulfate, 6-methyl pentadecanol ethoxylated sulfate, 7-methyl pentadecanol ethoxylated sulfate, 8-methyl pentadecanol ethoxylated sulfate, 9-methyl pentadecanol ethoxylated sulfate, 10-methyl pentadecanol ethoxylated sulfate, 11-methyl pentadecanol ethoxylated sulfate, 12-methyl pentadecanol ethoxylated sulfate, 13-methyl pentadecanol ethoxylated sulfate, 3-methyl hexadecanol ethoxylated sulfate, 4-methyl hexadecanol ethoxylated sulfate, 5-methyl hexadecanol ethoxylated sulfate, 6-methyl hexadecanol ethoxylated sulfate, 7-methyl hexadecanol ethoxylated sulfate, 8-methyl hexadecanol ethoxylated sulfate, 9-methyl hexadecanol ethoxylated sulfate, 10-methyl hexadecanol ethoxylated sulfate, 11-methyl hexadecanol ethoxylated sulfate, 12-methyl hexadecanol ethoxylated sulfate, 13-methyl hexadecanol ethoxylated sulfate, and mixtures thereof, wherein the compounds are ethoxylated with an average degree of ethoxylation of from about 0.1 to about 10.

Preferred di-methyl branched primary alkyl ethoxylated sulfates selected from the group consisting of: 2,3-dimethyl tetradeconol ethoxylated sulfate, 2,4-dimethyl tetradeconol ethoxylated sulfate, 2,5-dimethyl tetradeconol ethoxylated sulfate, 2,6-dimethyl tetradeconol ethoxylated sulfate, 2,7-dimethyl tetradeconol ethoxylated sulfate, 2,8-dimethyl tetradeconol ethoxylated sulfate, 2,9-dimethyl tetradeconol ethoxylated sulfate, 2,10-dimethyl tetradeconol ethoxylated sulfate, 2,11-dimethyl tetradeconol ethoxylated sulfate, 2,12-dimethyl tetradeconol ethoxylated sulfate, 2,3-dimethyl pentadecanol ethoxylated sulfate, 2,4-dimethyl pentadecanol ethoxylated sulfate, 2,5-dimethyl pentadecanol ethoxylated sulfate, 2,6-dimethyl pentadecanol ethoxylated sulfate, 2,7-dimethyl pentadecanol ethoxylated sulfate, 2,8-dimethyl pentadecanol ethoxylated sulfate, 2,9-dimethyl pentadecanol ethoxylated sulfate, 2,10-dimethyl pentadecanol ethoxylated sulfate.
ethoxylated sulfate, 2,11-methyl pentadecanol ethoxylated sulfate, 2,12-methyl pentadecanol ethoxylated sulfate, 2,13-methyl pentadecanol ethoxylated sulfate, and mixtures thereof, wherein the compounds are ethoxylated with an average degree of ethoxylation of from about 0.1 to about 10.

The paste can include adjunct surfactants such as those selected from anionics other than BAS, nonionic, zwitterionic, ampholytic and cationic classes and compatible mixtures thereof. Detergent surfactants useful herein are described in U.S. Patent 3,664,961, Norris, issued May 23, 1972, and in U.S. Patent 3,919,678, Laughlin et al., issued December 30, 1975, both of which are incorporated herein by reference. Useful cationic surfactants also include those described in U.S. Patent 4,222,905, Cockrell, issued September 16, 1980, and in U.S. Patent 4,239,659, Murphy, issued December 16, 1980, both of which are also incorporated herein by reference.

The following are representative examples of adjunct detergent surfactants useful in the present surfactant paste. Water-soluble salts of the higher fatty acids, i.e., "soaps", are useful anionic surfactants in the compositions herein. This includes alkali metal soaps such as the sodium, potassium, ammonium, and alkylolammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about 18 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

Additional anionic surfactants which suitable for use herein include the watersoluble salts, preferably the alkali metal, ammonium and alkylolammonium salts, of organic sulfuric reaction products having in their molecular structure a straight-chain alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic surfactants are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_{8-18} carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; and the sodium and potassium alkylbenzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain, e.g., those of the type described in U.S. Patents 2,220,099 and 2,477,383. Especially valuable are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 13, abbreviated as C_{11-13} LAS.

Other anionic surfactants suitable for use herein are the sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; sodium or potassium
of ethylene oxide per molecule and wherein the alkyl groups contain from about 8 to about 12 carbon atoms; and sodium or potassium salts of alkyl ethylene oxide ether sulfates containing about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl group contains from about 10 to about 20 carbon atoms.

In addition, suitable anionic surfactants include the water-soluble salts of esters of alpha-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxyalkane-i-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; alkyl ether sulfates containing from about 10 to 20 carbon atoms in the alkyl group and from about 1 to 30 moles of ethylene oxide; water-soluble salts of olefin and paraffin sulfonates containing from about 12 to 20 carbon atoms; and beta-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Preferred adjunct anionic surfactants are C_{10-18} linear alkylbenzene sulfonate and C_{10-18} alkyl sulfate. If desired, low moisture (less than about 25% water) alkyl sulfate paste can be the sole ingredient in the surfactant paste. Most preferred are C_{10-18} alkyl sulfates, linear or branched, and any of primary, secondary or tertiary. A preferred embodiment of the present invention is wherein the surfactant paste comprises from about 20% to about 40% of a mixture of sodium C_{10-13} linear alkylbenzene sulfonate and sodium C_{12-16} alkyl sulfate in a weight ratio of about 2:1 to 1:2. Another preferred embodiment of the detergent composition includes a mixture of C_{10-18} alkyl sulfate and C_{10-18} alkyl ethoxy sulfate in a weight ratio of about 80:20.

Water-soluble nonionic surfactants are also useful in the instant invention. Such nonionic materials include compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the polyoxyalkylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Suitable nonionic surfactants include the polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 15 carbon atoms, in either a straight chain or branched chain configuration, with from about 3 to 12 moles of ethylene oxide per mole of alkyl phenol. Included are the water-soluble and water-dispersible condensation products of aliphatic alcohols containing from 8 to 22 carbon atoms, in either straight chain or branched configuration, with from 3 to 12 moles of ethylene oxide per mole of alcohol.
An additional group of nonionics suitable for use herein are semi-polar nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to 18 carbon atoms and two moieties selected from the group of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of about 10 to 18 carbon atoms and two moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to 3 carbon atoms.

Preferred nonionic surfactants are of the formula $R^1(OC_2H_{4})_{n}OH$, wherein $R^1$ is a C$_{10-16}$ alkyl group or a C$_8-C_{12}$ alkyl phenyl group, and n is from 3 to about 80. Particularly preferred are condensation products of C$_{12-15}$ alcohols with from about 5 to about 20 moles of ethylene oxide per mole of alcohol, e.g., C$_{12-13}$ alcohol condensed with about 6.5 moles of ethylene oxide per mole of alcohol.

Additional suitable nonionic surfactants include polyhydroxy fatty acid amides. Examples are N-methyl N-1-deoxyglucitol cocoamide and N-methyl N-1-deoxyglucitol oleamide. Processes for making polyhydroxy fatty acid amides are known and can be found in Wilson, U.S. Patent No. 2,965,576 and Schwartz, U.S. Patent No. 2,703,798, the disclosures of which are incorporated herein by reference.

Ampholytic surfactants include derivatives of aliphatic or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic moiety can be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and at least one aliphatic substituent contains an anionic water-solubilizing group.

Zwitterionic surfactants include derivatives of aliphatic, quaternary, ammonium, phosphonium, and sulfonium compounds in which one of the aliphatic substituents contains from about 8 to 18 carbon atoms.

Cationic surfactants can also be included in the present invention. Cationic surfactants comprise a wide variety of compounds characterized by one or more organic hydrophobic groups in the cation and generally by a quaternary nitrogen associated with an acid radical. Pentavalent nitrogen ring compounds are also considered quaternary nitrogen compounds. Suitable anions are halides, methyl sulfate and hydroxide. Tertiary amines can have characteristics similar to cationic surfactants at washing solution pH values less than about 8.5. A more complete disclosure of these and other cationic surfactants useful herein can be found in U.S. Patent 4,228,044, Cambre, issued October 14, 1980, incorporated herein by reference.
Cationic surfactants are often used in detergent compositions to provide fabric softening and/or antistatic benefits. Antistatic agents which provide some softening benefit and which are preferred herein are the quaternary ammonium salts described in U.S. Patent 3,936,537, Baskerville, Jr. et al., issued February 3, 1976, the disclosure of which is incorporated herein by reference.
Dry Starting Detergent Ingredients

The compositions of the invention can contain all manner of organic, water-soluble detergent compounds, inasmuch as the builder material are compatible with all such materials. In addition to a detersive surfactant, at least one suitable adjunct detergent ingredient is preferably included in the detergent composition. The adjunct detergent ingredient is preferably selected from the group consisting of builders, enzymes, bleaching agents, bleach activators, suds suppressors, soil release agents, brighteners, perfumes, hydrotropes, dyes, pigments, polymeric dispersing agents, pH controlling agents, chelants, processing aids, crystallization aids, and mixtures thereof. The following list of detergent ingredients and mixtures thereof which can be used in the compositions herein is representative of the detergent ingredients, but is not intended to be limiting.

One or more builders can be used in conjunction with the builder material described herein to further improve the performance of the compositions described herein. For example, the builder can be selected from the group consisting of aluminosilicates, crystalline layered silicates, MAP zeolites, citrates, amorphous silicates, polycarboxylates, sodium carbonates and mixtures thereof. The sodium carbonate ingredient can serve as the inorganic alkaline material when a liquid acid precursor of the mid-chain branched surfactant is used. Other suitable auxiliary builders are described hereinafter.

Preferred builders include aluminosilicate ion exchange materials and sodium carbonate. The aluminosilicate ion exchange materials used herein as a detergent builder preferably have both a high calcium ion exchange capacity and a high exchange rate. Without intending to be limited by theory, it is believed that such high calcium ion exchange rate and capacity are a function of several interrelated factors which derive from the method by which the aluminosilicate ion exchange material is produced. In that regard, the aluminosilicate ion exchange materials used herein are preferably produced in accordance with Corkill et al, U.S. Patent No. 4,605,509 (Procter & Gamble), the disclosure of which is incorporated herein by reference.

Preferably, the aluminosilicate ion exchange material is in "sodium" form since the potassium and hydrogen forms of the instant aluminosilicate do not exhibit the as high of an exchange rate and capacity as provided by the sodium form. Additionally, the aluminosilicate ion exchange material preferably is in over dried form so as to facilitate production of crisp detergent agglomerates as described herein. The aluminosilicate ion exchange materials used herein preferably have particle size diameters which optimize their effectiveness as detergent builders. The term "particle size diameter" as used herein represents the average particle size diameter of a given aluminosilicate ion exchange material as determined by conventional analytical techniques, such as microscopic determination and scanning electron microscope (SEM). The preferred particle size
diameter of the aluminosilicate is from about 0.1 micron to about 10 microns, more preferably from about 0.5 microns to about 9 microns. Most preferably, the particle size diameter is from about 1 microns to about 8 microns.

Preferably, the aluminosilicate ion exchange material has the formula

$$Na_2[(AlO_2)_x(SiO_2)_y] \times H_2O$$

wherein \(x\) and \(y\) are integers of at least 6, the molar ratio of \(x\) to \(y\) is from about 1 to about 5 and \(x\) is from about 10 to about 264. More preferably, the aluminosilicate has the formula

$$Na_2[(AlO_2)_{12}(SiO_2)_{12}] \times H_2O$$

wherein \(x\) is from about 20 to about 30, preferably about 27. These preferred aluminosilicates are available commercially, for example under designations Zeolite A, Zeolite B and Zeolite X. Alternatively, naturally-occurring or synthetically derived aluminosilicate ion exchange materials suitable for use herein can be made as described in Krummell et al, U.S. Patent No. 3,985,669, the disclosure of which is incorporated herein by reference.

The aluminosilicates used herein are further characterized by their ion exchange capacity which is at least about 200 mg equivalent of CaCO₃ hardness/gram, calculated on an anhydrous basis, and which is preferably in a range from about 300 to 352 mg equivalent of CaCO₃ hardness/gram. Additionally, the instant aluminosilicate ion exchange materials are still further characterized by their calcium ion exchange rate which is at least about 2 grains Ca⁺⁺/gallon/minute/-gram/gallon, and more preferably in a range from about 2 grains Ca⁺⁺/gallon/minute/-gram/gallon to about 6 grains Ca⁺⁺/gallon/minute/-gram/gallon.

In order to make the present invention more readily understood, reference is made to the following examples, which are intended to be illustrative only and not intended to be limiting in scope.

**EXAMPLE I**

This Example illustrates the process of the invention which produces free flowing, crisp, high density detergent composition. Two feed streams of various detergent starting ingredients are continuously fed, at a rate of 2800 kg/hr, into a Lödige CB-30 mixer/densifier, one of which comprises a surfactant paste containing surfactant and water and the other stream containing starting dry detergent material containing aluminosilicate and sodium carbonate. The rotational speed of the shaft in the Lödige CB-30 mixer/densifier is about 1400 rpm and the mean residence time is about 10 seconds. The contents from the Lödige CB-30 mixer/densifier are continuously fed into a Lödige KM 600 mixer/densifier for further agglomeration during which the mean residence time is about 30 seconds. The resulting detergent agglomerates are then fed to a fluid bed dryer and then to
a fluid bed cooler, the mean residence time being about 10 minutes and 15 minutes, respectively. A coating agent, aluminosilicate, is fed after the Lödige KM 600 mixer/densifier to control and prevent over agglomeration. The detergent agglomerates are then screened with conventional screening apparatus resulting in a uniform particle size distribution. The composition of the detergent agglomerates exiting the fluid bed cooler for three process runs are set forth in Table I below:

<table>
<thead>
<tr>
<th>Component</th>
<th>% Weight of Total Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>C_{16.5} BAS</td>
<td>40.0</td>
</tr>
<tr>
<td>C_{14-15} AS</td>
<td>-</td>
</tr>
<tr>
<td>C_{12.3} LAS</td>
<td>1.1</td>
</tr>
<tr>
<td>Aluminosilicate</td>
<td>25.4</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>26.3</td>
</tr>
<tr>
<td>Polyethylene glycol (MW 4000)</td>
<td>1.1</td>
</tr>
<tr>
<td>Misc. (water, etc.)</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>100.0</td>
</tr>
</tbody>
</table>

Additional detergent ingredients including perfumes, enzymes, and other minors are sprayed onto the agglomerates described above in the finishing step to result in a finished detergent composition. The relative proportions of the overall finished detergent composition produced by the process of instant process is presented in Table II below:

<table>
<thead>
<tr>
<th>Component</th>
<th>(% weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{16.5} BAS, C_{14-15}AS and C_{12.3} LAS</td>
<td>39.8</td>
</tr>
<tr>
<td>Neodol 23-6.5</td>
<td>3.0</td>
</tr>
<tr>
<td>C_{12-14} N-methyl glucamide</td>
<td>0.9</td>
</tr>
<tr>
<td>Polyacrylate (MW=4500)</td>
<td>3.0</td>
</tr>
<tr>
<td>Polyethylene glycol (MW=4000)</td>
<td>1.2</td>
</tr>
<tr>
<td>Sodium Sulfate</td>
<td>8.9</td>
</tr>
<tr>
<td>Aluminosilicate</td>
<td>2.8</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>27.2</td>
</tr>
<tr>
<td>Protease enzyme</td>
<td>0.4</td>
</tr>
<tr>
<td>Amylase enzyme</td>
<td>0.1</td>
</tr>
<tr>
<td>Lipase enzyme</td>
<td>0.2</td>
</tr>
<tr>
<td>Cellulase enzyme</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Minors (water, perfume, etc.)

1 A mixture of a mid-chain branched C_{16.5} alkyl sulfate ("BAS"), C_{14-15} alkyl sulfate ("AS") and C_{12-13} linear alkylbenzene sulfonate ("LAS") surfactants.

2 C_{12-13} alkyl ethoxylate (EO=6.5) commercially available from Shell Oil Company.

The density of the resulting detergent composition is 796 g/l, the median particle size is 613 microns.

**EXAMPLE II-III**

Several detergent compositions made in accordance with the invention and specifically for top-loading washing machines are exemplified below. The base granule is prepared by a conventional spray drying process in which the starting ingredients are formed into a slurry and passed through a spray drying tower having a counter current stream of hot air (200-300°C) resulting in the formation of porous granules. The admixed agglomerates are formed from two feed streams of various starting detergent ingredients which are continuously fed, at a rate of 1400 kg/hr, into a L"odge CB-30 mixer/densifier, one of which comprises a surfactant paste containing surfactant and water and the other stream containing starting dry detergent material containing aluminosilicate and sodium carbonate. The rotational speed of the shaft in the L"odge CB-30 mixer/densifier is about 1400 rpm and the median residence time is about 5-10 seconds. The contents from the L"odge CB-30 mixer/densifier are continuously fed into a L"odge KM-600 mixer/densifier for further agglomeration during which the mean residence time is about 1-2 minutes. The resulting detergent agglomerates are then fed to a fluid bed dryer and to a fluid bed cooler before being admixed with the spray dried granules. The remaining adjunct detergent ingredients are sprayed on or dry added to the blend of agglomerates and granules.

<table>
<thead>
<tr>
<th>Base Granule</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{16.5} alkyl sulfate (mid-chain branched), Na</td>
<td>6.0</td>
<td>19.0</td>
</tr>
<tr>
<td>Aluminosilicate</td>
<td>15.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Sodium polyacrylate polymer</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>PolyethyleneGlycol (MW=4000)</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>C_{12-13} linear alkylbenzene sulfonate, Na</td>
<td>6.0</td>
<td>6.0</td>
</tr>
<tr>
<td>C_{14-15} alkyl ethoxylated sulfate, Na</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Sodium silicate</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Brightener 24^6</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>7.0</td>
<td>7.0</td>
</tr>
<tr>
<td>DTPA</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>
### Admixed Agglomerates

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>C14-15 alkyl sulfate, Na</th>
<th>3.0</th>
<th>5.0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C12-13 linear alkylbenzene sulfonate, Na</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>C16.5 alkyl sulfate (mid-chain branched), Na</td>
<td>3.0</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td>Sodium Carbonate</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>Polyethylene Glycol (MW=4000)</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

### Admix

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>C12-15 alkyl ethoxylate (EO = 7)</th>
<th>2.0</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Perfume</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>Polyvinylpyrrolidone</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Polyvinylpyridine N-oxide</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Polyvinylpyrrolidone-polyvinylimidazole</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Distearylamine &amp; Cumene sulfonic acid</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>Soil Release Polymer</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Lipolase Lipase (100,000 LU/L)</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Termamyl amylase (60 KNU/g)</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>CAREZYME® cellulase (1000 CEVU/g)</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>Protease (40mg/g)</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>NOBS</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>Sodium Percarbonate</td>
<td>12.0</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td>Polydimethylsiloxane</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Miscellaneous (water, etc.)</td>
<td><strong>balance</strong></td>
<td><strong>balance</strong></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>100.0</td>
<td></td>
</tr>
</tbody>
</table>

1 Diethylene Triamine Pentaacetic Acid

2 Made according to U.S. Patent 5,415,807, issued May 16, 1995 to Gosselink et al

3 Nonanoyloxybenzenesulfonate

4 Purchased from Novo Nordisk A/S

5 Purchased from Genencor

6 Purchased from Ciba-Geigy

Having thus described the invention in detail, it will be clear to those skilled in the art that various changes may be made without departing from the scope of the invention and the invention is not to be considered limited to what is described in the specification.
What is claimed is:

1. A process for continuously preparing a high density detergent composition characterized by the steps of:
(A) continuously mixing a detergent surfactant paste and dry starting detergent material into a high speed mixer/densifier to obtain detergent agglomerates, wherein the ratio of said surfactant paste to said dry detergent material is from 1:10 to 10:1, said surfactant paste containing mid-chain branched surfactant compounds of the formula:
\[ \text{A}^b \cdot \text{X} \cdot \text{B} \]
wherein:
(a) A\(^b\) is a hydrophobic C9 to C22, total carbons in the moiety, preferably from C12 to C18, mid-chain branched alkyl moiety having: (1) a longest linear carbon chain attached to the - X - B moiety in the range of from 8 to 21 carbon atoms; (2) one or more C\(_1\) - C\(_3\) alkyl moieties branching from this longest linear carbon chain; (3) at least one of the branching alkyl moieties is attached directly to a carbon of the longest linear carbon chain at a position within the range of position 2 carbon, counting from carbon \#1 which is attached to the - X - B moiety, to position \(\omega - 2\) carbon, the terminal carbon minus 2 carbons; and (4) the surfactant composition has an average total number of carbon atoms in the A\(^b\)-X moiety in the above formula within the range of greater than 14.5 to 18;
(b) B is a hydrophilic moiety selected from sulfates, sulfonates, amine oxides, polyoxyalkylene, alkoxylated sulfates, polyhydroxy moieties, phosphate esters, glycerol sulfonates, polyglucconates, polyphosphate esters, phosphonates, sulfosuccinates, sulfosuccaminates, polyalkoxylated carboxylates, glucamides, taurinates, sarcosinates, glycimates, isethianates, dialkanolamides, monoalkanolamides, monoalkanolamide sulfates, diglycolamides, diglycolamide sulfates, glycerol esters, glycerol ester sulfates, glycerol ethers, glycerol ether sulfates, polyglycerol ethers, polyglycerol ether sulfates, sorbitan esters, polyalkoxylated sorbitan esters, amminoalkanesulfonates, amidopropyl betaines, alkylated quats, alkylated/polyhydroxalkylated quats, alkylated quats, alkylated/polyhydroxylated oxypropyl quats, imidazolines, 2-yl-succinates, sulfonated alkyl esters, and sulfonated fatty acids; and
(c) X is \(-\text{CH}_2-\);
(B) mixing said detergent agglomerates in a moderate speed mixer/densifier to further densify and agglomerate said detergent agglomerates; and
(C) drying said detergent agglomerates so as to form said high density detergent composition.
2. A process according to claim 1 wherein the \( A^b \) moiety is a branched primary alkyl moiety having the formula:
\[
CH_3CH_2(CH_2)_wCH(CH_2)_xCH(CH_2)_yCH(CH_2)_z
\]
wherein the total number of carbon atoms in the branched primary alkyl moiety of this formula, including the \( R, R^1, \) and \( R^2 \) branching, is from 13 to 19; \( R, R^1, \) and \( R^2 \) are each independently selected from hydrogen and \( C_1-C_3 \) alkyl, preferably methyl, provided \( R, R^1, \) and \( R^2 \) are not all hydrogen and, when \( z \) is 0, at least \( R \) or \( R^1 \) is not hydrogen; \( w \) is an integer from 0 to 13; \( x \) is an integer from 0 to 13; \( y \) is an integer from 0 to 13; \( z \) is an integer from 0 to 13; and \( w + x + y + z \) is from 7 to 13.

3. A process according to claim 1 wherein the \( A^b \) moiety is a branched primary alkyl moiety having the formula selected from:
\[
(\text{I}) \quad CH_3
\]
\[
CH_3(\text{CH}_2)_aCH(\text{CH}_2)_b
\]
\[
(\text{II}) \quad CH_3 \quad CH_3
\]
\[
CH_3(\text{CH}_2)_dCH(\text{CH}_2)_eCH
\]
or mixtures thereof; wherein \( a, b, d, \) and \( e \) are integers, \( a+b \) is from 10 to 16, \( d+e \) is from 8 to 14 and wherein further
- when \( a + b = 10 \), \( a \) is an integer from 2 to 9 and \( b \) is an integer from 1 to 8;
- when \( a + b = 11 \), \( a \) is an integer from 2 to 10 and \( b \) is an integer from 1 to 9;
- when \( a + b = 12 \), \( a \) is an integer from 2 to 11 and \( b \) is an integer from 1 to 10;
- when \( a + b = 13 \), \( a \) is an integer from 2 to 12 and \( b \) is an integer from 1 to 11;
- when \( a + b = 14 \), \( a \) is an integer from 2 to 13 and \( b \) is an integer from 1 to 12;
- when \( a + b = 15 \), \( a \) is an integer from 2 to 14 and \( b \) is an integer from 1 to 13;
- when \( a + b = 16 \), \( a \) is an integer from 2 to 15 and \( b \) is an integer from 1 to 14;
- when \( d + e = 8 \), \( d \) is an integer from 2 to 7 and \( e \) is an integer from 1 to 6;
- when \( d + e = 9 \), \( d \) is an integer from 2 to 8 and \( e \) is an integer from 1 to 7;
- when \( d + e = 10 \), \( d \) is an integer from 2 to 9 and \( e \) is an integer from 1 to 8;
- when \( d + e = 11 \), \( d \) is an integer from 2 to 10 and \( e \) is an integer from 1 to 9;
- when \( d + e = 12 \), \( d \) is an integer from 2 to 11 and \( e \) is an integer from 1 to 10;
- when \( d + e = 13 \), \( d \) is an integer from 2 to 12 and \( e \) is an integer from 1 to 11;
- when \( d + e = 14 \), \( d \) is an integer from 2 to 13 and \( e \) is an integer from 1 to 12.
4. A process according to claim 1 wherein said dry starting detergent material is selected from the group consisting of aluminosilicates, crystalline layered silicates, sodium carbonate and mixtures thereof.

5. A process according to claim 1 further characterizing the step of extruding said surfactant paste in an extruder prior to said step (A).

6. A process according to claim 1 further characterizing the step of adding a coating agent after said moderate speed mixer/densifier.

7. A process according to claim 6 wherein said coating agent is selected from the group consisting of aluminosilicates, carbonates, silicates, said builder material, and mixtures thereof.

8. A process according to claim 1 wherein said ratio of said surfactant paste to said dry detergent material is from 1:4 to 4:1.

9. A process for continuously preparing a high density detergent composition characterizing the steps of:
   (A) spray drying an aqueous slurry containing a mid-chain branched surfactant and adjunct detergent ingredients to form spray dried granules, wherein said mid-chain branched surfactant has the formula:
   \[ A^b - X - B \]

   wherein:
   (a) \( A^b \) is a hydrophobic C9 to C22, total carbons in the moiety, preferably from C12 to C18, mid-chain branched alkyl moiety having: (1) a longest linear carbon chain attached to the -X-B moiety in the range of from 8 to 21 carbon atoms; (2) one or more C\(_1\) - C\(_3\) alkyl moieties branching from this longest linear carbon chain; (3) at least one of the branching alkyl moieties is attached directly to a carbon of the longest linear carbon chain at a position within the range of position 2 carbon, counting from carbon #1 which is attached to the -X-B moiety, to position \( \omega \) - 2 carbon, the terminal carbon minus 2 carbons; and (4) the surfactant composition has an average total number of carbon atoms in the \( A^b \)-X moiety in the above formula within the range of greater than 14.5 to 18;

   (b) B is a hydrophilic moiety selected from sulfates, sulfonates, amine oxides, polyoxyalkylene, alkoxyalkylated sulfates, polyhydroxy moieties, phosphate esters, glycerol sulfonates, polyglyconates, polyphosphate esters, phosphonates, sulfosuccinates, sulfosuccaminates, polyalkoxylated carboxylates, glucamides, taurinates, sarcosinates,
glycinates, isethionates, dialkanolamides, monoalkanolamides, monoalkanolamide sulfates, diglycolamides, diglycolamide sulfates, glycerol esters, glycerol ester sulfates, glycerol ethers, glycerol ether sulfates, polyglycerol ethers, polyglycerol ether sulfates, sorbitan esters, polyalkoxylated sorbitan esters, ammonioalkanesulfonates, amidopropyl betaines, alkylated quats, alkyated/polyhydroxalkylated quats, alkylated quats, alkylated/polyhydroxylated oxypropyl quats, imidazolines, 2-yl-succinates, sulfonated alkyl esters, and sulfonated fatty acids; and

(c) X is \(-\text{CH}_2\)-;

(B) continuously mixing a detergent surfactant paste and dry starting detergent material into a high speed mixer/densifier to obtain detergent agglomerates, wherein the ratio of said surfactant paste to said dry detergent material is from 1:10 to 10:1;

(C) mixing said detergent agglomerates in a moderate speed mixer/densifier to further densify and agglomerate said detergent agglomerates; and

(D) blending said granules and said detergent agglomerates together so as to form said high density detergent composition.

10. A process for continuously preparing a high density detergent composition characterizing the steps of:

(A) continuously mixing an acid precursor of an anionic surfactant and dry starting detergent material containing an alkaline inorganic material capable of neutralizing said acid precursor into a high speed mixer/densifier to obtain detergent agglomerates, wherein the ratio of said surfactant paste to said dry detergent material is from 1:10 to 10:1, said surfactant paste containing mid-chain branched surfactant compounds of the formula:

\[ A^b - X - B \]

wherein:

(a) \(A^b\) is a hydrophobic C9 to C22, total carbons in the moiety, preferably from C12 to C18, mid-chain branched alkyl moiety having: (1) a longest linear carbon chain attached to the \(-X-B\) moiety in the range of from 8 to 21 carbon atoms; (2) one or more \(C_1 - C_3\) alkyl moieties branching from this longest linear carbon chain; (3) at least one of the branching alkyl moieties is attached directly to a carbon of the longest linear carbon chain at a position within the range of position 2 carbon, counting from carbon \#1 which is attached to the \(-X-B\) moiety, to position \(\omega - 2\) carbon, the terminal carbon minus 2 carbons; and (4) the surfactant composition has an average total number of carbon atoms in the \(A^b-X\) moiety in the above formula within the range of greater than 14.5 to 18;

(b) \(B\) is a hydophilic moiety selected from sulfates, sulfonates, amine oxides, polyoxyalkylene, alkoxyated sulfates, polyhydroxy moieties, phosphate esters, glycerol sulfonates, polygluconates, polyphosphate esters, phosphonates, sulfosuccinates,
sulfosuccinamates, polyalkoxylated carboxylates, glucamides, taurinates, sarcosinates, glycinites, isethionates, dialkanolamides, monoalkanolamides, monoalkanolamide sulfates, diglycolamides, diglycolamide sulfates, glycerol esters, glycerol ester sulfates, glycerol ethers, glycerol ether sulfates, polyglycerol ethers, polyglycerol ether sulfates, sorbitan esters, polyalkoxylated sorbitan esters, ammonioalkanesulfonates, amidopropyl betaines, alkylated quats, alkylated/polyhydroxyalkylated quats, alkylated quats, alkylated/polyhydroxylated oxypropyl quats, imidazolines, 2-yl-succinates, sulfonated alkyl esters, and sulfonated fatty acids; and

(c) X is \(-\text{CH}_2\);
## A. CLASSIFICATION OF SUBJECT MATTER

| IPC 6 | C11D17/06 | C11D1/00 | C11D1/14 | C11D1/29 | C11D11/00 |

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

| IPC 6 | C11D |

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>WO 96 38531 A (PROCTER &amp; GAMBLE) 5 December 1996 see claims 1-12; examples I-VI</td>
<td>1-9</td>
</tr>
<tr>
<td>Y</td>
<td>see claims 1-12; examples I-VI</td>
<td>1-9</td>
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<td>P,A</td>
<td>WO 97 39090 A (CONNOR DANIEL STEDMAN ;VINSON PHILLIP KYLE (US); WILLMAN KENNETH W) 23 October 1997 see page 83, line 23 - page 84, line 22; example 4</td>
<td>1-4,6,8</td>
</tr>
<tr>
<td>Y</td>
<td>see page 83, line 23 - page 84, line 22; example 4</td>
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Date of the actual completion of the international search: 8 February 1999

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