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(54) **PROCEDE D'AGGLOMERATION POUR PRODUIRE DES
COMPOSITIONS DETERGENTES NECESSITANT LE
PREMIX DE POLYMERES POLYAMINES MODIFIES**

(54) **AGGLOMERATION PROCESS FOR PRODUCING DETERGENT
COMPOSITIONS INVOLVING PREMIXING MODIFIED
POLYAMINE POLYMERS**

(57) A process is provided in which selected modified polyamines are incorporated into fully formulated detergent compositions in a manner that unexpectedly results in enhanced cleaning performance. The process involves premixing the modified polyamine with a deterative surfactant or acid precursor thereof, and thereafter, agglomerating with dry detergent materials such as builders.



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(54) Title: AGGLOMERATION PROCESS FOR PRODUCING DETERGENT COMPOSITIONS INVOLVING PREMIXING MODIFIED POLYAMINE POLYMERS		
(57) Abstract <p>A process is provided in which selected modified polyamines are incorporated into fully formulated detergent compositions in a manner that unexpectedly results in enhanced cleaning performance. The process involves premixing the modified polyamine with a deterative surfactant or acid precursor thereof, and thereafter, agglomerating with dry detergent materials such as builders.</p>		

**AGGLOMERATION PROCESS FOR PRODUCING DETERGENT
COMPOSITIONS INVOLVING PREMIXING MODIFIED POLYAMINE
POLYMERS**

FIELD OF THE INVENTION

The present invention relates to an agglomeration process for producing laundry detergent compositions that contain modified polyamines especially useful as cotton soil release and/or dispersant agents. More specifically, the process involves premixing the modified polyamine with a surfactant paste or an acid precursor thereof prior to subsequent agglomeration with a builder and optional adjunct detergent ingredients. The premixture is subjected to an agglomeration step which can be carried forth in a two serially positioned mixer/densifiers so as to provide an agglomerated detergent composition having improved performance.

BACKGROUND OF THE INVENTION

Various fabric surface modifying agents have been commercialized and are currently used in detergent compositions and fabric softener/antistatic articles and compositions. Examples of surface modifying agents are soil release polymers. Soil release polymers typically comprise an oligomeric or polymeric ester "backbone" and are generally very effective on polyester or other synthetic fabrics where the grease or similar hydrophobic stains form an attached film and are not easily removed in an aqueous laundering process. The soil release polymers have a less dramatic effect on "blended" fabrics, that is, on fabrics that comprise a mixture of cotton and synthetic material, and have little or no effect on cotton articles.

Extensive research in this area has yielded significant improvements in the effectiveness of polyester soil release agents yielding materials with enhanced product performance and capability of being incorporated into detergent formulations. Modifications of the polymer backbone as well as the selection of proper end-capping groups have produced a wide variety of polyester soil release polymers. For example, end-cap modifications, such as the use of sulfoaryl moieties and especially the low cost isethionate-derived end-capping units, have increased the range of solubility and adjunct ingredient compatibility of these polymers without sacrifice to soil release effectiveness. Many polyester soil release polymers can now be formulated into both liquid as well as solid (i.e., granular) detergents.

As in the case of polyester soil release agents, producing an oligomeric or polymeric material that mimics the structure of cotton has not resulted in a cotton soil release polymer. Although cotton and polyester fabric are both comprised of long chain

polymeric materials, they are chemically very different. Cotton is comprised of cellulose fibers that consist of anhydroglucose units joined by 1-4 linkages. These glycosidic linkages characterize the cotton cellulose as a polysaccharide whereas polyester soil release polymers are generally a combination of terephthalate and ethylene/propylene oxide residues. These differences in composition account for the difference in the fabric properties of cotton versus polyester fabric. Cotton is hydrophilic relative to polyester. Polyester is hydrophobic and attracts oily or greasy dirt and can be easily "dry cleaned". Importantly, the terephthalate and ethyleneoxy/propyleneoxy backbone of polyester fabric does not contain reactive sites, such as the hydroxyl moieties of cotton, that react with stains in a different manner than synthetics. Many cotton stains become "fixed" and can only be resolved by bleaching the fabric.

Until recently, the development of effective fabric surface modifying agents for use on cotton fabrics has been elusive. Attempts by others to apply the paradigm of matching the structure of a soil release polymer with the structure of the fabric, a method successful in the polyester soil release polymer field, have nevertheless yielded marginal results when applied to other fabric surface modifying agents, especially for cotton fabrics. For example, the use of methylcellulose, a cotton polysaccharide with modified oligomeric units, proved to be more effective on polyesters than on cotton.

Additionally, detergent formulators have been faced with the task of devising products to remove a broad spectrum of soils and stains from fabrics. The varieties of soils and stains ranges within a spectrum spanning from polar soils, such as proteinaceous, clay, and inorganic soils, to non-polar soils, such as soot, carbon-black, by-products of incomplete hydrocarbon combustion, and organic soils. To that end, detergent compositions have become more complex as formulators attempt to provide products which handle all types of such soils concurrently. Formulators have been highly successful in developing traditional dispersants which are particularly useful in suspending polar, highly charged, hydrophilic particles such as clay. As yet, however, dispersants designed to disperse and suspend non-polar, hydrophobic-type soils and particulates have been more difficult to develop.

It has been surprisingly discovered that effective soil release agents for cotton articles and dispersants can be prepared from certain modified polyamines. This unexpected result has yielded compositions that are key to providing these benefits once available to only synthetic and synthetic-cotton blended fabric. However, the manner in which such modified polyamines may be included into fully formulated detergent compositions so as to retain, and preferably, improve performance has remained unresolved. Detergent compositions which contain these modified polyamines and are produced via prior art processes do not perform at the desired level of performance.

Accordingly, there remains a need in the art for a detergent-making process which provides a means by which selected modified polyamines can be incorporated into fully formulated detergent compositions that have enhanced cleaning performance.

BACKGROUND ART

U.K. 1,314,897, published April 26, 1973 teaches a hydroxypropyl methyl cellulose material for the prevention of wet-soil redeposition and improving stain release on laundered fabric. U. S. Patent No. 3,897,026 issued to Kearney, discloses cellulosic textile materials having improved soil release and stain resistance properties obtained by reaction of an ethylene-maleic anhydride co-polymer with the hydroxyl moieties of the cotton polymers. U.S. Patent No. 3,912,681 issued to Dickson teaches a composition for applying a non-permanent soil release finish comprising a polycarboxylate polymer to a cotton fabric. U.S. Patent No. 3,948,838 issued to Hinton, *et alia* describes high molecular weight (500,000 to 1,500,000) polyacrylic polymers for soil release. U.S. Patent 4,559,056 issued to Leigh, *et alia* discloses a process for treating cotton or synthetic fabrics with a composition comprising an organopolysiloxane elastomer, an organosiloxaneoxyalkylene copolymer crosslinking agent and a siloxane curing catalyst. See also U.S. Patent Nos. 4,579,681 and 4,614,519. These disclose vinyl caprolactam materials have their effectiveness limited to polyester fabrics, blends of cotton and polyester, and cotton fabrics rendered hydrophobic by finishing agents.

In addition to the above cited art, the following disclose various soil release polymers or modified polyamines; U.S. Patent 4,548,744, Connor, issued October 22, 1985; U.S. Patent 4,597,898, Vander Meer, issued July 1, 1986; U.S. Patent 4,877,896, Maldonado, et al., issued October 31, 1989; U.S. Patent 4,891,160, Vander Meer, issued January 2, 1990; U.S. Patent 4,976,879, Maldonado, et al., issued December 11, 1990; U.S. Patent 5,415,807, Gosselink, issued May 16, 1995; U.S. Patent 4,235,735, Marco, et al., issued November 25, 1980; U.K. Patent 1,537,288, published December 29, 1978; U.K. Patent 1,498,520, published January 18, 1978; WO 95/32272, published November 30, 1995; European Patent Application 206,513; German Patent DE 28 29 022, issued January 10, 1980; Japanese Kokai JP 06313271, published April 27, 1994.

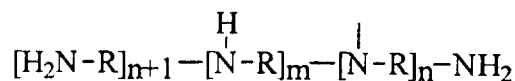
The following references are directed to densifying spray-dried granules: Appel et al, U.S. Patent No. 5,133,924 (Lever); Bortolotti et al, U.S. Patent No. 5,160,657 (Lever); Johnson et al, British patent No. 1,517,713 (Unilever); and Curtis, European Patent Application 451,894. The following references are directed to producing detergents by agglomeration: Capeci et al, U.S. Patent 5,366,652, issued November 22, 1994 and Capeci et al, U.S. Patent 5,486,303, issued January 23, 1996; Beerse et al, U.S. Patent No. 5,108,646 (Procter & Gamble); Hollingsworth et al, European Patent Application 351,937 (Unilever); and Swatling et al, U.S. Patent No. 5,205,958.

SUMMARY OF THE INVENTION

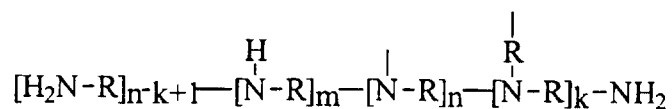
The aforementioned needs in the art are met by the present invention which provides a process in which selected modified polyamines are incorporated into fully

formulated detergent compositions that unexpectedly exhibit enhanced dispersancy and cleaning performance, especially relative to cotton-containing fabrics. In essence, the process invention involves premixing the modified polyamine with a deterative surfactant or acid precursor thereof, and thereafter, agglomerating the premix in a high speed mixer/densifier followed by a moderate speed mixer/densifier with builders and optional adjunct detergent ingredients.

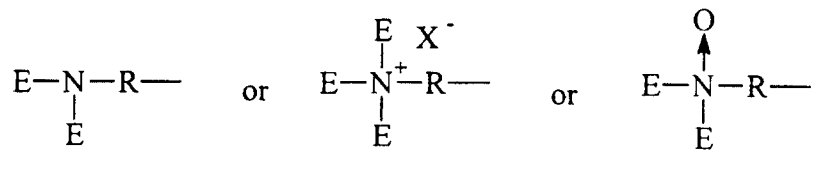
In accordance with one aspect of the invention, a process for an agglomerated detergent composition is provided. The process comprises the steps of: (a) premixing a deterative surfactant paste, dry detergent material and a water-soluble or dispersible, modified polyamine in a premixer to form a premix, the modified polyamine having a polyamine backbone corresponding to the formula:



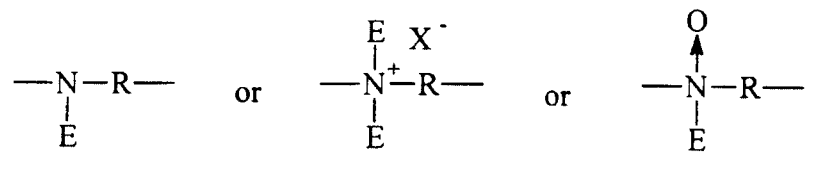
having a modified polyamine formula $V_{(n+1)}W_mY_nZ$ or a polyamine backbone corresponding to the formula:



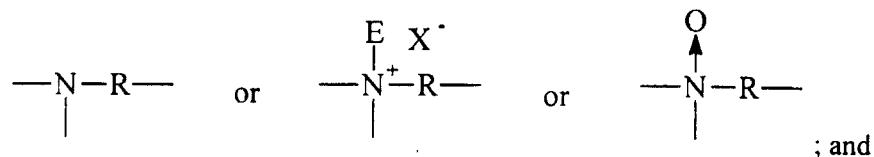
having a modified polyamine formula $V_{(n-k+1)}W_mY_nY'_kZ$, wherein k is less than or equal to n , the polyamine backbone prior to modification has a molecular weight greater than about 200 daltons, wherein i) V units are terminal units having the formula:



ii) W units are backbone units having the formula:

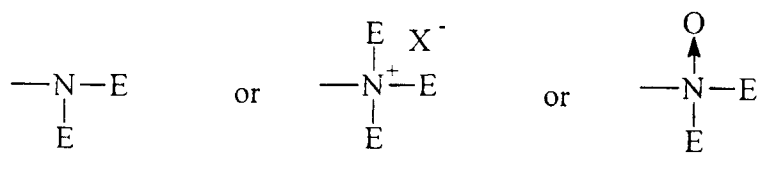


iii) Y units are branching units having the formula:



iv) Z units are terminal units having the formula:

6



wherein backbone linking R units are selected from the group consisting of C₂-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxy-alkylene, C₈-C₁₂ dialkylarylene, -(R¹O)_xR¹-, -(R¹O)_xR⁵(OR¹)_x-, -(CH₂CH(OR²)CH₂O)_z(R¹O)_yR¹(OCH₂CH(OR²)CH₂)_w-, -C(O)(R⁴)_rC(O)-, -CH₂CH(OR²)CH₂-, and mixtures thereof; wherein R¹ is C₂-C₆ alkylene and mixtures thereof; R² is hydrogen, -(R¹O)_xB, and mixtures thereof; R³ is C₁-C₁₈ alkyl, C₇-C₁₂ arylalkyl, C₇-C₁₂ alkyl substituted aryl, C₆-C₁₂ aryl, and mixtures thereof; R⁴ is C₁-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₈-C₁₂ arylalkylene, C₆-C₁₀ arylene, and mixtures thereof; R⁵ is C₁-C₁₂ alkylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxy-alkylene, C₈-C₁₂ dialkylarylene, -C(O)-, -C(O)NHR⁶NHC(O)-, -R¹(OR¹)-, -C(O)(R⁴)_rC(O)-, -CH₂CH(OH)CH₂-, -CH₂CH(OH)CH₂O(R¹O)_yR¹OCH₂CH(OH)CH₂-, and mixtures thereof; R⁶ is C₂-C₁₂ alkylene or C₆-C₁₂ arylene; E units are selected from the group consisting of hydrogen, C₁-C₂₂ alkyl, C₃-C₂₂ alkenyl, C₇-C₂₂ arylalkyl, C₂-C₂₂ hydroxyalkyl, -(CH₂)_pCO₂M, -(CH₂)_qSO₃M, -CH(CH₂CO₂M)CO₂M, -(CH₂)_pPO₃M, -(R¹O)_xB, -C(O)R³, and mixtures thereof; oxide; B is hydrogen, C₁-C₆ alkyl, -(CH₂)_qSO₃M, -(CH₂)_pCO₂M, -(CH₂)_q(CHSO₃M)CH₂SO₃M, -(CH₂)_q-(CHSO₂M)CH₂SO₃M, -(CH₂)_pPO₃M, -PO₃M, and mixtures thereof; M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance; X is a water soluble anion; m has the value from 4 to about 400; n has the value from 0 to about 200; p has the value from 1 to 6, q has the value from 0 to 6; r has the value of 0 or 1; w has the value 0 or 1; x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1; and (b) agglomerating the premix initially in a high speed mixer/densifier and subsequently in a moderate speed mixer/densifier so as to form agglomerates, thereby resulting in the detergent composition.

In accordance with another aspect of the invention, a process for producing an agglomerated detergent composition. This process comprises the steps of: (a) premixing an acid precursor of a deterative surfactant, dry detergent material and a water-soluble or dispersible, modified polyamine in a mixer to form a premix, wherein the modified polyamine has a polyamine backbone as described above; (b) inputting the premix into a high speed mixer/densifier and neutralizing the acid precursor to form agglomerates; and (c) agglomerating the agglomerates further in a moderate speed mixer/densifier so as to form the detergent composition. Also provided by the invention are the detergent compositions made by any of the processes described herein.

As used herein, the term "agglomerates" refers to particles formed by agglomerating detergent granules or particles which typically have a smaller median particle size than the formed agglomerates. All documents cited herein are incorporated by reference, and all percentages used herein are expressed as "percent-by-weight" unless indicated otherwise. All viscosities described herein are measured at 70°C and at shear rates between about 10 to 100 sec⁻¹.

Accordingly, it is an object of the invention to provide a process for producing an agglomerated detergent composition which provides a means by which selected modified polyamine can be incorporated into fully formulated detergent compositions. It is also an object of the invention to provide such a process which minimizes or eliminates degradation of the selected modified polyamines as a result of the fully formulated detergent-making process so as to provide enhanced cleaning performance. 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 detailed description of the preferred embodiment and the appended claims.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The process of the instant invention involves premixing selected modified polyamines and a surfactant paste prior to, or during, neutralization of an acid precursor of a surfactant. While not intending to be bound by theory, it is believed that the selected modified poly-amines described more fully hereinafter form a complex with the deterative surfactant in the surfactant paste or liquid acid precursor thereof. In order to achieve the maximum benefits of the process, the surfactant paste will preferably comprise an anionic surfactant, and optionally a nonionic surfactant, but preferably will not contain a cationic surfactant. This polyamine/surfactant complex typically has a higher oxidative degradation temperature as compared to the degradation temperature of the modified polyamines by themselves. As a consequence of this complex formation, the selected modified polyamines unexpectedly result in improved performance of the fully formulated granular detergent composition into which these modified polyamines are incorporated.

To this end, the modified polyamine and surfactant paste or acid precursor thereof is mixed for at least about 5 seconds, preferably from about 5 seconds to about 1 minute in any acceptable known mixing apparatus such as an in-line static mixer, twin-screw extruder, stirred mixing tanks and the like. The temperature at which the premixing step using the surfactant paste is performed typically is at a temperature of from about 25°C to about 80°C. Also, it is preferred to maintain the pH of the premix at from about 8 to about 10 without other detergent ingredients other than the surfactant paste and modified polyamine. In the case of the use of an acid precursor, the pH is typically from about 1 to about 3 and the temperature is typically from about 50°C to about 90°C. The modified

polyamine is preferably present in an amount of from about 0.01% to about 10%, more preferably from about 0.05% to about 5%, and most preferably from about 0.1% to about 1.0%, by weight of the overall detergent composition. Further, in the premixing step, the deterative surfactant paste preferably comprises from about 1% to about 70%, more preferably from about 20% to about 60%, and most preferably from about 25% to about 50%, by weight of a deterative surfactant the balance water and other minor ingredients. The preferred surfactants used in the surfactant paste are anionic surfactants as detailed hereinafter. With the aforementioned selections, the process provides a detergent composition unexpectedly exhibits improved cleaning performance as compared to direct addition of the modified polyamine to the composition.

In the embodiment involving the surfactant paste, the premix of modified polyamine and paste are initially agglomerated in a high speed mixer/densifier followed by a moderate speed mixer/densifier. The high speed mixer/densifier is a Lödige CB 30 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 100 rpm to about 2500 rpm, more preferably from about 300 rpm to about 1600 rpm. Preferably, the mean residence time of the detergent ingredients in the high speed mixer/densifier is preferably in range from about 2 seconds to about 45 seconds, and most preferably from about 5 seconds to about 15 seconds.

Preferably, the resulting detergent agglomerates formed in the high speed mixer/densifier are then fed into a lower or moderate speed mixer/densifier during which further agglomeration and densification is carried forth. This particular moderate speed mixer/densifier used in the present process should include liquid distribution and agglomeration tools so that both techniques can occur simultaneously. It is preferable to have the moderate speed mixer/densifier be, for example, a Lödige KM 600 (Ploughshare) mixer, Drais® K-T 160 mixer or similar brand mixer. The residence time in the moderate speed mixer/densifier is preferably from about 0.5 minutes to about 15 minutes, most preferably the residence time is about 1 to about 10 minutes. The liquid distribution can be accomplished by cutters, generally smaller in size than the rotating shaft, which preferably operate at about 3600 rpm. It should be understood that while the processing described herein is relative to formation of high density agglomerates, the same equipment and processing steps may be used to produce less or moderately dense agglomerates. Of course, agglomerates produced by the process regardless of the density can be admixed with less dense spray-dried granules in the final detergent product, if desired.

The detergent agglomerates produced by the process preferably have a surfactant level of from about 25% to about 55%, more preferably from about 35% to about 55% and,

most preferably from about 45% to about 55%. The particle porosity of the resulting detergent agglomerates produced according to the process of the invention is preferably in a range from about 5% to about 20%, more preferably at about 10%. In addition, an attribute of dense or densified agglomerates is the relative particle size. The present process typically provides detergent agglomerates having a median particle size of from about 400 microns to about 700 microns, and more preferably from about 400 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 650 g/l and higher. Alternatively, the particle size and porosity can be adjusted to produce agglomerates having lower densities, as well (e.g., 300 g/l to 500 g/l). Such features are especially useful in the production of low as well as high or conventional dosage laundry detergents as well as other granular compositions such as dishwashing compositions.

In the embodiment involving the acid precursor of a surfactant, the premix of acid precursor and modified polyamine is neutralized with a neutralizing agent, preferably a dry agent selected from the group consisting of carbonates, silicates and mixtures thereof, with sodium carbonate being the most preferred. This neutralization occurs in the high speed mixer/densifier previously mentioned. If the surfactant paste is used, the neutralization step is not necessary, and the dry detergent material is inputted into the high speed mixer/densifier with the premix. In both embodiments, agglomerates are formed in the high speed mixer/densifier. However, it is preferable to send these agglomerates to the aforementioned moderate speed mixer/densifier for further build-up of particle size and additional agglomeration. Preferably, the dry detergent material includes sodium sulfate and a detergent builder selected from the group consisting of aluminosilicates, carbonates, phosphates and mixtures thereof. Optional adjunct detergent ingredients as described more fully hereinafter can be added in any step of the process to provide a more fully formulated detergent composition.

Optional Process Steps

In an optional step of the present process, the detergent agglomerates formed by the process are dried in a fluid bed dryer and/or further conditioned by cooling the agglomerates in a fluid bed cooler 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 or dryer; (2) the coating agent may be added between the fluid bed dryer and the fluid bed cooler; (3) the coating agent may be added between the fluid bed dryer and the mixer/densifier(s); and/or (4) the coating agent may be added directly to one

or more of the mixer/densifiers. The coating agent is preferably selected from the group consisting of aluminosilicates, silicates, carbonates and mixtures thereof. 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 mixer/densifier(s). 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.

Other optional steps in the present process involve recycling oversized and undersized agglomerates as described in Capeci et al, U.S. Patent Nos. 5,489,392 and 5,516,448 (Procter & Gamble). Also, the step of including an anhydrous material at selected points in the process can be incorporated as described by Capeci et al, U.S. Patent No. 5,366,652 and 5,486,303 (Procter & Gamble). Optionally, the agglomerates exiting the moderate speed mixer/densifier can be dried in a spray drying tower as described in Capeci et al, U.S. Patent 5,496,487 (Procter & Gamble).

Optionally, the process can comprise the step of spraying an additional binder in the mixer/densifier(s). 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), the disclosure of which is incorporated herein by reference.

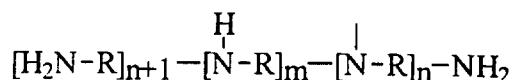
Another optional step of the instant process entails finishing the resulting detergent agglomerates by a variety of processes including spraying and/or admixing other conventional detergent ingredients. For example, the finishing step encompasses spraying on perfumes, and the addition of brighteners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

Modified Polyamines

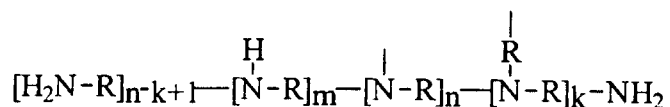
The modified polyamines used in the process invention are water-soluble or dispersible, especially useful for cleaning cotton-containing fabrics or as a dispersant. These polyamines comprise backbones that can be either linear or cyclic. The polyamine backbones can also comprise polyamine branching chains to a greater or lesser degree. In general, the polyamine backbones described herein are modified in such a manner that each nitrogen of the polyamine chain is thereafter described in terms of a unit that is substituted, quaternized, oxidized, or combinations thereof.

For the purposes of the present invention the term "modification" is defined as replacing a backbone -NH hydrogen atom by an E unit (substitution), quaternizing a backbone nitrogen (quaternized) or oxidizing a backbone nitrogen to the N-oxide (oxidized). The terms "modification" and "substitution" are used interchangeably when referring to the process of replacing a hydrogen atom attached to a backbone nitrogen with an E unit. Quaternization or oxidation may take place in some circumstances without substitution, but preferably substitution is accompanied by oxidation or quaternization of at least one backbone nitrogen.

The linear or non-cyclic polyamine backbones that comprise the polymers used in the process have the general formula:

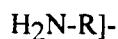


said backbones prior to subsequent modification, comprise primary, secondary and tertiary amine nitrogens connected by R "linking" units. The cyclic polyamine backbones have the general formula:



said backbones prior to subsequent modification, comprise primary, secondary and tertiary amine nitrogens connected by R "linking" units

For the purpose of the present invention, primary amine nitrogens comprising the backbone or branching chain once modified are defined as V or Z "terminal" units. For example, when a primary amine moiety, located at the end of the main polyamine backbone or branching chain having the structure



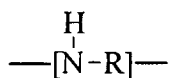
is modified according to the present invention, it is thereafter defined as a V "terminal" unit, or simply a V unit. However, for the purposes of the present invention, some or all of the primary amine moieties can remain unmodified subject to the restrictions further described herein below. These unmodified primary amine moieties by virtue of their position in the backbone chain remain "terminal" units. Likewise, when a primary amine moiety, located at the end of the main polyamine backbone having the structure



is modified according to the present invention, it is thereafter defined as a Z "terminal" unit, or simply a Z unit. This unit can remain unmodified subject to the restrictions further described herein below.

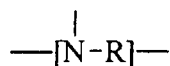
In a similar manner, secondary amine nitrogens comprising the backbone or branching chain once modified are defined as W "backbone" units. For example, when a

secondary amine moiety, the major constituent of the backbones and branching chains of the present invention, having the structure



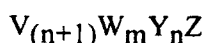
is modified according to the present invention, it is thereafter defined as a W "backbone" unit, or simply a W unit. However, for the purposes of the present invention, some or all of the secondary amine moieties can remain unmodified. These unmodified secondary amine moieties by virtue of their position in the backbone chain remain "backbone" units.

In a further similar manner, tertiary amine nitrogens comprising the backbone or branching chain once modified are further referred to as Y "branching" units. For example, when a tertiary amine moiety, which is a chain branch point of either the polyamine backbone or other branching chains or rings, having the structure

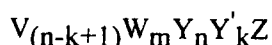


is modified according to the present invention, it is thereafter defined as a Y "branching" unit, or simply a Y unit. However, for the purposes of the present invention, some or all of the tertiary amine moieties can remain unmodified. These unmodified tertiary amine moieties by virtue of their position in the backbone chain remain "branching" units. The R units associated with the V, W and Y unit nitrogens which serve to connect the polyamine nitrogens, are described herein below.

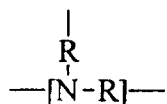
The final modified structure of the polyamines of the present invention can be therefore represented by the general formula



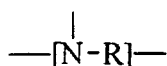
for linear polyamines, by the general formula



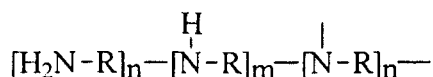
for cyclic polyamine polymers. For the case of polyamines comprising rings, a Y' unit of the formula



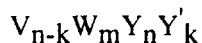
serves as a branch point for a backbone or branch ring. For every Y' unit there is a Y unit having the formula



that will form the connection point of the ring to the main polymer chain or branch. In the unique case where the backbone is a complete ring, the polyamine backbone has the formula

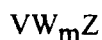


therefore comprising no Z terminal unit and having the formula



wherein k is the number of ring forming branching units. Preferably the polyamine backbones of the present invention comprise no rings.

In the case of non-cyclic polyamines, the ratio of the index n to the index m relates to the relative degree of branching. A fully non-branched linear modified polyamine according to the present invention has the formula

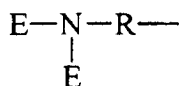


that is, n is equal to 0. The greater the value of n (the lower the ratio of m to n), the greater the degree of branching in the molecule. Typically the value for m ranges from a minimum value of 4 to about 400, however larger values of m, especially when the value of the index n is very low or nearly 0, are also preferred.

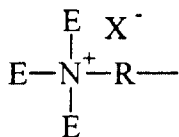
Each polyamine nitrogen whether primary, secondary or tertiary, once modified according to the present invention, is further defined as being a member of one of three general classes; simple substituted, quaternized or oxidized. Those polyamine nitrogen units not modified are classed into V, W, Y, or Z units depending on whether they are primary, secondary or tertiary nitrogens. That is unmodified primary amine nitrogens are V or Z units, unmodified secondary amine nitrogens are W units and unmodified tertiary amine nitrogens are Y units for the purposes of the present invention.

Modified primary amine moieties are defined as V "terminal" units having one of three forms:

- a) simple substituted units having the structure:

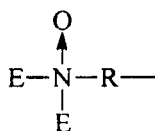


- b) quaternized units having the structure:



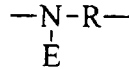
wherein X is a suitable counter ion providing charge balance; and

- c) oxidized units having the structure:

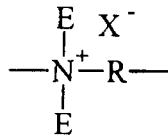


Modified secondary amine moieties are defined as W "backbone" units having one of three forms:

- a) simple substituted units having the structure:

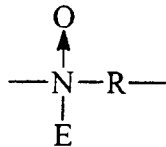


- b) quaternized units having the structure:



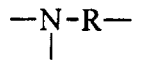
wherein X is a suitable counter ion providing charge balance; and

- c) oxidized units having the structure:

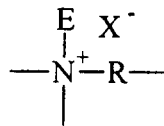


Modified tertiary amine moieties are defined as Y "branching" units having one of three forms:

- a) unmodified units having the structure:

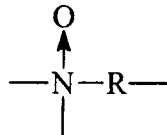


- b) quaternized units having the structure:



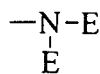
wherein X is a suitable counter ion providing charge balance; and

- c) oxidized units having the structure:



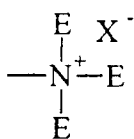
Certain modified primary amine moieties are defined as Z "terminal" units having one of three forms:

- a) simple substituted units having the structure:



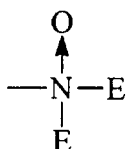
- b) quaternized units having the structure:

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wherein X is a suitable counter ion providing charge balance; and

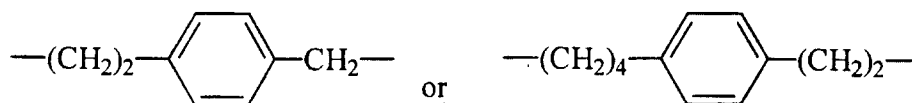
c) oxidized units having the structure:



When any position on a nitrogen is unsubstituted or unmodified, it is understood that hydrogen will substitute for E. For example, a primary amine unit comprising one E unit in the form of a hydroxyethyl moiety is a V terminal unit having the formula (HOCH₂CH₂)HN-

For the purposes of the present invention there are two types of chain terminating units, the V and Z units. The Z "terminal" unit derives from a terminal primary amino moiety of the structure -NH₂. Non-cyclic polyamine backbones according to the present invention comprise only one Z unit whereas cyclic polyamines can comprise no Z units. The Z "terminal" unit can be substituted with any of the E units described further herein below, except when the Z unit is modified to form an N-oxide. In the case where the Z unit nitrogen is oxidized to an N-oxide, the nitrogen must be modified and therefore E cannot be a hydrogen.

The polyamines of the present invention comprise backbone R "linking" units that serve to connect the nitrogen atoms of the backbone. R units comprise units that for the purposes of the present invention are referred to as "hydrocarbyl R" units and "oxy R" units. The "hydrocarbyl" R units are C₂-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₃-C₁₂ hydroxyalkylene wherein the hydroxyl moiety may take any position on the R unit chain except the carbon atoms directly connected to the polyamine backbone nitrogens; C₄-C₁₂ dihydroxyalkylene wherein the hydroxyl moieties may occupy any two of the carbon atoms of the R unit chain except those carbon atoms directly connected to the polyamine backbone nitrogens; C₈-C₁₂ dialkylarylene which for the purpose of the present invention are arylene moieties having two alkyl substituent groups as part of the linking chain. For example, a dialkylarylene unit has the formula



although the unit need not be 1,4-substituted, but can also be 1,2 or 1,3 substituted C₂-C₁₂ alkylene, preferably ethylene, 1,2-propylene, and mixtures thereof, more preferably ethylene. The "oxy" R units comprise $-(R^1O)_xR^5(OR^1)_x-$, $-(CH_2CH(OR^2)CH_2O)_z(R^1O)_yR^1(OCH_2CH(OR^2)CH_2)_w-$, $-CH_2CH(OR^2)CH_2-$, $-(R^1O)_xR^1-$, and mixtures thereof. Preferred R units are C₂-C₁₂ alkylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxyalkylene, C₈-C₁₂ dialkylarylene, $-(R^1O)_xR^1-$, $-CH_2CH(OR^2)CH_2-$, $-(CH_2CH(OH)CH_2O)_z(R^1O)_yR^1(OCH_2CH(OH)CH_2)_w-$, $-(R^1O)_xR^5(OR^1)_x-$, more preferred R units are C₂-C₁₂ alkylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxyalkylene, $-(R^1O)_xR^1-$, $-(R^1O)_xR^5(OR^1)_x-$, $-(CH_2CH(OH)CH_2O)_z(R^1O)_yR^1(OCH_2CH(OH)CH_2)_w-$, and mixtures thereof, even more preferred R units are C₂-C₁₂ alkylene, C₃ hydroxyalkylene, and mixtures thereof, most preferred are C₂-C₆ alkylene. The most preferred backbones of the present invention comprise at least 50% R units that are ethylene.

R¹ units are C₂-C₆ alkylene, and mixtures thereof, preferably ethylene. R² is hydrogen, and $-(R^1O)_xB$, preferably hydrogen.

R³ is C₁-C₁₈ alkyl, C₇-C₁₂ arylalkylene, C₇-C₁₂ alkyl substituted aryl, C₆-C₁₂ aryl, and mixtures thereof, preferably C₁-C₁₂ alkyl, C₇-C₁₂ arylalkylene, more preferably C₁-C₁₂ alkyl, most preferably methyl. R³ units serve as part of E units described herein below.

R⁴ is C₁-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₈-C₁₂ arylalkylene, C₆-C₁₀ arylene, preferably C₁-C₁₀ alkylene, C₈-C₁₂ arylalkylene, more preferably C₂-C₈ alkylene, most preferably ethylene or butylene.

R⁵ is C₁-C₁₂ alkylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxyalkylene, C₈-C₁₂ dialkylarylene, $-C(O)-$, $-C(O)NHR^6NHC(O)-$, $-C(O)(R^4)_rC(O)-$, $-R^1(OR^1)-$, $-CH_2CH(OH)CH_2O(R^1O)_yR^1OCH_2CH(OH)CH_2-$, $-C(O)(R^4)_rC(O)-$, $-CH_2CH(OH)CH_2-$, R⁵ is preferably ethylene, $-C(O)-$, $-C(O)NHR^6NHC(O)-$, $-R^1(OR^1)-$, $-CH_2CH(OH)CH_2-$, $-CH_2CH(OH)CH_2O(R^1O)_yR^1OCH_2CH(OH)CH_2-$, more preferably $-CH_2CH(OH)CH_2-$.

R⁶ is C₂-C₁₂ alkylene or C₆-C₁₂ arylene.

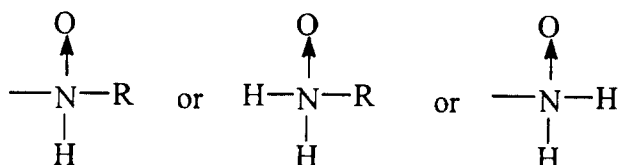
The preferred "oxy" R units are further defined in terms of the R¹, R², and R⁵ units. Preferred "oxy" R units comprise the preferred R¹, R², and R⁵ units. The preferred modified polyamines comprise at least 50% R¹ units that are ethylene. Preferred R¹, R², and R⁵ units are combined with the "oxy" R units to yield the preferred "oxy" R units in the following manner.

- i) Substituting more preferred R⁵ into $-(CH_2CH_2O)_xR^5(OCH_2CH_2)_x-$ yields $-(CH_2CH_2O)_xCH_2CHOHCH_2(OCH_2CH_2)_x-$.

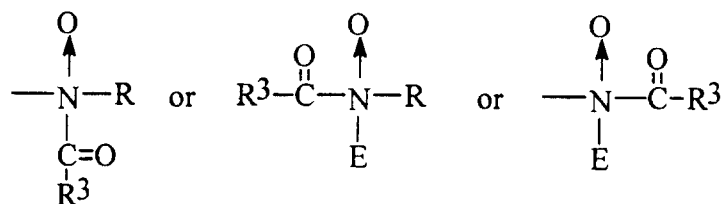
- ii) Substituting preferred R^1 and R^2 into $-(CH_2CH(OR^2)CH_2O)_z-$
 $(R^1O)_yR^1O(CH_2CH(OR^2)CH_2)_w-$ yields $-(CH_2CH(OH)CH_2O)_z-$
 $(CH_2CH_2O)_yCH_2CH_2O(CH_2CH(OH)CH_2)_w-$.
- iii) Substituting preferred R^2 into $-CH_2CH(OR^2)CH_2-$ yields $-CH_2CH(OH)CH_2-$.

E units are selected from the group consisting of hydrogen, C_1 - C_{22} alkyl, C_3 - C_{22} alkenyl, C_7 - C_{22} arylalkyl, C_2 - C_{22} hydroxyalkyl, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, $-(CH_2)_pPO_3M$, $-(R^1O)_mB$, $-C(O)R^3$, preferably hydrogen, C_2 - C_{22} hydroxyalkylene, benzyl, C_1 - C_{22} alkylene, $-(R^1O)_mB$, $-C(O)R^3$, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, more preferably C_1 - C_{22} alkylene, $-(R^1O)_xB$, $-C(O)R^3$, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, most preferably C_1 - C_{22} alkylene, $-(R^1O)_xB$, and $-C(O)R^3$. When no modification or substitution is made on a nitrogen then hydrogen atom will remain as the moiety representing E.

E units do not comprise hydrogen atom when the V, W or Z units are oxidized, that is the nitrogens are N-oxides. For example, the backbone chain or branching chains do not comprise units of the following structure:



Additionally, E units do not comprise carbonyl moieties directly bonded to a nitrogen atom when the V, W or Z units are oxidized, that is, the nitrogens are N-oxides. According to the present invention, the E unit $-C(O)R^3$ moiety is not bonded to an N-oxide modified nitrogen, that is, there are no N-oxide amides having the structure



or combinations thereof.

B is hydrogen, C_1 - C_6 alkyl, $-(CH_2)_qSO_3M$, $-(CH_2)_pCO_2M$, $-(CH_2)_q-$
 $(CHSO_3M)CH_2SO_3M$, $-(CH_2)_q(CHSO_2M)CH_2SO_3M$, $-(CH_2)_pPO_3M$, $-PO_3M$,
 preferably hydrogen, $-(CH_2)_qSO_3M$, $-(CH_2)_q(CHSO_3M)CH_2SO_3M$, $-(CH_2)_q-$
 $(CHSO_2M)CH_2SO_3M$, more preferably hydrogen or $-(CH_2)_qSO_3M$.

M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance. For example, a sodium cation equally satisfies $-(CH_2)_pCO_2M$, and $-(CH_2)_qSO_3M$, thereby resulting in $-(CH_2)_pCO_2Na$, and $-(CH_2)_qSO_3Na$ moieties. More than one monovalent cation, (sodium, potassium, etc.) can be combined to satisfy the

required chemical charge balance. However, more than one anionic group may be charge balanced by a divalent cation, or more than one mono-valent cation may be necessary to satisfy the charge requirements of a poly-anionic radical. For example, a $-(\text{CH}_2)_p\text{PO}_3\text{M}$ moiety substituted with sodium atoms has the formula $-(\text{CH}_2)_p\text{PO}_3\text{Na}_3$. Divalent cations such as calcium (Ca^{2+}) or magnesium (Mg^{2+}) may be substituted for or combined with other suitable mono-valent water soluble cations. Preferred cations are sodium and potassium, more preferred is sodium.

X is a water soluble anion such as chlorine (Cl^-), bromine (Br^-) and iodine (I^-) or X can be any negatively charged radical such as sulfate (SO_4^{2-}) and methosulfate (CH_3SO_3^-).

The formula indices have the following values: p has the value from 1 to 6, q has the value from 0 to 6; r has the value 0 or 1; w has the value 0 or 1, x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1; k is less than or equal to the value of n; m has the value from 4 to about 400, n has the value from 0 to about 200; m + n has the value of at least 5.

The preferred modified polyamines comprise polyamine backbones wherein less than about 50% of the R groups comprise "oxy" R units, preferably less than about 20%, more preferably less than 5%, most preferably the R units comprise no "oxy" R units.

The most preferred polyamines which comprise no "oxy" R units comprise polyamine backbones wherein less than 50% of the R groups comprise more than 3 carbon atoms. For example, ethylene, 1,2-propylene, and 1,3-propylene comprise 3 or less carbon atoms and are the preferred "hydrocarbyl" R units. That is when backbone R units are C_2 - C_{12} alkylene, preferred is C_2 - C_3 alkylene, most preferred is ethylene.

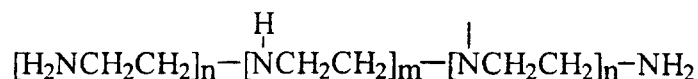
The polyamines of the present invention comprise modified homogeneous and non-homogeneous polyamine backbones, wherein 100% or less of the -NH units are modified. For the purpose of the present invention the term "homogeneous polyamine backbone" is defined as a polyamine backbone having R units that are the same (i.e., all ethylene). However, this sameness definition does not exclude polyamines that comprise other extraneous units comprising the polymer backbone which are present due to an artifact of the chosen method of chemical synthesis. For example, it is known to those skilled in the art that ethanolamine may be used as an "initiator" in the synthesis of polyethyleneimines, therefore a sample of polyethyleneimine that comprises one hydroxyethyl moiety resulting from the polymerization "initiator" would be considered to comprise a homogeneous polyamine backbone for the purposes of the present invention. A polyamine backbone comprising all ethylene R units wherein no branching Y units are present is a homogeneous backbone. A polyamine backbone comprising all ethylene R units is a homogeneous backbone regardless of the degree of branching or the number of cyclic branches present.

For the purposes of the present invention the term "non-homogeneous polymer backbone" refers to polyamine backbones that are a composite of various R unit lengths and R unit types. For example, a non-homogeneous backbone comprises R units that are a mixture of ethylene and 1,2-propylene units. For the purposes of the present invention a mixture of "hydrocarbyl" and "oxy" R units is not necessary to provide a non-homogeneous backbone. The proper manipulation of these "R unit chain lengths" provides the formulator with the ability to modify the solubility and fabric substantivity of the modified polymers.

Preferred polyamines of the present invention comprise homogeneous polyamine backbones that are totally or partially substituted by polyethyleneoxy moieties, totally or partially quaternized amines, nitrogens totally or partially oxidized to N-oxides, and mixtures thereof. However, not all backbone amine nitrogens must be modified in the same manner, the choice of modification being left to the specific needs of the formulator. The degree of ethoxylation is also determined by the specific requirements of the formulator.

The preferred polyamines that comprise the backbone of the compounds of the present invention are generally polyalkyleneamines (PAA's), polyalkyleneimines (PAI's), preferably polyethyleneamine (PEA's), polyethyleneimines (PEI's), or PEA's or PEI's connected by moieties having longer R units than the parent PAA's, PAI's, PEA's or PEI's. A common polyalkyleneamine (PAA) is tetrabutylpentamine. PEA's are obtained by reactions involving ammonia and ethylene dichloride, followed by fractional distillation. The common PEA's obtained are triethylenetetramine (TETA) and tetraethylenepentamine (TEPA). Above the pentamines, i.e., the hexamines, heptamines, octamines and possibly nonamines, the cogenerically derived mixture does not appear to separate by distillation and can include other materials such as cyclic amines and particularly piperazines. There can also be present cyclic amines with side chains in which nitrogen atoms appear. See U.S. Patent 2,792,372, Dickinson, issued May 14, 1957, which describes the preparation of PEA's.

Preferred amine polymer backbones comprise R units that are C₂ alkylene (ethylene) units, also known as polyethylenimines (PEI's). Preferred PEI's have at least moderate branching, that is the ratio of m to n is less than 4:1, however PEI's having a ratio of m to n of about 2:1 are most preferred. Preferred backbones, prior to modification have the general formula:



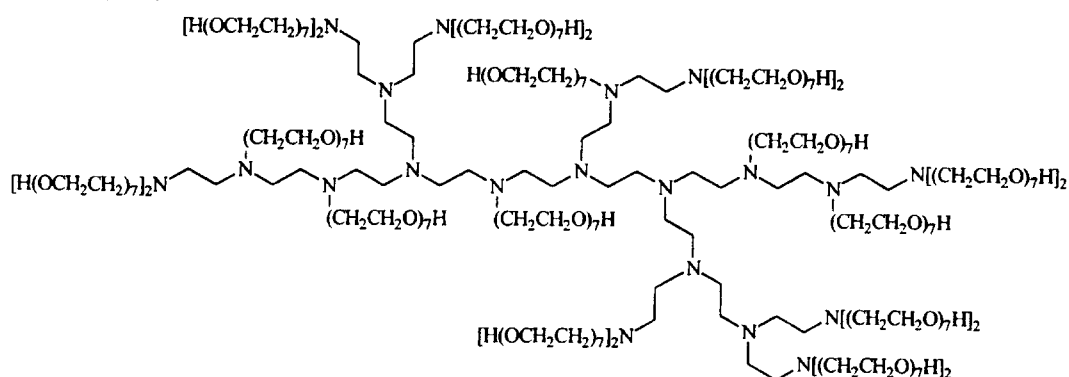
wherein m and n are the same as defined herein above. Preferred PEI's, prior to modification, will have a molecular weight greater than about 200 daltons.

The relative proportions of primary, secondary and tertiary amine units in the polyamine backbone, especially in the case of PEI's, will vary, depending on the manner of preparation. Each hydrogen atom attached to each nitrogen atom of the polyamine backbone chain represents a potential site for subsequent substitution, quaternization or oxidation.

These polyamines can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing these polyamine backbones are disclosed in U.S. Patent 2,182,306, Ulrich et al., issued December 5, 1939; U.S. Patent 3,033,746, Mayle et al., issued May 8, 1962; U.S. Patent 2,208,095, Esselmann et al., issued July 16, 1940; U.S. Patent 2,806,839, Crowther, issued September 17, 1957; and U.S. Patent 2,553,696, Wilson, issued May 21, 1951; all herein incorporated by reference.

Examples of modified polyamines of the present invention comprising PEI's, are illustrated in Formulas I - IV:

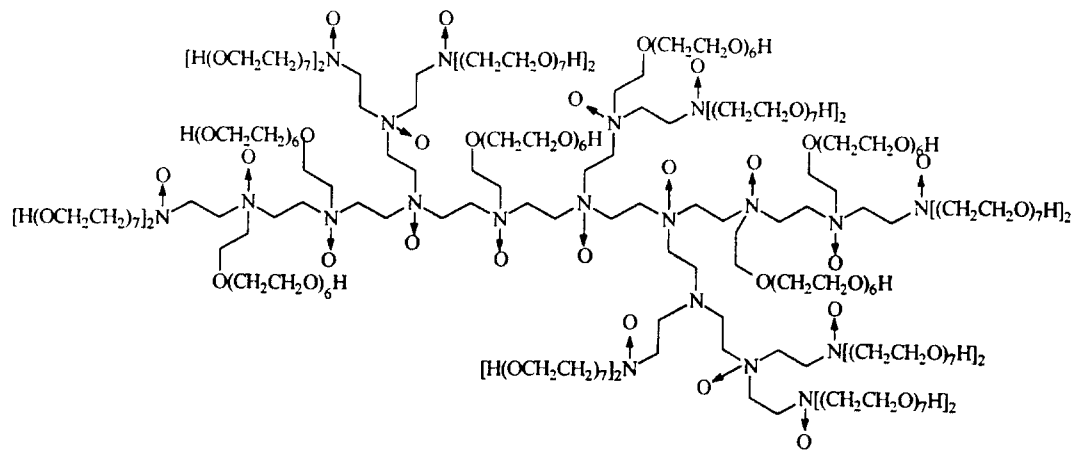
Formula I depicts a polymer comprising a PEI backbone wherein all substitutable nitrogens are modified by replacement of hydrogen with a polyoxyalkyleneoxy unit, $-(\text{CH}_2\text{CH}_2\text{O})_7\text{H}$, having the formula



Formula I

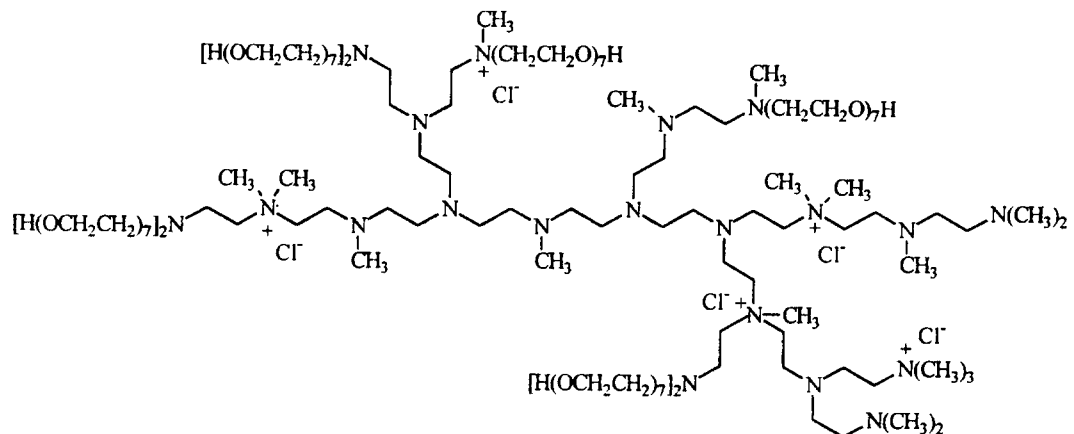
This is an example of a polymer that is fully modified by one type of moiety.

Formula II depicts a polymer comprising a PEI backbone wherein all substitutable primary amine nitrogens are modified by replacement of hydrogen with a polyoxyalkyleneoxy unit, $-(\text{CH}_2\text{CH}_2\text{O})_7\text{H}$, the molecule is then modified by subsequent oxidation of all oxidizable primary and secondary nitrogens to N-oxides, said polymer having the formula



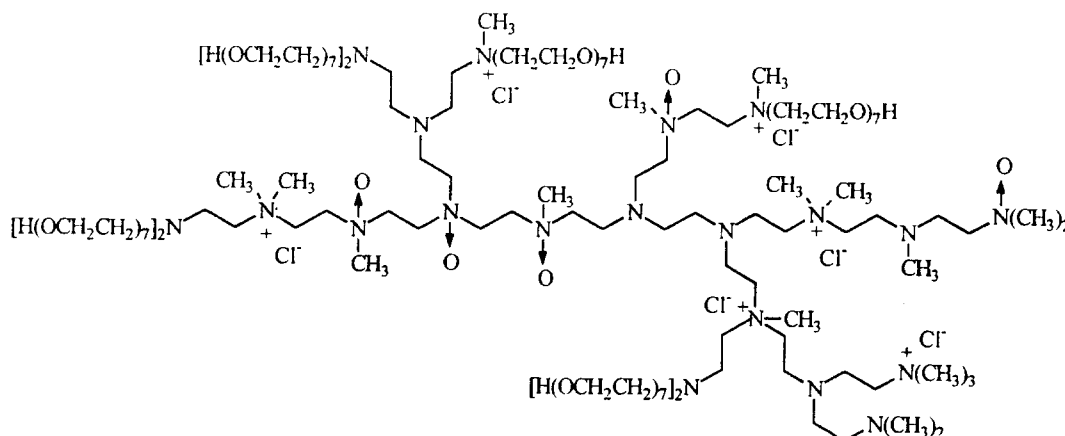
Formula II

Formula III depicts a polymer comprising a PEI backbone wherein all backbone hydrogen atoms are substituted and some backbone amine units are quaternized. The substituents are polyoxyalkyleneoxy units, $-(\text{CH}_2\text{CH}_2\text{O})_7\text{H}$, or methyl groups. The modified PEI polymer has the formula



Formula III

Formula IV depicts a polymer comprising a PEI backbone wherein the backbone nitrogens are modified by substitution (i.e. by $-(\text{CH}_2\text{CH}_2\text{O})_7\text{H}$ or methyl), quaternized, oxidized to N-oxides or combinations thereof. The resulting polymer has the formula



Formula IV

In the above examples, not all nitrogens of a unit class comprise the same modification. The present invention allows the formulator to have a portion of the secondary amine nitrogens ethoxylated while having other secondary amine nitrogens oxidized to N-oxides. This also applies to the primary amine nitrogens, in that the formulator may choose to modify all or a portion of the primary amine nitrogens with one or more substituents prior to oxidation or quaternization. Any possible combination of E groups can be substituted on the primary and secondary amine nitrogens, except for the restrictions described herein above.

Detersive Surfactant Paste Or Acid Precursor

The process employs a surfactant paste in which a detersive surfactant and water are included. This surfactant paste typically has a viscosity of from about 5,000 cps to about 100,000 cps, more preferably from about 10,000 cps to about 80,000 cps, and contains at least about 10% water, more typically at least about 30% water. The viscosity is measured at 70°C and at shear rates of about 10 to 100 sec.⁻¹. Alternatively, the process may employ a liquid acid precursor of an anionic detersive surfactant which is eventually neutralized in the process to contain the surfactant salt and water. Typically, this anionic surfactant will be linear alkylbenzene sulfonate. Optionally, other structuring agents, viscosity modifiers and various other minors may be included in the surfactant paste or acid precursor thereof.

Nonlimiting examples of surfactants useful in the surfactant paste include the conventional C₁₁-C₁₈ alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C₁₀-C₂₀ alkyl sulfates ("AS"), the C₁₀-C₁₈ secondary (2,3) alkyl sulfates of the formula CH₃(CH₂)_x(CHOSO₃⁻M⁺)CH₃ and CH₃(CH₂)_y(CHOSO₃⁻M⁺)CH₂CH₃ where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C₁₀-C₁₈ alkyl alkoxy sulfates ("AE_xS"; especially EO 1-7 ethoxy sulfates), C₁₀-C₁₈ alkyl

alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C₁₀₋₁₈ glycerol ethers, and C₁₂₋₁₈ alpha-sulfonated fatty acid esters or mixtures thereof.

If desired, the conventional nonionic and amphoteric surfactants may be included as adjunct surfactants in the surfactant paste which are the C₁₂₋₁₈ alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C₆₋₁₂ alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy), C₁₂₋₁₈ betaines; the C₁₀₋₁₈ alkyl polyglycosides and their corresponding sulfated polyglycosides, and sulfobetaines ("sultaines"), C₁₀₋₁₈ amine oxides, and the like. The C₁₀₋₁₈ N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C₁₂₋₁₈ N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀₋₁₈ N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C₁₂₋₁₈ glucamides can be used for low sudsing. C₁₀₋₂₀ conventional soaps may also be used. If high sudsing is desired, the branched-chain C₁₀₋₁₆ soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts.

Dry Detergent Material

Dry detergent material such as sodium sulfate or other fillers and a detergent builder are also employed in the process to provide fully formulated detergent compositions. The builder controls the effects of mineral hardness during typical laundering operations. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

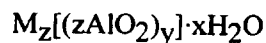
The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least about 1% builder. Granular formulations typically comprise from about 10% to about 80%, more typically from about 15% to about 50% by weight, of the detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the alkali metal silicates, particularly those having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent No. 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6® is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta- Na_2SiO_5 morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $\text{NaMSi}_x\text{O}_{2x+1}\cdot y\text{H}_2\text{O}$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5®, NaSKS-7® and NaSKS-11®, as the alpha, beta and gamma forms. As noted above, the delta- Na_2SiO_5 (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crisping agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

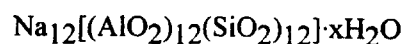
Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:



wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent No. 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites ($x = 0 - 10$) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent No. 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent No. 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent No. 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patent Nos. 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C₅-C₂₀ alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent No. 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent No. 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent No. 3,723,322.

Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundering operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patent Nos. 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

Adjunct Detergent Ingredients

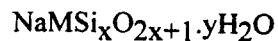
One or more adjunct detergent ingredients can be incorporated in the detergent composition during subsequent steps of the present process invention. These adjunct ingredients include other surfactants such as cationic surfactants, other detergency builders, suds boosters or suds suppressers, anti-tarnish and anticorrosion agents, soil suspending agents, soil release agents, germicides, pH adjusting agents, non-builder alkalinity sources, chelating agents such as diethylene triamine penta acetic acid (DTPA) and diethylene triamine penta(methylene phosphonic acid), smectite clays, enzymes, enzyme-stabilizing agents, dye transfer inhibitors and perfumes. See U.S. Patent 3,936,537, issued February 3, 1976 to Baskerville, Jr. et al., incorporated herein by reference.

Other builders can be generally selected from the various water-soluble, alkali metal, ammonium or substituted ammonium phosphates, polyphosphates, phosphonates, polyphosphonates, carbonates, borates, polyhydroxy sulfonates, polyacetates, carboxylates, and polycarboxylates. Preferred are the alkali metal, especially sodium, salts of the above. Preferred for use herein are the phosphates, carbonates, C₁₀₋₁₈ fatty acids, polycarboxylates, and mixtures thereof. More preferred are sodium tripolyphosphate, tetrasodium pyrophosphate, citrate, tartrate mono- and di-succinates, and mixtures thereof (see below).

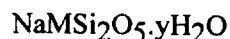
In comparison with amorphous sodium silicates, crystalline layered sodium silicates exhibit a clearly increased calcium and magnesium ion exchange capacity. In addition, the layered sodium silicates prefer magnesium ions over calcium ions, a feature necessary to insure that substantially all of the "hardness" is removed from the wash water. These crystalline layered sodium silicates, however, are generally more expensive than amorphous

silicates as well as other builders. Accordingly, in order to provide an economically feasible laundry detergent, the proportion of crystalline layered sodium silicates used must be determined judiciously.

The crystalline layered sodium silicates suitable for use herein preferably have the formula



wherein M is sodium or hydrogen, x is from about 1.9 to about 4 and y is from about 0 to about 20. More preferably, the crystalline layered sodium silicate has the formula



wherein M is sodium or hydrogen, and y is from about 0 to about 20. These and other crystalline layered sodium silicates are discussed in Corkill et al, U.S. Patent No. 4,605,509, previously incorporated herein by reference.

Specific examples of inorganic phosphate builders are sodium and potassium tripolyphosphate, pyrophosphate, polymeric metaphosphate having a degree of polymerization of from about 6 to 21, and orthophosphates. Examples of polyphosphonate builders are the sodium and potassium salts of ethylene diphosphonic acid, the sodium and potassium salts of ethane 1-hydroxy-1, 1-diphosphonic acid and the sodium and potassium salts of ethane, 1,1,2-triphosphonic acid. Other phosphorus builder compounds are disclosed in U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,422,137; 3,400,176 and 3,400,148, all of which are incorporated herein by reference.

Examples of nonphosphorus, inorganic builders are tetraborate decahydrate and silicates having a weight ratio of SiO_2 to alkali metal oxide of from about 0.5 to about 4.0, preferably from about 1.0 to about 2.4. Water-soluble, nonphosphorus organic builders useful herein include the various alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates and polyhydroxy sulfonates. Examples of polyacetate and polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylene diamine tetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid.

Polymeric polycarboxylate builders are set forth in U.S. Patent 3,308,067, Diehl, issued March 7, 1967, the disclosure of which is incorporated herein by reference. Such materials include the water-soluble salts of homo- and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and methylene malonic acid. Some of these materials are useful as the water-soluble anionic polymer as hereinafter described, but only if in intimate admixture with the non-soap anionic surfactant.

Other suitable polycarboxylates for use herein are the polyacetal carboxylates described in U.S. Patent 4,144,226, issued March 13, 1979 to Crutchfield et al, and U.S.

Patent 4,246,495, issued March 27, 1979 to Crutchfield et al, both of which are incorporated herein by reference. These polyacetal carboxylates can be prepared by bringing together under polymerization conditions an ester of glyoxylic acid and a polymerization initiator. The resulting polyacetal carboxylate ester is then attached to chemically stable end groups to stabilize the polyacetal carboxylate against rapid depolymerization in alkaline solution, converted to the corresponding salt, and added to a detergent composition. Particularly preferred polycarboxylate builders are the ether carboxylate builder compositions comprising a combination of tartrate monosuccinate and tartrate disuccinate described in U.S. Patent 4,663,071, Bush et al., issued May 5, 1987, the disclosure of which is incorporated herein by reference.

Suitable smectite clays for use herein are described in U.S. Patent 4,762,645, Tucker et al, issued August 9, 1988, Column 6, line 3 through Column 7, line 24, incorporated herein by reference. Suitable additional detergency builders for use herein are enumerated in the Baskerville patent, Column 13, line 54 through Column 16, line 16, and in U.S. Patent 4,663,071, Bush et al, issued May 5, 1987, both incorporated herein by reference.

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

Preparation of PEI 1800 E7

This Example illustrates a method by which one of the selected modified polyamines is made. The ethoxylation is conducted in a 2 gallon stirred stainless steel autoclave equipped for temperature measurement and control, pressure measurement, vacuum and inert gas purging, sampling, and for introduction of ethylene oxide as a liquid. A ~20 lb. net cylinder of ethylene oxide (ARC) is set up to deliver ethylene oxide as a liquid by a pump to the autoclave with the cylinder placed on a scale so that the weight change of the cylinder could be monitored.

A 750 g portion of polyethyleneimine (PEI) (Nippon Shokubai, Epomin SP-018 having a listed average molecular weight of 1800 equating to about 0.417 moles of polymer and 17.4 moles of nitrogen functions) is added to the autoclave. The autoclave is then sealed and purged of air (by applying vacuum to minus 28" Hg followed by pressurization with nitrogen to 250 psia, then venting to atmospheric pressure). The autoclave contents are heated to 130 °C while applying vacuum. After about one hour, the autoclave is charged with nitrogen to about 250 psia while cooling the autoclave to about 105 °C. Ethylene oxide is then added to the autoclave incrementally over time while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate. The ethylene oxide pump is turned off and cooling is applied to limit any temperature increase resulting

from any reaction exotherm. The temperature is maintained between 100 and 110 °C while the total pressure is allowed to gradually increase during the course of the reaction. After a total of 750 grams of ethylene oxide has been charged to the autoclave (roughly equivalent to one mole ethylene oxide per PEI nitrogen function), the temperature is increased to 110 °C and the autoclave is allowed to stir for an additional hour. At this point, vacuum is applied to remove any residual unreacted ethylene oxide.

Next, vacuum is continuously applied while the autoclave is cooled to about 50 °C while introducing 376 g of a 25% sodium methoxide in methanol solution (1.74 moles, to achieve a 10% catalyst loading based upon PEI nitrogen functions). The methoxide solution is sucked into the autoclave under vacuum and then the autoclave temperature controller setpoint is increased to 130 °C. A device is used to monitor the power consumed by the agitator. The agitator power is monitored along with the temperature and pressure. Agitator power and temperature values gradually increase as methanol is removed from the autoclave and the viscosity of the mixture increases and stabilizes in about 1 hour indicating that most of the methanol has been removed. The mixture is further heated and agitated under vacuum for an additional 30 minutes.

Vacuum is removed and the autoclave is cooled to 105 °C while it is being charged with nitrogen to 250 psia and then vented to ambient pressure. The autoclave is charged to 200 psia with nitrogen. Ethylene oxide is again added to the autoclave incrementally as before while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate while maintaining the temperature between 100 and 110 °C and limiting any temperature increases due to reaction exotherm. After the addition of 4500 g of ethylene oxide (resulting in a total of 7 moles of ethylene oxide per mole of PEI nitrogen function) is achieved over several hours, the temperature is increased to 110 °C and the mixture stirred for an additional hour.

The reaction mixture is then collected in nitrogen purged containers and eventually transferred into a 22 L three neck round bottomed flask equipped with heating and agitation. The strong alkali catalyst is neutralized by adding 167 g methanesulfonic acid (1.74 moles). The reaction mixture is then deodorized by passing about 100 cu. ft. of inert gas (argon or nitrogen) through a gas dispersion frit and through the reaction mixture while agitating and heating the mixture to 130 °C. The final reaction product is cooled slightly and collected in glass containers purged with nitrogen. In other preparations the neutralization and deodorization is accomplished in the reactor before discharging the product.

EXAMPLE II

Formation of amine oxide of PEI 1800 E7

This Example illustrates another method by which one of the selected modified polyamines is made. To a 500 mL Erlenmeyer flask equipped with a magnetic stirring bar is added polyethyleneimine having a molecular weight of 1800 and ethoxylated to a degree of about 7 ethoxy groups per nitrogen (PEI-1800, E₇) (209 g, 0.595 mole nitrogen, prepared as in Example I), and hydrogen peroxide (120 g of a 30 wt % solution in water, 1.06 mole). The flask is stopped, and after an initial exotherm the solution is stirred at room temperature overnight. ¹H-NMR (D₂O) spectrum obtained on a sample of the reaction mixture indicates complete conversion. The resonances ascribed to methylene protons adjacent to unoxidized nitrogens have shifted from the original position at ~2.5 ppm to ~3.5 ppm. To the reaction solution is added approximately 5 g of 0.5% Pd on alumina pellets, and the solution is allowed to stand at room temperature for approximately 3 days. The solution is tested and found to be negative for peroxide by indicator paper. The material as obtained is suitably stored as a 51.1% active solution in water.

EXAMPLE III

Preparation of PEI 1200 E₇

This Example illustrates yet another method by which one of the selected modified polyamines is made. The ethoxylation is conducted in a 2 gallon stirred stainless steel autoclave equipped for temperature measurement and control, pressure measurement, vacuum and inert gas purging, sampling, and for introduction of ethylene oxide as a liquid. A ~20 lb. net cylinder of ethylene oxide (ARC) is set up to deliver ethylene oxide as a liquid by a pump to the autoclave with the cylinder placed on a scale so that the weight change of the cylinder could be monitored. A 750 g portion of polyethyleneimine (PEI) (having a listed average molecular weight of 1200 equating to about 0.625 moles of polymer and 17.4 moles of nitrogen functions) is added to the autoclave. The autoclave is then sealed and purged of air (by applying vacuum to minus 28" Hg followed by pressurization with nitrogen to 250 psia, then venting to atmospheric pressure). The autoclave contents are heated to 130 °C while applying vacuum. After about one hour, the autoclave is charged with nitrogen to about 250 psia while cooling the autoclave to about 105 °C. Ethylene oxide is then added to the autoclave incrementally over time while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate. The ethylene oxide pump is turned off and cooling is applied to limit any temperature increase resulting from any reaction exotherm. The temperature is maintained between 100 and 110 °C while the total pressure is allowed to gradually increase during the course of the reaction. After a total of 750 grams of ethylene oxide has been charged to the autoclave (roughly equivalent to one mole ethylene oxide per PEI nitrogen function), the temperature is increased to 110 °C and the autoclave is allowed to stir for an additional hour. At this point, vacuum is applied to remove any residual unreacted ethylene oxide.

Next, vacuum is continuously applied while the autoclave is cooled to about 50 °C while introducing 376 g of a 25% sodium methoxide in methanol solution (1.74 moles, to achieve a 10% catalyst loading based upon PEI nitrogen functions). The methoxide solution is sucked into the autoclave under vacuum and then the autoclave temperature controller setpoint is increased to 130 °C. A device is used to monitor the power consumed by the agitator. The agitator power is monitored along with the temperature and pressure. Agitator power and temperature values gradually increase as methanol is removed from the autoclave and the viscosity of the mixture increases and stabilizes in about 1 hour indicating that most of the methanol has been removed. The mixture is further heated and agitated under vacuum for an additional 30 minutes.

Vacuum is removed and the autoclave is cooled to 105 °C while it is being charged with nitrogen to 250 psia and then vented to ambient pressure. The autoclave is charged to 200 psia with nitrogen. Ethylene oxide is again added to the autoclave incrementally as before while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate while maintaining the temperature between 100 and 110 °C and limiting any temperature increases due to reaction exotherm. After the addition of 4500 g of ethylene oxide (resulting in a total of 7 moles of ethylene oxide per mole of PEI nitrogen function) is achieved over several hours, the temperature is increased to 110 °C and the mixture stirred for an additional hour. The reaction mixture is then collected in nitrogen purged containers and eventually transferred into a 22 L three neck round bottomed flask equipped with heating and agitation. The strong alkali catalyst is neutralized by adding 167 g methanesulfonic acid (1.74 moles). The reaction mixture is then deodorized by passing about 100 cu. ft. of inert gas (argon or nitrogen) through a gas dispersion frit and through the reaction mixture while agitating and heating the mixture to 130 °C. The final reaction product is cooled slightly and collected in glass containers purged with nitrogen. In other preparations the neutralization and deodorization is accomplished in the reactor before discharging the product.

EXAMPLE IV

A modified polyamine is made in accordance with Example I ("PEI1800 E7") and used in the process of the current invention to form an agglomerated detergent composition. An in-line static mixer is used into which the PEI1800 E7 is added continuously along with a sodium linear alkylbenzene sulfonate ("LAS") surfactant paste (60% LAS and balance water) at about 60°C in order to completely mix the ingredients, wherein the pH of the premix is maintained at about 7 to 10. Thereafter, the premix are continuously fed to a high speed mixer/densifier (Lödige CB-30, commercially available from Lödige) along with sodium aluminosilicate (zeolite) 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 6 minutes. 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 is set forth in Table I below:

TABLE I

<u>Component</u>	<u>% Weight</u>
C ₁₂₋₁₃ linear alkylbenzene sulfonate	29.1
Sodium aluminosilicate	34.4
Sodium carbonate	17.5
Polyethylene glycol (MW 4000)	1.3
PEI1800 E7	1.0
Misc. (water, etc.)	<u>15.7</u>
	100.0

Performance testing for multi-cycle whiteness maintenance is conducted using standard laundry testing techniques with test swatches of fabrics with various fiber contents. Unexpectedly, the agglomerated detergent compositions made by a process in accordance with the invention wherein the PEI1800 E7 is premixed with LAS in the premixer exhibit significantly improved cleaning performance compared to compositions made by process outside the scope of the present invention.

EXAMPLE V

A modified polyamine polymer is made in accordance with Example I ("PEI1800E7") and used in another aspect of the current invention to form an agglomerated detergent composition. An in-line static mixer is used into which the PEI1800E7 is added continuously along with the acid form of linear alkylbenzene sulfonate ("HLAS") in order to form a completely mixed premix. Thereafter the premix is continuously fed to a high speed mixer/densifier (Lödige CB-30, commercially available from Lödige), along with sodium carbonate and other dry detergent materials. Non-limiting examples of useful dry detergent materials include sodium aluminosilicate (zeolite) sodium tripoly phosphate (STPP) and sodium sulfate.

The rotational speed of the shaft in the Lödige CB-30 mixer/densifier is about 1400 rpm and the mean residence time about 10 seconds. The contents from 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 6 minutes. The detergent agglomerates are then screened with conventional screening apparatus resulting in a uniform particle size distribution. The composition of the detergent agglomerates exiting is set forth in Table 2 below:

Table 2

<u>Component</u>	<u>% Weight</u>
C ₁₂₋₁₃ linear alkylbenzene sulfonate	20.0 %
Sodium Carbonate	18.0 %
PEI1800E7	0.5 %
Sodium aluminosilicate	16.0 %
Sodium tripoly phosphate	35.0 %
Sodium sulfate	3.5 %
Misc. (Water, etc.)	<u>7.0%</u>
Total:	100.0 %

Performance testing for multi-cycle whiteness maintenance is conducted using standard laundry testing techniques with test swatches of fabrics with various fiber contents.

Unexpectedly, the agglomerated detergent compositions made by a process in accordance with this aspect of the invention wherein the PEI1800E7 is premixed with the HLAS in the premixer exhibits significantly improved cleaning performance compared to compositions made by process outside the scope of the present invention.

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.

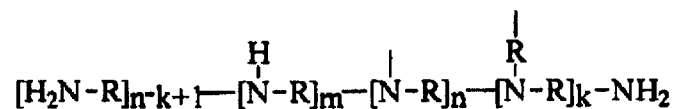
WHAT IS CLAIMED IS:

1. A process for producing an agglomerated detergent composition characterized by the steps of:

- (a) premixing a deterative surfactant paste, dry detergent material and a water-soluble or dispersible, modified polyamine in a premixer to form a premix, said modified polyamine having a polyamine backbone corresponding to the formula:

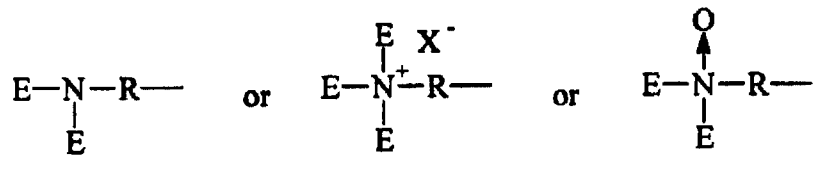


having a modified polyamine formula $V_{(n+1)}W_mY_nZ$ or a polyamine backbone corresponding to the formula:

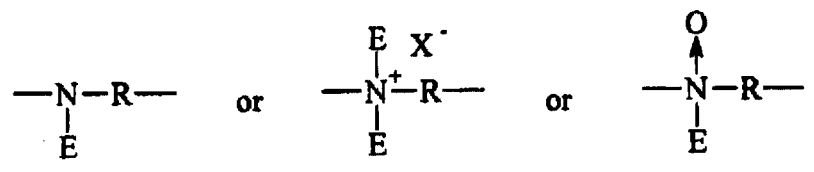


having a modified polyamine formula $V_{(n-k+1)}W_mY_nY'_kZ$, wherein k is less than or equal to n , said polyamine backbone prior to modification has a molecular weight greater than 200 daltons, wherein

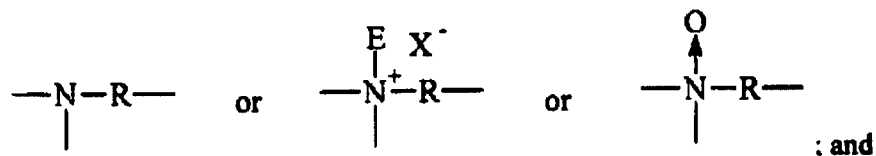
- i) V units are terminal units having the formula:



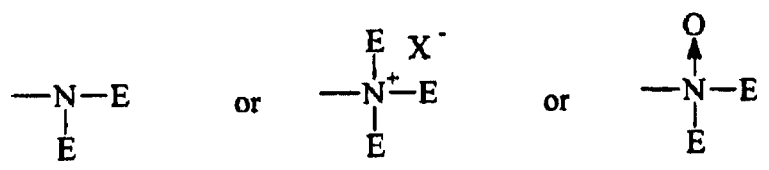
- ii) W units are backbone units having the formula:



- iii) Y units are branching units having the formula:



- iv) Z units are terminal units having the formula:



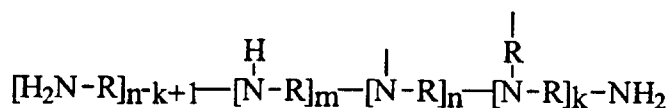
wherein backbone linking R units are selected from the group consisting of C₂-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxy-alkylene, C₈-C₁₂ dialkylarylene, $-(R^1O)_xR^1-$, $-(R^1O)_xR^5(OR^1)_x-$, $-(CH_2CH(OR^2)CH_2O)_z(R^1O)_yR^1(OCH_2CH(OR^2)CH_2)_w-$, $-C(O)(R^4)_rC(O)-$, $-CH_2CH(OR^2)CH_2-$, and mixtures thereof; wherein R¹ is C₂-C₆ alkylene and mixtures thereof; R² is hydrogen, $-(R^1O)_xB$, and mixtures thereof; R³ is C₁-C₁₈ alkyl, C₇-C₁₂ arylalkyl, C₇-C₁₂ alkyl substituted aryl, C₆-C₁₂ aryl, and mixtures thereof; R⁴ is C₁-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₈-C₁₂ arylalkylene, C₆-C₁₀ arylene, and mixtures thereof; R⁵ is C₁-C₁₂ alkylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxy-alkylene, C₈-C₁₂ dialkylarylene, $-C(O)-$, $-C(O)NHR^6NHC(O)-$, $-R^1(OR^1)-$, $-C(O)(R^4)_rC(O)-$, $-CH_2CH(OH)CH_2-$, $-CH_2CH(OH)CH_2O(R^1O)_yR^1OCH_2CH(OH)CH_2-$, and mixtures thereof; R⁶ is C₂-C₁₂ alkylene or C₆-C₁₂ arylene; E units are selected from the group consisting of hydrogen, C₁-C₂₂ alkyl, C₃-C₂₂ alkenyl, C₇-C₂₂ arylalkyl, C₂-C₂₂ hydroxy-alkyl, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, $-(CH_2)_pPO_3M$, $-(R^1O)_xB$, $-C(O)R^3$, and mixtures thereof; oxide; B is hydrogen, C₁-C₆ alkyl, $-(CH_2)_qSO_3M$, $-(CH_2)_pCO_2M$, $-(CH_2)_q(CHSO_3M)CH_2SO_3M$, $-(CH_2)_q-(CHSO_2M)CH_2SO_3M$, $-(CH_2)_pPO_3M$, $-PO_3M$, and mixtures thereof; M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance; X is a water soluble anion; m has the value from 4 to 400; n has the value from 0 to 200; p has the value from 1 to 6, q has the value from 0 to 6; r has the value of 0 or 1; w has the value 0 or 1; x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1; and

- (b) agglomerating said premix initially in a high speed mixer/densifier and subsequently in a moderate speed mixer/densifier so as to form agglomerates, thereby resulting in said detergent composition.
2. The process of claim 1 wherein the pH of said premix is in a range from 8 to 10.
 3. The process of claims 1-2 wherein said modified polyamine is present in an amount of from 0.01% to 10% by weight of said detergent composition.
 4. The process of claims 1-3 wherein said premixing step is performed for at least 5 seconds.

5. The process of claims 1-4 wherein said surfactant paste has a viscosity of from 5,000 cps to 100,000 cps and contains from 70% to 95%, by weight of said surfactant paste, of a deterative surfactant and the balance water and adjunct ingredients.
6. The process of claims 1-5 wherein said dry detergent material includes a detergent builder selected from the group consisting of carbonates, phosphates, citrates, aluminosilicates, and mixtures thereof.
7. The process of claims 1-6 further characterized by the step of drying said agglomerates.
8. The process of claims 1-7 wherein said agglomerates have a density of at least 650 g/l.
9. The process of claims 1-9 wherein R is C₂-C₁₂ alkylene.
10. A process for producing an agglomerated detergent composition characterized by the steps of:
- (a) premixing an acid precursor of a deterative surfactant, dry detergent material and a water-soluble or dispersible, modified polyamine in a mixer to form a premix, said modified polyamine having a polyamine backbone corresponding to the formula:

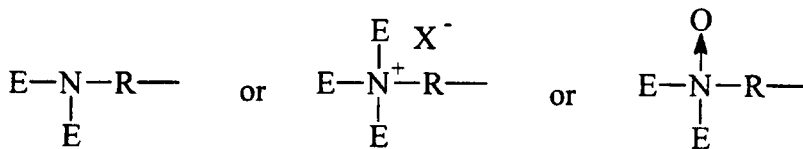


having a modified polyamine formula $V_{(n+1)}W_mY_nZ$ or a polyamine backbone corresponding to the formula:

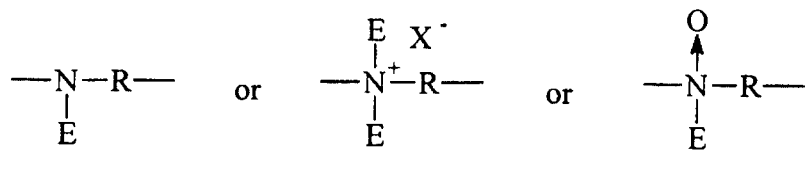


having a modified polyamine formula $V_{(n-k+1)}W_mY_nY'_kZ$, wherein k is less than or equal to n, said polyamine backbone prior to modification has a molecular weight greater than 200 daltons, wherein

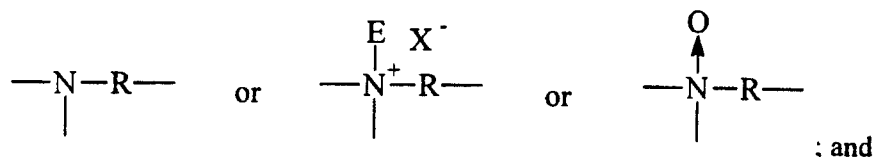
- i) V units are terminal units having the formula:



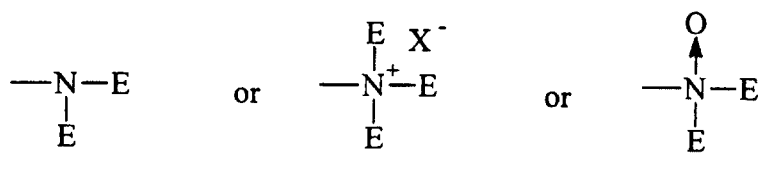
- ii) W units are backbone units having the formula:



iii) Y units are branching units having the formula:



iv) Z units are terminal units having the formula:



wherein backbone linking R units are selected from the group consisting of C₂-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxy-alkylene, C₈-C₁₂ dialkylarylene, -(R¹O)_xR¹-, -(R¹O)_xR⁵(OR¹)_x-, -(CH₂CH(OR²)CH₂O)_z(R¹O)_yR¹(OCH₂CH(OR²)CH₂)_w-, -C(O)(R⁴)_rC(O)-, -CH₂CH(OR²)CH₂-, and mixtures thereof; wherein R¹ is C₂-C₆ alkylene and mixtures thereof; R² is hydrogen, -(R¹O)_xB, and mixtures thereof; R³ is C₁-C₁₈ alkyl, C₇-C₁₂ arylalkyl, C₇-C₁₂ alkyl substituted aryl, C₆-C₁₂ aryl, and mixtures thereof; R⁴ is C₁-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₈-C₁₂ arylalkylene, C₆-C₁₀ arylene, and mixtures thereof; R⁵ is C₁-C₁₂ alkylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxy-alkylene, C₈-C₁₂ dialkylarylene, -C(O)-, -C(O)NHR⁶NHC(O)-, -R¹(OR¹)-, -C(O)(R⁴)_rC(O)-, -CH₂CH(OH)CH₂-, -CH₂CH(OH)CH₂O(R¹O)_yR¹OCH₂CH(OH)CH₂-, and mixtures thereof; R⁶ is C₂-C₁₂ alkylene or C₆-C₁₂ arylene; E units are selected from the group consisting of hydrogen, C₁-C₂₂ alkyl, C₃-C₂₂ alkenyl, C₇-C₂₂ arylalkyl, C₂-C₂₂ hydroxyalkyl, -(CH₂)_pCO₂M, -(CH₂)_qSO₃M, -CH(CH₂CO₂M)CO₂M, -(CH₂)_pPO₃M, -(R¹O)_xB, -C(O)R³, and mixtures thereof; oxide; B is hydrogen, C₁-C₆ alkyl, -(CH₂)_qSO₃M, -(CH₂)_pCO₂M, -(CH₂)_q(CHSO₃M)CH₂SO₃M, -(CH₂)_q-(CHSO₂M)CH₂SO₃M, -(CH₂)_pPO₃M, -PO₃M, and mixtures thereof; M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance; X is a water soluble anion; m has the value from 4 to 400; n has the value from 0 to 200; p has the value from 1 to 6, q has the value from 0 to 6; r has the value of 0 or 1; w has the value 0 or 1; x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1;

- (b) inputting said premix into a high speed mixer/densifier and neutralizing said acid precursor to form agglomerates; and
- (c) agglomerating said agglomerates further in a moderate speed mixer/densifier so as to form said detergent composition.