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[54] **PARTICULATE SILICATE-HYDROXYALKYL IMINODIACETATE BUILT DETERGENT COMPOSITIONS OF IMPROVED PROPERTIES**

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[57] **ABSTRACT**

A particulate heavy duty synthetic organic detergent which has improved aging properties includes a synthetic organic detergent of the anionic or nonionic type or a mixture thereof and a builder which is a hydroxyalkyl iminodicarboxylate hydrate. In preferred compositions the iminodicarboxylate hydrate is disodium 2-hydroxyethyl iminodiacetate hexahydrate, the detergent is a mixture of linear higher alkyl benzene sulfonate and higher fatty alcohol polyethoxylate and the detergent composition includes sodium silicate, sodium carbonate, sodium carboxymethyl cellulose, sodium sulfate and moisture. The described products are of better storage and aging properties than products of similar formulas in which the iminodicarboxylate is present but not as a hydrate.

Also within the invention are methods for the manufacture of the described compositions in which all the formula except the iminodicarboxylate hydrate is spray dried from an aqueous crutcher mix to globular particles which are then mixed with iminodicarboxylate hydrate particles of similar sizes.

14 Claims, No Drawings

PARTICULATE SILICATE-HYDROXYALKYL IMINODIACETATE BUILT DETERGENT COMPOSITIONS OF IMPROVED PROPERTIES

This invention relates to heavy duty synthetic organic detergent compositions and methods for their manufacture. More particularly, it is of such detergent compositions which are of reduced caking tendencies despite their contents of an iminodicarboxylate builder salt which would normally be expected to cause caking of the detergent or aging.

Synthetic organic detergent compositions, whether based on anionic or nonionic organic detergent products, usually include a builder salt to improve detergency. Various phosphates, borax compounds, carbonates and silicates have been found to have building properties and of these, the phosphates, especially pentasodium tripolyphosphate, until recent years was acknowledged to be far superior. However, due to opinions that phosphates in detergents contribute to eutrophication of inland waters, causing excessive algae growths, and because of government regulations, efforts have been made to produce non-phosphate detergents including substitutes for pentasodium tripolyphosphate. One such substitute, trisodium nitrilotriacetate (NTA), is not being used in the United States because of an interpretation of certain test results as indicating that it would, under certain circumstances, be carcinogenic.

Experiments have been run using iminodicarboxylates as builders for anionic and nonionic detergents in non-phosphate compositions and while such materials allow the production of detergents which wash satisfactorily, they possess other disadvantages which have interfered with their large scale acceptance. In another patent application, entitled MANUFACTURE OF IMPROVED AQUEOUS ALKALI METAL SILICATE-ALKALI METAL HYDROXYALKYL IMINODIACETATE COMPOSITIONS, filed by me concurrently with the present application, a method of avoiding production of gels and precipitates when admixing iminodicarboxylates and silicate components of detergent compositions has been described. In addition to the gelation or precipitation problem it has also been noted that the iminodicarboxylates tend to become tacky or to cake on storage, possibly due to hydrate formation. Therefore, the product used by the consumer may be in unacceptable physical condition, being caked into a solid or exhibiting a lumpy appearance. Accordingly, efforts have been made to improve the caking and flow properties of such detergents, leading to the discovery of the present solution which, surprisingly, allows the production of the desired phosphate-free built heavy duty detergent compositions based on iminodicarboxylate builder salts by utilization of a hydrate of such iminodicarboxylate and post addition thereof to the rest of the detergent composition.

In accordance with the present invention a particulate heavy duty synthetic organic detergent composition of reduced caking tendency (compared to a control composition containing anhydrous iminodiacetate) comprises a synthetic organic detergent selected from the group consisting of anionic and nonionic synthetic organic detergents and mixtures thereof and, as a builder therefor, a hydroxyalkyl iminodicarboxylate hydrate. Preferably, the detergent is phosphate-free and NTA-free and includes from 5 to 30 parts of sodium linear higher alkyl benzene sulfonate, 1 to 8 parts of higher fatty alcohol poly-lower alkoxylate detergent, 5 to 30 parts of sodium silicate of an $Na_2O:SiO_2$ ratio in the range of 1:2.0 to 1:2.7, 4 to 20 parts of sodium carbonate, 0.3 to 3 parts of sodium carboxymethyl cellulose, 1 to 15 parts of moisture and 5 to 40 parts of sodium sulfate in spray dried detergent beads and 15 to 50 parts of disodium 2-hydroxyethyl iminodiacetate hexahydrate in separate particles, all of the particles being within the range of 6 to 100 mesh, U.S. Standard Sieve Series.

A method of manufacture of the desired detergents comprises making particles of the heavy duty synthetic organic detergent composition components exclusive of the hydroxyalkyl iminodicarboxylate, preferably by spray drying such materials, and admixing with them particles of hydroxyalkyl iminodicarboxylate hydrate of approximately the same particle size, usually within the 6 to 140 mesh range.

The detergent compositions of the present invention include as a primary detersive constituent an anionic synthetic organic detergent or a nonionic organic detergent but preferably, these are employed in mixture. The anionic detergent may include the various materials listed in that category, as described in McCutcheon's *Detergents and Emulsifiers* 1969 *Annual*, in which such compounds are listed by chemical formulas and trade names. They may also include those anionic detergents described in the test *Surface Active Agents and Detergents*, Vol. II, by Schwartz, Perry and Berch (Interscience Publishers, 1958). In short, such materials include hydrophilic and lipophilic groupings, the lipophilic portions whereof normally contain a higher hydrocarbyl chain, usually of 10 to 20 carbon atoms and the hydrophilic portions of which include a salt-forming ion, preferably an alkali metal salt. Most of such useful detergents are sulfates or sulfonates but corresponding phosphates, phosphonates and other suitable detergent salts are also useful. Included among the anionic detergents, for example, are the linear higher alkyl benzene sulfonates, the branched chain higher alkyl benzene sulfonates (although these are not usually sufficiently biodegradable to be acceptable in modern detergent formulations), the higher fatty alkyl sulfates, the higher fatty acid monoglyceride sulfates, the higher olefin sulfonates, the higher alkyl sulfonates, the sulfated phenoxy polyethoxyethanols, the sulfated higher fatty alcohol poly-lower alkoxy alkanols, paraffin sulfonates and the corresponding phosphates and phosphonates. The hydrocarbyls, alkyls and higher fatty acyl groups of such compounds will generally be of 12 to 18 carbon atoms and the salt-forming ions thereof will preferably be alkali metal, although alkanolamines and alkylamines may also be utilized. The sulfated nonionics are preferably those in which the alkyls are of two or three carbon atoms per unit. Specific exemplifications of such compounds include sodium linear tridecyl benzene sulfonate; triethanolamine lauryl sulfate; potassium stearate; sodium phenoxy polyethoxyethanol wherein the polyethoxyethanol chain is of 15 units; sodium coconut oil fatty acids monoglyceride sulfate; and potassium tallow sulfonate. Of these materials it is highly preferred to employ the linear higher alkyl benzene sulfonates wherein the alkyls are of 12 to 15 carbon atoms, most preferably about 13 carbon atoms, and in which the salt-forming ion is alkali metal, preferably sodium. The sodium salts tend to make harder detergent products which are

more freely flowing than those of the alkylamines, alkanolamines and potassium. They also tend to cake less.

Instead of the anionic detergents or in addition to them nonionic detergents may also be utilized. These include condensation products of higher fatty alcohols with polyoxy-lower alkylene glycols, such as Neodol 45-11, Plurafac B-26 and Alfonic 1618-65. Also useful, normally as a proportion of a nonionic detergent content, are Neodols 25-3 and 25-7. Such compounds are hydroxy-containing linear polymers of lower (1–4 C's) alkylene oxides and are normally liquid or semi-solid at room temperature. Also useful are the block copolymers of propylene glycol, propylene oxide and ethylene oxide, such as the Pluronics, e.g., Pluronic L-44 and Pluronic F-68; and the middle alkyl phenyl polyoxyethylene ethanols, such as those sold as Igepals. Normally, the content of nonionic detergents, such as those which are condensation products of higher fatty alcohol and alkylene oxide, e.g., the Neodols of 12 to 15 carbon atoms in the higher fatty alcohol and including from 3 to 15 moles of alkylene oxide per mole of fatty alcohol, will be less than the anionic detergent content of the product and preferably will be about one-half or less of such content, e.g., 10 to 50% thereof.

Although the anionic detergents may be employed alone and solid forms of nonionic detergents may be utilized by themselves, the nonionic detergents are normally liquid or pasty in nature and do not make as satisfactory primary detergent constituents as the anionic compounds. Yet, they do contribute desirable cleaning properties and accordingly, are preferably employed in admixture with the anionic detergents, normally with the nonionic component being present to a greater extent.

An important constituent of the detergents is the alkali metal silicate component. Such compounds are water soluble and are useful as builders for the synthetic organic detergents. They exert alkalizing effects, help to counteract water hardness and have both an independent detersive effect and the property of improving the effect of the anionic and nonionic detergents utilized, especially when these are employed in mixture. When the particular higher fatty alcohol-polylower alkylene oxide nonionic detergent condensates of the present invention are employed with the silicates and linear higher alkyl benzene sulfonates a product can be made which is comparable to previously highly superior phosphate-built linear alkyl benzene sulfonate (LAS) compositions. Additionally, the silicates have a corrosion inhibiting effect.

The silicates employed are water soluble. Of the inorganic silicates those which are water soluble are the silicates of alkali metals, e.g., sodium, potassium. Silicates of $M_2O:SiO_2$ ratios are available in the range of 1:1 to 1:4 but for practical purposes those which are used for detergent compositions are generally of such ratios of 1:1.6 to 1:3, preferably 1:2 to 1:2.4 and most preferably about 1:2.0. In the preceding formulas M stands for alkali metal, preferably sodium or potassium. The sodium silicates are preferred for use in solid or particulate detergent products and the potassium silicates are generally preferred in liquid compositions, although, especially when mixtures are utilized, either may be employed in both types of compositions.

The various silicates described are usually supplied as aqueous solutions although it is within the present invention to employ solid or particulate silicates too, normally after dissolving them in water. The concentrations of the aqueous solutions will usually be those which are as high as possible and at which the solution is readily pumpable. Normally, from 20 to 50% by weight of sodium silicate will be employed, preferably from 35 to 45% by weight thereof. With respect to a preferred silicate, that of $Na_2O:SiO_2$ ratio of 1:2.4, the concentration will most preferably be from 40 to 45%.

Another detergent builder found to be highly desirable in the non-tacky and free flowing particulate compositions is alkali metal carbonate. This will normally be utilized in the anhydrous form but hydrates such as washing soda may also be employed, providing that the excess moisture will be removed therefrom during the drying process. Alkali metal sesquicarbonates and bicarbonates may be employed as substitutes for the carbonates providing that the crutching and drying operations will essentially convert these to the alkali metal carbonate. Of the alkali metals, e.g., sodium, potassium, it is generally preferable to employ the sodium salt. Sodium carbonate has the useful effects of increasing the pH of the crutcher mix before spray drying and of giving the detergent product and the wash water desirable high pH's. It also helps to improve product flow and storage properties, serving to sorb moisture without objectionable caking.

To improve the cleaning power of the detergent and to help to maintain the beads in smooth, regular, globular and stable form an organic gum anti-redeposition agent such as sodium carboxymethyl cellulose, polyvinyl alcohol, hydroxymethyl ethyl cellulose, polyvinyl pyrrolidone, polyacrylamide or hydroxypropyl ethyl cellulose or mixtures thereof may be utilized. Such materials are well known in the art and other equivalents need not be described at length here.

Also of importance in improving flowability of detergent particles, in addition to the carbonates, are the filler salts, which are often used. These include primarily sodium sulfate and sodium chloride, although other such alkali metal sulfates chlorides, nitrates, borates, acetates, gluconates, citrates and many other water soluble salts may be employed as fillers and in some cases may have additional functions in the detergent, e.g., sequestering, solubilizing and buffering actions. Finally, suitable adjuvants may also be utilized such as sanitizers, e.g., trichlorocarbanalide; coloring agents, e.g., dyes and pigments; foam improvers, e.g., lauric diethanolamide; foam depressants, e.g., silicones; fungicides, e.g., polyhalosalicylanilides; antioxidants, e.g., stannic chloride; stabilizers; chelating agents; optical bleaches or fluorescent brighteners; solvents; hydrotropes; and perfumes.

The materials previously described may for the most part be compounded together in a mixture and spray dried into homogeneous detergent beads absent any iminodicarboxylate. In some cases it may be desirable to post-add some of these materials or proportions thereof and such processing method will be described at greater length later herein.

The iminodicarboxylate compounds of this invention are water soluble hydroxylalkyl iminodicarboxylates wherein the carboxyls are of 2 to 4 carbon atoms, preferably 2 to 3 carbon atoms and most preferably from actetic acid. Such materials are found to be excellent builders for synthetic organic detergents and have desirable sequestering effects against water hardness ions, such calcium and magnesium, which might otherwise interfere with detersive actions of the organic detergent. The hydroxyalkyl iminodiacetates generally em-

ployed are alkali metal salts, usually diacetates, although other solubilizing cations may also be present, at least in partial substitution for the alkali metal salts. Of the alkali metal salts the sodium and potassium salts are preferred, with the sodium salt being that of greater preference for solid or particulate compositions and the potassium salts being better for liquid preparations. Exemplary of other solubilizing cations are mono-, di- and tri-alkanolammonium and mono-, di- and trialkylammonium, where the alkyls and alkanols are lower, usually of 1 to 4 carbon atoms and preferably of 1 to 3 carbon atoms, most preferably being of 2 carbon atoms. Examples of such materials are di-triethanolammonium 2-hydroxyethyl iminodiacetate and dimonoisopropylammonium 3-hydroxypropyl-N-iminodiacetate. Di-ammonium iminodiacetates substituted with the hydroxyalkyls are also used.

The hydroxyalkyl of the hydroxyalkyl iminodiacetate is hydroxy-lower alkyl wherein the lower alkyl is of 1 to 4 carbon atoms, preferably of 2 to 3 carbon atoms and most preferably, ethanol. Although the hydroxyl needs not be terminal on the ethyl, for best effects this positioning is desirable.

Although the described iminodicarboxylates are available in solutions and sometimes as anhydrous solids and are useful in such forms in various detergent compositions or processes, in accordance with the present invention it is important that the anhydrous form not be utilized and that the iminodicarboxylates be present in the final detergent compositions as hydrates. Such hydrates are usually polyhydrates, of which the most preferred is disodium 2-hydroxyethyl iminodiacetate hexahydrate. Generally, the various polyhydrates will contain from 3 to 10 moles of water per mole of iminodicarboxylate.

The non-iminodiacetate portion of the detergent composition will usually comprise from 5 to 30 parts of the anionic detergent and/or 1 to 10 parts of nonionic detergent, 5 to 30 parts of alkali metal silicate, 4 to 20 parts of alkali metal carbonate, 0.3 to 3 parts of organic gum anti-redeposition agent, 1 to 20 parts of moisture and 5 to 40 parts of alkali metal sulfate and/or alkali metal chloride in the particles or spray dried beads thereof. The proportions of adjuvants and supplementing materials present in such beads will usually not exceed 20% of the total composition (including iminodiacetate), normally will be less than 10% and preferably will be less than 5% thereof, with none of the constituents being more than 5%, preferably with each being less than 2% and most preferably, less than 1% thereof. Of course, some of the less stable components of the particular detergents or those which might interfere with drying or flow properties if dried with the major proportion of detergent composition, may be added after drying is completed. Most preferred proportions and materials are from 5 to 30 parts of sodium linear higher alkyl benzene sulfonate, 1 to 8 parts of higher fatty alcohol poly-lower alkoxylate detergent, 5 to 30 parts of a sodium silicate of an $Na_2O:SiO_2$ ratio in the range of 1:2.0 to 1:2.4, 4 to 20 parts of sodium carbonate, 0.3 to 3 parts of sodium carboxymethyl cellulose, 1 to 10 parts of moisture and 5 to 40 parts of sodium sulfate.

The other component of the final detergent product, the iminodicarboxylate hydrate, should usually constitute about 15 to 50 parts, preferably 20 to 40 parts thereof. Such material, most preferably disodium-2-hydroxyethyl iminodiacetate hexahydrate, may be in separate pure iminodicarboxylate particles or may have filler salts or other suitable such components of the total composition mixed with it. Generally, it is preferred that the pure iminodicarboxylate material should be utilized. In some instances some of the iminodicarboxylate may be in the major proportion of the detergent even in anhydrous or lower hydrate form but for better flow and caking properties this should be only a minor proportion of the total iminodicarboxylate builder content, e.g., less than 30%.

To avoid separation during storage and shipment, it is highly desirable that the particles of detergent composition constituents and those of iminodicarboxylate hydrate should be of about equal particle sizes. Although various ranges of particle sizes utilized in the detergent industry may be employed it has been found that it is preferable that the particles be in the 6 to 140 mesh range, U.S. Standard Sieve Series, preferably from 6 to **100** mesh. That means that the particles will pass through the 6 to 8 mesh sieve and rest on the 100 or 140 mesh sieve. With particles of such sizes and of approximately the same particle size distribution little settling results and the finished detergent is flowable and of an acceptable degree of tackiness and tendency to cake in contrast to similar compositions in which the non-hydrated iminodicarboxylate is employed or in which an iminodicarboxylate solution is spray dried or otherwise dried with the rest of the detergent composition.

The products of this invention are preferably made by spray drying most of the detergent compositions, except for the hydroxyalkyl iminodicarboxylate, in a conventional spray drying apparatus so as to produce beads of the desired particle sizes, 6 to 140 and preferably 8 to 100 mesh. Such a spray operation is usually effected by crutching an aqueous mixture of the various components at an elevated temperature, e.g., 50° to 90°C. for a suitable period of time, e.g., three minutes to one hour, and then forcing the crutcher mix at high pressure, e.g., 200 to 1,000 lbs./sq. in., through restricted orifices so as to result in a production of a spray of crutcher mix droplets into a spray tower in which the droplets fall while being contacted by a countercurrent hot air flow, which dries them. The crutcher mix will usually contain from 20 to 50% of water and may include some small solid particles which are pumpable through the spray orifices at the high pressure. The orifices will be of a cross-section equivalent to a circular area of 1 to 5 millimeters in diameter. The drying air entering the spray drying tower will be of an initial temperature in the range of 200° to 500°C. and at exit from the tower will usually be at a temperature of 110° to 200°C. The detergent particles removed will be of a moisture content of 1 to 20% and more often will be 15% or less in moisture. The drying operation will be controlled, as by drying gas temperatures and tower throughput rates, to make detergent beads of such moisture contents that together with the moisture in the iminodicarboxylate hydrate the moisture of the product will be in the 1 to 20% range, preferably 1 to 15% and most preferably about 1 to 10%.

The spray nozzle sizes and spraying pressures or atomizing means employed will be chosen so as to produce particles of the desired sizes for detergent compositions. Oversize and fine particles may be removed by screening or other classification technique so that the product is correctly sized. Such off-size particles may be size-reduced or reworked so as to avoid waste.

In the crutching operation the order of addition of the mentioned components is not critical but it is preferred to dissolve the anti-redeposition agent gum in water or in an aqueous solution of other constituent before addition to the main crutcher mix, to avoid lumping or the production of hard gel sections in the crutcher mix. Generally, water, liquid detergent, anionic detergent solution, silicate solution and carbonate may be added in that order, followed by the gum solution or dispersion and various heat stable adjuvants. Any components which exhibit an undesirable reaction to the heat of the crutcher or the spray drying operation are preferably post-added.

In some cases proportions of components are crutched and the remainders are post-added. For example, it has been found that larger proportions of nonionic detergents, silicate and anti-redeposition gum than 2% of the detergent (Neodol 45-11), 15% of sodium silicate and 0.5% of carboxymethyl cellulose, on a final product anhydrous basis may interfere with drying, flow and non-caking properties of the product. Therefore, such materials will be preferably limited in the crutcher mix to the amounts mentioned. However, additional nonionic detergent or surface active agent and aqueous solution of sodium silicate may be sprayed onto particles after manufacture and additional sodium carboxymethyl cellulose or other gum, in powdered form, may be admixed with them. These operations preferably take place in a tumbling drum shortly after production of the detergent beads. Such tumbling is preferably at room temperature but is suitably effected at temperatures above that, e.g., 30° to 50°C.

The extra operation of blending in powdered anti-redeposition agent may be avoided in the present processes by maintaining the limit of anti-redeposition agent at 0.5% or thereabout. It has been noted that good anti-redeposition effects are obtained with such small proportion of the agent, apparently due to additional anti-redeposition properties of the iminodicarboxylate builder in the present compositions.

The iminodicarboxylate hydrate is preferably in globule form and of the same size distribution as the spray dried particles of the other detergent constituents. Particles of this type may be made by drying an iminodicarboxylate solution or slurry in conventional spray drying equipment and then hydrating it by treating it with water or by subjecting it to air of a relative humidity about the same as or higher than the equilibrium humidity for the hydrate. For example, when exposed to a humidity of from 65 to 75% at room temperature, a preferred iminodicarboxylate, disodium 2-hydroxyethyl iminodiacetate, will take up moisture until it reaches the hexahydrate stage. At relative humidities of 80% or more, which are rarely encountered, if by itself the hydrate may absorb water but in the present compositions sorption is minimized and caking problems are not common. Considering that almost all storage is at humidities less than 80% and at temperatures of 20° to 27°C., the employment of a hexahydrate in the present detergent compositions substantially prevents caking of the iminodicarboxylate and allows the production of a free flowing product.

Instead of adding moisture to the anhydrous form by subjecting spray beads to air of higher relative humidities, controlled addition of water thereto may also be practiced. Solutions of the iminodicarboxylate may be spray cooled to the hexahydrate form while maintaining globular particle shapes. Alternatively, granular hexahydrate may be made in manners known in the art and the granules may be size-reduced to the proper particle size range, with oversize particles and fines being removed. In a less preferred application of the invention a powdered iminodicarboxylate hydrate may be employed. Although the use of the hexahydrate in this form avoids some of the caking problems noted with the anhydrous iminodicarboxylate particles it introduces a disparity in particle sizes which may, under extreme conditions, cause sifting or settling and could make a boxed detergent product heterogenous, so that poor washing effects would be obtained because product employed would not have the proper balance of detersive and builder components. Such balance is important because the iminodicarboxylates improve the cleaning power of the organic detergents and other builders and with either an excess or deficiency of the iminodicarboxylate less desirable cleaning results.

Although the preferred forms of both the detergent base particles and the iminodicarboxylate builder particles are globular and in the particle size ranges mentioned it is within the broader ambit of this invention to utilize more finely divided or powdered components. Normally, such components do not flow as readily and have a greater tendency to cake during storage and so are not preferred but by using the process of this invention, with post-addition of the iminodicarboxylate hydrate, improvements in flow properties are obtained and there is less of a tendency toward caking. The "base" powder is preferably produced by drying a mix of all the detergent components except the iminodicarboxylate but the use of individual powdered materials is also within the broad invention of improving flowability and caking properties by post-addition of the iminodicarboxylate hydrate. Of course, where components are liquid, they may either be mixed with powdered carriers initially or may be blended with the powdered product at a later stage in the production. In some manufacturing processes a proportion, usually a minor proportion, generally less than 30%, of the iminodicarboxylate may be mixed in with the other detergent components before drying but there is generally little advantage in following such a procedure and it is highly preferred that the detergent "base" beads be free of iminodicarboxylate since such material can hydrate during the storage and cause caking and poor flow. In fact, post-adding of the iminodicarboxylate avoids a manufacturing roblem for which another solution is described in my concurrently filed patent application entitled MANUFACTURE OF IMPROVED AQUEOUS ALKALI METAL SILICATE-ALKALI METAL HYDROXYALKYL IMINODIACETATE COMPOSITIONS. In short, the gelation or precipitation often noted when iminodicarboxylate and silicate are admixed is avoided by initially raising the pH of the iminodicarboxylate solution to above 12, preferably to 12.5 to 13.5.

The admixing of the detergent base beads or particles and the hydrated iminodicarboxylate may be effected by any convenient means, the most preferable of which is an inclined tumbling drum or a twin shell blender. The main consideration is that the mixing apparatus should not unduly fragment the particles. In the mixing apparatus, as was previously indicated, other components of the detergent composition may be added in liquid, droplet, powder or other form and additional quantities of components may be added. In such cases it would be desirable to utilize materials of the same

particle sizes, whenever possible. Materials such as sodium carboxymethyl cellulose may be agglomerated to particles of the correct size, although it has been found acceptable to utilize this material, in the small proportion in which it is present, as a finely divided powder having particles in the range of 100 to 200 mesh. Preferably, all mixing, spraying and other forms of treatments in the mixer will be at about room temperature.

The iminodicarboxylate particles made are added to the base particles before or after addition of post-addition materials. The post-addition substances may be added to either the iminodicarboxylate or the base composition particles first and then the other component particles may be admixed. In some instances, as where starting materials include fines or are of particle sizes smaller than desired, partial agglomeration may take place in the tumbling drum, aided by the application of solutions of gums or silicates, or nonionic detergents or surface active agents. In any such cases, care will be taken to maintain the particles in the desired range of sizes and to prevent any dehydration of the iminodicarboxylate hydrate.

After production of the final detergent product it may be stored prior to filling into cartons or may be directly filled. The cartons used may be of moisture barrier or non-barrier types and it has been found that in the ordinary, non-barrier cardboard cartons, stored at room temperature, detergent compositions containing the post-added hexahydrate are of a lesser tendency to cake on storage than similar products in which anhydrous iminodiacetate is present (made from a spray dried crutcher mix).

In use it is found that the products are excellent detergents, effectively washing out soils of the various types normally encountered, such as particulate (clay) soils, sebum soils, greasy and carbonaceous soils, from cotton and synthetic organic fiber-based materials and articles made from them. The iminodicarboxylate builders function better in this respect than all of the builder substitutes for pentasodium tripolyphosphate and trisodium nitrilotriacetate that have been tried and the detersive, soil-suspending and whitening effects of the present detergent compositions are comparable to those obtained with phosphate-based formulations, even at much higher levels of the phosphate (with compensating lower levels of synthetic organic detergent content). The products are competitive in price with other commercial detergent formulations. Additionally, they do not contain excessive quantities of potentially toxic or harmful constituents.

The following examples illustrate the invention but do not limit it. Unless otherwise indicated, all parts are by weight and all temperatures are in °C.

EXAMPLE 1

	Parts by weight
* Higher fatty alcohol poly-lower alkoxylate nonionic surface active agent	5
** Higher fatty alcohol poly-lower alkoxylate detergent	3
Linear tridecyl benzene sulfonate, sodium salt (90% active ingredient)	15
Aqueous sodium silicate solution ($Na_2O:SiO_2$ = 1:2.35; solids content = 44%)	36
Sodium carbonate, anhydrous	13
Sodium carboxymethyl cellulose (85% active ingredient)	0.7
Sodium sulfate	20
Water	7

* Neodol 25-3S, a higher fatty alcohol polyisopropoxylate made by Shell Chemical Company, wherein the higher fatty alcohol is of 12 to 15 carbon atoms and there are present three moles of propylene oxide per mole of higher fatty alcohol.
** Neodol 45-11, a higher fatty alcohol polyethoxylate made by Shell Chemical Company, wherein the higher fatty alcohol is of 14 to 15 carbon atoms and there are present eleven moles of ethylene oxide per mole of higher fatty alcohol.

About four parts of the water are added to a detergent composition crutcher, followed by the silicate solution, sodium carbonate, anionic detergent, nonionic surface active agent, nonionic detergent, and sodium chloride and the contents are mixed over a period of about five minutes. The sodium carboxymethyl cellulose is dissolved and dispersed in the remaining water and the aqueous solution-dispersion is admixed with the rest of the crutcher mix. After continuing mixing for an additional 5 minutes after all the materials are present in the crutcher the mix is pumped by a Triplex pump at a pressure of 600 lbs./sq. in. through a plurality of spray nozzles, each of which has an orifice of about 1.5 millimeter diameter, into the top of a countercurrent spray drying tower wherein the falling droplets of detergent composition base are dried in heated drying air which passes upwardly through the tower. The drying air has an initial temperature of about 400°C. and a final temperature of 130°C. The dried beads have a moisture content of about 3%. The resulting product, in the form of spray dried globules, is screened and sized so the particles thereof pass through a No. 8 sieve, U.S. Standard Sieve Series, and rest on a No. 100 mesh sieve.

After removal from the spray tower and cooling to a temperature of about 40°C., 100 parts of the spray dried detergent base beads are added to a tumbling drum and 23 parts of disodium 2-hydroxyethyl iminodiacetate hexahydrate, in granular form of particle sizes in the 8 to 100 mesh range, are mixed with tumbling so as to evenly distribute them throughout the particulate mass. Next, 0.15% of perfume is sprayed onto the particles and mixing is continued until the perfume is completely distributed, which takes about an additional minute beyond the 5 minutes earlier mixing time.

In use it is found that the above composition is comparable in detergency with high phosphate compositions based on 10 to 25% of active anionic detergent and 30 to 45% of pentasodium tripolyphosphate. Yet, the product is non-eutrophying and does not contain any phosphates nor does it contain unusual quantities of surface active agents, detergents, builders or anti-redeposition agents. Utilizing standard concentrations of detergents in automatic washing machines, 0.15% of the particulate detergent, the product is tested and found to be acceptable, good or superior in washing ability in both hot and cold water, in both hard and soft water, and when tested against varying types of soils, including clay soils, carbon soils, greasy soils, and phospholipid or sebum soils, as compared to phosphate-containing commercial detergents.

Compared to formulations in which the anhydrous disodium 2-hydroxyethyl iminodiacetate is employed instead of the hexahydrate (with the proportions thereof being diminished to allow for the extra water content of the hexahydrate), the present products are

of reduced caking tendency in non-barrier boxes or cartons when subjected to normal use and aging conditions. They flow more freely than "control" compositions based on the anhydrous iminodicarboxylate, after storage in ordinary non-barrier boxes at room temperature (20–27°C.) and ordinary humidities (30–60%).

Variations in the formula to increase or decrease the various components within the ranges previously given result in the productions of satisfactory detergent compositions, which are or improved flowability and anti-caking properties, compared to control detergents. Similarly, changes in the processing whereby an additional 15 parts of sodium silicate solution are sprayed onto the tumbling detergent beads and an additional 0.5% of sodium carboxymethyl cellulose powder, in finely divided form (100 to 200 mesh) is blended in with the product after application of the sodium silicate solution, also result in a product of improved flowability and anti-caking properties, compared to the control. In such compositions the moisture content of the base detergent beads may be reduced to 0.5 to 1% initially, to compensate for the additional moisture post-added with the silicate solution. When, in addition to the processing changes described, the Neodol 25-3S is omitted from the crutcher mix and the same proportion of Neodol 45-11, in liquid form, at an elevated temperature, is sprayed onto the detergent and iminodicarboxylate beads after application of the silicate, an equivalent product is made. Such product avoids the problem of pluming from the spray tower of some of the nonionic surface active and detergent materials when higher nonionic content formulations (greater than 2%) are spray dried. Replacement of the sodium sulfate with the potassium sulfate or mixtures of sodium and potassium sulfates also makes a good product but it may tend to cake slightly more. Use of sodium chloride instead of sodium sulfate is acceptable when corrosion of metal equipment is no problem. The products are also satisfactory detergents against the various mentioned soils on the different types of fabric substrates.

EXAMPLE 2

	Parts		
	2-1	2-2	2-3
Neodol 25-3S	0	4	0
Neodol 45-11	6	2	2
Sodium linear tridecyl benzene sulfonate	11	11	11
Aqueous sodium silicate solids (applied as a solution with $Na_2O:SiO_2$= 1:2, solids content = 44%)	15	12	12
Sodium carbonate, anhydrous	10	10	10
Moisture	4	4	4
Disodium 2-hydroxyethyl iminodiacetate hexahydrate	15	12	25
Adjuvants (0.5 part sodium carboxymethyl cellulose, 0.5 part calcined aluminum silicate flow-improving agent, 1.0% fluorescent brightener mixture, 0.2% perfume and 0.1% stabilizer)	2.3	2.3	2.3
Sodium sulfate, anhydrous	36.7	42.7	33.7

Repeated experimentation indicates that the best concentrations for the sodium linear tridecyl benzene sulfonate, sodium silicate, sodium carbonate, moisture and adjuvants contents are about 11%, 12–15%, 10%, 4% and 2–3%, respectively, with nonionic detergent contents in 2 to 6% range and other anionic organic detergent contents of about 0 to 4%. Concentrations of iminodiacetate hexahydrate in the product are preferably in the 10 to 30% range, preferably 12 to 25%.

The detergent compositions described above are made substantially as related in Example 1, with the spray drying of the intermediate products being effected after the described pre-mixing and with no more than 2% of Neodol 45-11 being incorporated in the product during spray drying operations. The hexahydrate is post-added also, following the procedure of Example 1 and producing products of about the same size. In some experiments the nonionic detergent is completely post-sprayed onto the other particles, optionally with sodium carboxymethyl cellulose (or with it being pre-mixed with the intermediate), and the calcined aluminum silicate is dusted onto the product afterward. In other experiments a proportion of the nonionic detergent is post-sprayed and another proportion, up to 2% thereof, is spray dried with the balance of the detergent composition formula. Control runs are also made, using the iminodiacetate in the final product, holding the final product moisture content essentially the same (except for hydrate moisture). The iminodiacetate may be employed in any suitable form but usually will be the alkali metal salt (or as ions form such a salt) in the completed crutcher mix.

The products made are compared for tackiness and caking. It is observed that when stored in normal containers, without barriers, under normal storage conditions (not excessively high temperatures), there is a noticeable improvement in characteristics of the final product. Control products, not utilizing the hexahydrate, cake significantly worse and are much more difficult to pour out of cartons. On the other hand, the compositions to which the hexahydrate is post-added, whether with post-addition of nonionic detergent or not, are of improved aging characteristics. Although they can sometimes produce noticeable lumping, they will flow much more freely than the "controls", after storage.

When the formulations given above are changed, substituting the corresponding iminodipropionate or hydroxypropyl iminodiacetate, useful detergents are obtained for which the hydrated iminodialkanoates are of improved non-caking and subsequent flow properties. This is also the case when the previously named anionic detergents are substituted for the sum of the Neodol 25-3S and sodium linear tridecyl benzene sulfonate and when proportions of these specific detergents are halved and/or doubled. Similarly, when Neodol 45-11 is replaced by Neodol 25-7, in minor part or is partially or completely replaced by Plurafac B-26, Alfonic or Conoco 1618-65, a mixture of Pluronics L-44 and F-68 or other suitable nonionic detergent, essentially the same type of result is obtained. This is also true when in the various experiments described the proportion of carbonate is increased to 15% and when 5% of bicarbonate is added to the 10% of carbonate. Of course, changing of the silicates to $Na_2O:SiO_2$ ratios of 1:2.35 and 1:2.2 yields essentially the same types of products, too.

Instead of the sodium salts, a minor proportion of the total of builder, detergent and filler salts may be replaced by the corresponding potassium salts without harm to the production of an acceptable product.

Although the product obtained is better than corresponding non-phosphate built detergents that are al-

lowed to be marketed in the United States, with respect to cleaning and brightening abilities, as shown in comparative testings against controls containing no iminoalkanoate, and although there is a decided improvement in subsequent flow and aging properties in non-barrier boxes on ordinary storage, efforts are being made to improve the aging characteristics of the detergent further, to which end starch or other additional flow improving agent may be utilized and, in some cases, the iminodialkanoate, either as a hydrate or as a mixture thereof with the corresponding anhydrous form, may be at least partially encapsulated to further diminish any tendency toward caking or lazy flow after packaging.

EXAMPLE 3

The formulation of Example 2–3 is followed with the exception that the proportion of sulfate is diminished 5% and that of the hydroxyethyl iminodiacetate hexahydrate is increased 5% and the iminodiacetate and nonionic detergent are post-sprayed onto and post-mixed with the rest of the previously spray dried detergent constituents. In similar experiments, the entire mixture is blended together, without intermediate spray drying. Products made are compared to controls in which the entire compositions are spray dried. Subsequently, the products are stored in open jars for 3 and 7 days at 100°C. and 80% humidity, after which time they are observed for caking characteristics. It is found that the control products are very heavily caked and in essence, are brick-like, whereas the "experimental" products flow but contain some medium sized lumps. Utilizing plant production equipment, lower initial moisture content, encapsulating means, favorable carton designs and improved storage conditions, the proportion of such caking is diminished further.

From this experiment, the various modifications of the processes thereof which may be carried out in accordance with the teaching of the previous specification and the results thereof it is evident that the use in these detergent compositions of hydrated iminodialkanoates improves storage and subsequent flow characteristics of the detergents. It does so without harming the washing abilities or otherwise affecting the products and those resulting are superior in washing power to other permissible non-phosphate detergents and sometimes are superior to comparable heavy duty built detergents based on pentasodium tripolyphosphate.

The invention has been desribed with respect to examples and illustrations of embodiments thereof but is not to be considered as limited to them, since it will be clear to one of skill in the art how to substitute equivalents and modify the operations without departing from the spirit of the invention.

What is claimed is:

1. A particulate heavy duty synthetic organic detergent composition which comprises 5 to 30 parts of anionic detergent and/or 1 to 10 parts of nonionic detergent and, as a builder therefor, 15 to 50 parts of a water-soluble salt of a hydroxy C_2–C_4 alkyl iminodi C_2–C_4 carboxylic acid hydrated by 3 to 10 moles of water per mole of iminodicarboxylate.

2. A heavy duty detergent composition according to claim **1** wherein the builder salt is a dialkali metal iminodiacetate polyhydrate.

3. A detergent composition according to claim **2** wherein the iminodiacetate polyhydrate is disodium 2-hydroxyethyl iminodiacetate hexahydrate.

4. A detergent composition according to claim **3** wherein the particles of synthetic organic detergent are in the form of spray dried beads.

5. A detergent composition according to claim **1** which comprises from 5 to 30 parts of anionic detergent and/or 1 to 10 parts of nonionic detergent, 5 to 30 parts of alkali metal silicate, 4 to 20 parts of alkali metal carbonate, 0.3 to 3 parts of organic gum anti-redeposition agent, 1 to 20 parts of moisture, 5 to 40 parts of alkali metal sulfate and 15 to 50 parts of builder salt hydrate.

6. A detergent composition according to claim **4** which comprises from 5 to 30 parts of anionic detergent, 1 to 8 parts of nonionic detergent, 5 to 30 parts of alkali metal silicate, 4 to 20 parts of alkali metal carbonate, 0.3 to 3 parts or organic gum anti-redeposition agent, 1 to 20 parts of moisture, 5 to 40 parts of alkali metal sulfate in the beads and 15 to 50 parts of disodium 2-hydroxyethyl iminodiacetate hexahydrate.

7. A phosphate-free and NTA-free detergent composition according to claim **6** which comprises from 5 to 30 parts of sodium linear alkyl benzene sulfonate, 1 to 8 parts of higher fatty alcohol poly-lower alkoxylate detergent, 5 to 15 parts of sodium silicate of an Na_2O:-SiO_2 ratio in the range of 1:2.0 to 1:2.4, 4 to 20 parts of sodium carbonate, 0.3 to 3 parts of sodium carboxymethyl cellulose, 1 to 15 parts of moisture and 5 to 40 parts of sodium sulfate in the beads and 15 to 30 parts of disodium 2-hydroxyethyl iminodiacetate hexahydrate, with the particles being within the range of 6 to 100 mesh.

8. A method of making a free flowing, particulate heavy duty synthetic organic detergent composition which comprises 5 to 30 parts of anionic detergent and/or 1–10 parts of nonionic detergent and, as a builder therefor, 15 to 50 parts of a water-soluble salt of a hydroxy C_2–C_4 alkyl iminodi C_2–C_4 carboxylic acid hydrated by 3 to 10 moles of water per mole of iminodicarboxylate, which comprises making particles of the heavy duty synthetic organic detergent composition components exclusive of the said builder salt and admixing with them particles of said builder salt hydrate.

9. A method according to claim **8** wherein the builder salt is a di-alkali metal iminodiacetate polyhydrate.

10. A method according to claim **9** wherein the builder salt is 2-hydroxyethyl iminodiacetate hexahydrate.

11. A method according to claim **10** wherein the organic detergent is spray dried and after spray drying the particles of 2-hydroxyethyl iminodiacetate hexahydrate are post-added and mixed with such particles.

12. A method according to claim **11** wherein the spray dried particles of the detergent comprise from 5 to 30 parts of anionic detergent and/or 1 to 10 parts of nonionic detergent, 5 to 30 parts of alkali metal silicate, 4 to 20 parts of alkali metal carbonate, 0.3 to 3 parts of organic gum anti-redeposition agent, 1 to 10 parts of moisture and 5 to 40 parts of alkali metal sulfate and/or alkali metal chloride, to which are post-added particles of about the same size of 2-hydroxyethyl iminodiacetate hexahydrate, after which addition the particles are mixed.

13. A method according to claim **12** wherein an aqueous detergent composition crutcher mix is spray dried to detergent beads of particle sizes in the 6 to 100 mesh range, which beads comprise from 5 to 30 parts sodium linear higher alkyl benzene sulfonate, 1 to 8 parts of higher fatty alcohol poly-lower alkoxylated

detergent, 5 to 15 parts of sodium silicate of an Na_2O:SiO_2 ratio in the range of 1:2.0 to 1:2.4, 4 to 20 parts of sodium carbonate, 0.3 to 1 part of sodium carboxymethyl cellulose, 1 to 10 parts of moisture and 5 to 40 parts of sodium sulfate and such spray dried beads resulting are admixed with 15 to 30 parts of disodium 2-hydroxyethyl iminodiacetate hexahydrate of particle sizes in the 6 to 100 mesh range.

14. A method according to claim **13** in which additional nonionic detergent, sodium silicate and sodium carboxymethyl cellulose are post-added to the spray dried product, the silicate as an aqueous solution and thereafter nonionic detergent being sprayed onto the product surfaces in liquid droplet form and the sodium carboxymethyl cellulose being admixed therewith as a finely divided powder, with particles in the range of 100 to 200 mesh, during tumbling of the beads, the proportions of silicate, detergent and sodium carboxymethyl cellulose added being such that the total proportions thereof in the product are 1 to 8 parts of higher alcohol poly-lower alkoxylate, 5 to 30 parts sodium silicate and 0.3 to 3 parts of sodium carboxymethyl cellulose.

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