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## DETERGENT COMPOSITIONS AND PROCESSES INCORPORATING N-(2 - HYDROXY HYDRO- CARBYL) IMINODICARBOXYLATES

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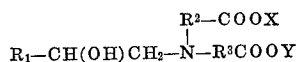
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12 Claims

### ABSTRACT OF THE DISCLOSURE

Built synthetic organic detergent compositions comprise N-(2-hydroxy hydrocarbyl) iminocarboxylates or the corresponding carboxylic acids of the formula:



wherein R<sup>1</sup> is an aliphatic hydrocarbon radical of 4 to 20 carbon atoms, R<sup>2</sup> and R<sup>3</sup> are divalent aliphatic or aromatic hydrocarbon radicals of 1 to 9 carbon atoms and X and Y are either hydrogen or salt-forming elements or radicals. In preferred embodiments of the invention, R<sup>1</sup> is a saturated radical of 12 to 20 carbon atoms, R<sup>2</sup> and R<sup>3</sup> are identical alkylene radicals of 1 to 2 carbon atoms, and X and Y are the same monovalent metals, or lower alkanolamines, e.g., sodium, triethanolamine. In addition to the iminodicarboxylates, such compositions comprise an inorganic builders salt, such as sodium tripolyphosphate or potassium pyrophosphate, and also may include other adjuvant materials, such as trisodium nitrilotriacetate, enzymes, anti-redeposition agents, bleaches or bluing agents, germicides, hydrotropes, auxiliary detergents and softening agents, etc. Usually, the iminodicarboxylate comprises from 3 to 30% of the composition and the inorganic builder salt is from 10 to 70% thereof.

The products made may be in liquid or solid form and are preferably employed as liquids or powders. They may be utilized as washing-softening agents in laundering or may be employed in pre-soaking or after-soaking of laundry, to improve the softening of the washed material. The iminodicarboxylate can be used without inorganic builder salt, in which case it normally functions primarily as a softening agent and is preferably utilized in the rinse water, after completion of washing, although it may also be used alone in a pre-soaking or washing operations.

This invention relates to compositions and processes for the treatment of textiles, clothing or laundry, to clean and soften such items and to impart anti-static properties to them. The invented compositions and processes incorporate or utilize N-(2-hydroxy hydrocarbyl) iminodicarboxylates or the corresponding carboxylic acids and are particularly suitable for treatment of cotton and cotton-containing materials, although they are also useful for application to other natural and synthetic products.

In recent years much research has been undertaken in an attempt to improve the physical properties of washed materials. It has been a principal object of such research to improve the whiteness of the materials being washed, by better removal of soil and stains. To this end, improved cleaning agents, builders, anti-redeposition agents, enzymes for stain removal, brighteners, and bleaches have been employed, sometimes as separate treatments and at other times incorporated with the principal detergent agent. Although it is recognized that the primary function of a detergent must be to clean, the substantial attainment of this objective has caused industry scientists to explore other research areas, in an attempt to improve further

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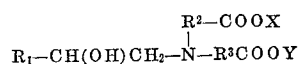
other qualities of their products. Thus, it has been found that laundry, such as cotton clothing articles, when washed with built synthetic organic detergents and air dried, sometimes develops a roughness that makes it scratchy to the wearer's skin. To counteract this effect, which also has been noted as a result of washing clothing or other items, such as diapers, with soap or unbuilt synthetic detergents, softening agents have been produced, which are usually added to the rinse water, after completion of machine washing. Research has been conducted to discover and develop improved softeners and to obtain such materials which might be employed in detergent compositions so that they would not have to be added in a special operation, after completion of washing.

Another area of research, especially with respect to synthetic fabrics such as those made from nylon, polyesters and polyvinyl halides, has been prevention of annoying static charge build-up on textiles. It has been found that by applying certain anti-static chemicals to the textiles, electric charges thereon and annoying shocks to a wearer or one who contacts such material will be diminished.

The present invented processes and compositions, utilizing the N-(2-hydroxy hydrocarbyl) iminodicarboxylate described herein, allow improved washing of textiles and laundry, with the washed materials being of greater softness and having antistatic properties. Such results are obtainable by applying the mentioned compounds, either in built or unbuilt compositions, to the materials to be treated, either before, during or after washing. It appears that the present iminodicarboxylates are exceptionally substantive to fabrics and a sufficient proportion thereof remains on the fabric so as to make it soft and impart antistatic properties to it. This action is especially surprising because the active ingredients themselves are detergents and serve to remove materials from substrates, rather than to deposit them thereon.

Other advantages of the present compositions and methods include their usefulness in hard and soft waters and at high and low washing temperatures. Thus, surprisingly, it has been found that effective detergency, softness and anti-static properties are obtained under such conditions. Furthermore, the compounds are generally of the controlled foaming type, resulting in a visible foam which is not "clogging" in an automatic washing machine. The processes may be used in conjunction with various other treatments of textiles or laundry and the compositions may be modified to include other detergents and adjuvants, without interfering with the desirable activities thereof. In the washing of synthetic materials, such as nylon, which yellow when contacted with rubber goods in the pre-soak or wash, the present compositions, including the N-(2-hydroxyhydrocarbyl) iminodicarboxylates or the corresponding acids, counteract this tendency toward discoloration. Nylon is only very slightly yellowed by such contact, with present solutions.

In accordance with the present invention, built synthetic organic detergent compositions comprise an inorganic builder salt and an N-(2-hydroxyhydrocarbyl) iminodicarboxylate or corresponding acid of the formula:



wherein R<sup>1</sup> is an aliphatic hydrocarbon radical of 4 to 20 carbon atoms, R<sup>2</sup> and R<sup>3</sup> are divalent, aliphatic or aromatic hydrocarbon radicals of 1 to 9 carbon atoms and X and Y are hydrogen or a salt-forming element or radical. R<sup>2</sup> and R<sup>3</sup> may be the same or different and X and Y may be the same or different. If either X or Y is an element, it is preferred that it should be an alkali metal, an alkaline earth metal or other suitable salt-forming metal, capable

of making the compounds water soluble. If X or Y is a radical, it is preferred that such be ammonium, alkylamine or alkanolamine, either mono-, di-, or tri-alkylamine or mono-, di- tri-alkanolamine, in which the alkyl and alkanol groups of the salt-forming amines are of 1 to 4 carbon atoms, preferably 2 to 3 carbon atoms.

In preferred embodiments of the invention, the compounds are those wherein R<sup>1</sup> is an aliphatic hydrocarbon radical of 12 to 20 carbon atoms, R<sup>2</sup> and R<sup>3</sup> are aliphatic alkylene radicals of 1 to 2 carbon atoms, and X and Y are monovalent salt-forming ions, including alkali metal, ammonium, mono-, di- and tri-alkylamine and mono-, di- and tri-alkanolamine. In such preferred compounds, it is additionally preferred that R<sup>2</sup> and R<sup>3</sup> are same and that X and Y are the same.

With respect to X and Y, it will be noted that in the above formula there has been no allowance made for divalent or polyvalent salt-forming ions. Nevertheless, it may be considered that X and Y stand for a monovalent portion of any salt-forming ion. Thus, if a divalent ion, such as magnesium, is employed, it could be joined to both the carboxylic groups of the present compounds or could be joined to only one of them, with another valence bond either otherwise tied up, as with a different anion, or with it joined to the carboxylic groups of different iminodicarboxylic acids. In such a way, mixed salts may be formed, as may be acid-salt compounds.

In addition to the mixed salts formed, mixtures of different iminodicarboxylates may also be used. Also contemplated as useful for purposes of this invention are other compositions and methods wherein the hydroxy substituted hydrocarbon radical is a hydroxy substituted higher aliphatic hydrocarbon radical, preferably a hydroxy-higher linear alkyl, and in which the R<sup>2</sup> and R<sup>3</sup> are lower or higher hydrocarbon radicals. The compounds so described, which may be outside the range of normally used compounds, are considered to be useful in some built detergent-softener compositions and in textile-treating methods, to clean, soften or make anti-static, various textiles contacted therewith. The preferred compositions and methods mentioned above are found to be excellent for softening textiles, especially for cotton articles which are washed with them, even in the presence of various builders, other detergents and adjuvants. They may also be used in normal washing procedures, including rinsing and presoaking operations. With respect to the softening properties observed, the most preferred compounds of the compositions and processes are the salts of N-(2-hydroxy-higher alkyl) iminodilower carboxylic acids, wherein the higher alkyl is of 14 to 22 carbon atoms and is of straight chain structure. Of such compounds, it is preferred to employ the sodium and potassium salts, with the sodium salt being that which is generally considered most useful. Of the lower carboxylic acids, the most preferred is acetic acid, so that the most preferred of these compounds are the N-(2-hydroxy-higher alkyl)-iminodiacetates. The use of these compounds in the present compositions and methods results in a surprisingly effective textile-softening action and detergency, especially with cotton, even when applied to the textile or laundry in the washing operation and even when no additional active synthetic organic detergent materials are present.

The preferred and highly preferred embodiments of the invention have been described above, which compositions have exceptionally good softening activities on textiles and laundry. Other compositions within the scope of the present invention are also useful as surface active agents, wetting agents, emulsifiers and detergents, although they might not produce to the same extent the extremely desirable softening activity shown by the most preferred compositions. In fact, in some instances, such compositions may be only moderately effective as softeners, although they will often have the advantage of being very useful because of their other surface active properties, such as detergency, often in both hard and soft

waters and at elevated and comparatively low washing temperatures.

Among the compositions within the scope of the invention, in which the compounds are within the formula previously given, are those built detergents containing active compounds such as

- N-(2-hydroxy-n-hexyl)-iminodiacetic acid, mono-n-propanolamine salt;
- N-(2-hydroxy-n-heptyl)-iminodiacetic acid, di-triethanolamine salt;
- N-(2-hydroxy-n-octyl)-iminodiacetic acid, disodium salt;
- N-(2-hydroxy-propylene tetramer)-iminodiacetic acid, dipotassium salt;
- N-(2-hydroxydodecyl)-iminodipropionic acid, dilithium salt;
- N-(2-hydroxy-propylene pentamer)-iminodiacetic acid, magnesium salt;
- N-(2-hydroxyhexadecyl)-iminodiacetic acid, disodium salt;
- N-(2-hydroxydocosyl)-iminodiacetic acid, disodium salt;
- N-(2-hydroxytetradecyl)-iminodiacetic acid;
- N-(2-hydroxyoctadecyl)-iminodiacetic acid;
- N-(2-hydroxy-n-hexyl)-iminodi-n-propionic acid, monopotassium salt;
- N-(2-hydroxy-6-ethyl-n-decyl)-imino-n-butyric acid, di-diethanolamine salt;
- N-(2-hydroxydodecyl)-iminodi-p-benzoic acid, magnesium salt;
- N-(2-hydroxyhexadecyl)-iminoacetic-propionic acid, calcium salt;
- N-(2-hydroxyoctadecenyl)-iminobenzoic-toluic acid, diisopropylamine salt;
- N-(2-hydroxyoctadecyl)-iminodipentanoic acid, mixed sodium and potassium salt;
- N-(2-hydroxytetradecyl)-iminodiacetic acid, mono-ammonium salt;
- N-(2-hydroxyhexadecyl)-iminopropionic-butyric acid, mono-monoethanolamine salt;
- N-(2-hydroxytetradecyl)-imino-benzoic-o-isopropylbenzoic acid, mixed magnesium and calcium salt;
- N-(2-hydroxyoctadecyl)-iminoacetic-toluic acid, mixed sodium and triethanolamine salt;
- N-(2-hydroxydocosyl)-iminodiacetic acid, aluminum salt;
- N-(2-hydroxy-mixed higher linear alkyl of 14-16 carbon atoms)-iminodiacetic acid, disodium salt;
- N-(2-hydroxy-n-tetradecyl)-iminodi-n-decanoic acid, disodium salt; and
- N-(2-hydroxyoctadecyl)-imino-n-pentanoic-n-heptanoic acid, mixed sodium and potassium salts.

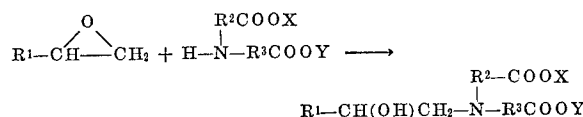
The above-mentioned compounds are illustrative of those within the formulas given but it will be clear to those of skill in the art that other compounds are within the scope of such formulas and are also useful. In many cases, they may possess properties superior to those specifically listed above. Also, variations may be made in the above specific compounds, wherein other mentioned constituents are employed to replace those specifically illustrated. In some cases, additional non-interfering substituents may be present, usually on the longer chain portions of the molecules, such as on the R<sup>1</sup> group, where they do not affect the properties of the final product as significantly as they might if placed on shorter chain portions. Among useful substituents are amino, hydroxy, halogen, e.g., chlorine, bromine, fluorine, and hydroxy-lower alkyl wherein the alkyl is up to four carbon atoms. The number of such substituents present will usually be small, often no more than four per molecule and usually, less than three. It is generally preferable that the compounds be unsubstituted but many of the substituted compounds are often of utilities similar to those of the compounds literally within the formulas given and therefore, are also contemplated as relevant to this invention. As has been illustrated by recitation of the specific compounds within the formulas given above, mixed salts may be employed, as may be acid salts.

From the recitation of the above compounds, it is seen that the hydrocarbonyl groups,  $R^1$ , include both saturated and relatively slightly unsaturated radicals. Thus, one or two double bonds per  $R^1$  are acceptable and are within the present invention, although it is preferred to employ alkyl groups as  $R^1$ . Of the alkyl groups, straight chain alkyls, which are terminally joined to the carbon to which the hydroxy group is attached, are highly preferred, and are intended to be described herein, unless otherwise indicated, although those alkyl groups which are not terminally joined also possess utility, as do various alkyl groups of non-linear structures. For example, medially joined keryl (alkyl derived from kerosene) may be used for  $R^1$ . Also useful are various polymeric radicals, such as propylene tetramer and pentamer, a preferred form of which is often such a mixture thereof as to average 13 carbon atoms per group. In some instances, it may be desirable to have cycloalkyl groups employed, either alone or with linear alkyls, e.g., cyclohexyldecyl.

R<sup>2</sup> and R<sup>3</sup> are preferably short chain alkylene, usually of 1 to 2 carbon atoms, but longer chain alkenes and divalent hydrocarbyl radicals containing aromatic moieties are also useful to make detergent and softener products. Normally, the alkenes will be present with a carbon content of the alkylene groups, R<sup>2</sup> and R<sup>3</sup>, of four or less but in some instances as many as nine carbon atoms may be found in such group to be good for making the novel and useful surface active products. When aromatic materials are employed, it is preferred that they be derivatives of benzene, usually with no more than two substituents on the benzene ring, in addition to joinder of the benzene ring to the rest of the present molecule.

X and Y, while they may be hydrogen, are preferably salt-forming ions. Of course, mixed substitution of hydrogen and salt-forming ions is within the invention. The salts made are usually more stable and freer flowing than the acids and because the product is most frequently employed in alkaline solutions, it is therefore preferably in the salt form. Of the salt-forming ions, those which are monovalent are generally preferred, usually because of their greater water solubility, which is an important feature in the use of the present compositions in aqueous systems. However, even if water solubility is low, salts of low solubility can be employed as washing agents in other polar media and may be useful in an aqueous medium, especially if solvents or solubilizers are present.

The N-substituted iminodicarboxylates of the present compositions and methods can be prepared by reaction of a hydrocarbon-1,2-epoxide with an iminodicarboxylic acid, usually in the form of a salt. The reaction is shown in the following equation:



The described reaction is normally effected in aqueous solution, wherein the hydrocarbon-1,2-epoxide is added in stoichiometric proportion to a solution of a salt of the iminodicarboxylic acid. Sometimes, a hydrotrope or auxiliary solvent, such as alcohol, may be employed to assist in solubilizing the epoxide. The reaction will ordinarily occur at elevated temperature and to minimize foaming, may be effected under pressure. After completion of the reaction and cooling, solvent may be removed by any convenient means, e.g., freeze drying, and the product may be recrystallized from a suitable solvent, e.g., alcohol.

The iminodiacids and their salts are known compounds, as are the hydrocarbon epoxides. Methods for making such compounds from readily available starting materials are also known to those of skill in the art and accordingly, they need not be described here. Further details relevant to the manufacture of the present N-(2-hydroxy-

hydrocarbyl)-N-iminodicarboxylates and the corresponding acids are given in our application for patent entitled N-(2-Hydroxyhydrocarbyl) Iminodicarboxylates, U.S. application Ser. No. 880,992, filed by us in the U.S. Patent Office on the same date as the present application. As described in said application in the reaction of the epoxy compound and the iminodiacid although stoichiometric proportions are preferred, it is within the present invention to employ an excess of either reagent, depending upon the circumstances, with the usual excess not exceeding 50% and rarely exceeding 20%. Although the reaction may be effected at various temperature, it is normally preferred to initiate it at approximately room temperature, e.g., 15–30° C. Ordinarily, the iminodiacid reactant is dissolved in an aqueous medium and it is preferred to utilize deionized water for such medium. The proportion of water employed may be relatively small, and usually it is preferred to use from 25 to 200% of the total weight of the reactants. In any case, sufficient water is employed to dissolve the iminodiacid, and the epoxide, usually as a liquid, is admixed with the dissolved reagent. Such admixing may take from ten seconds to one hour and during mixing the temperature of the reaction mixture is held within the mentioned room temperature range. After initial reaction, the temperature is usually raised to from 50° C. to 110° C., depending upon the materials being reacted. The temperature most conveniently employed is the reflux temperature of the reaction mix. The reaction mixture is held at such temperature for a period of from about one hour to about 42 hours, after which it is considered that the reaction is complete. After that time, a one-phase system is found, from which the product may be obtained by precipitating with a suitable lower ketone, e.g., acetone, methyl ethyl ketone, diisopropyl ketone or other ketone having one to four carbon atoms in the alkyl groups thereof. Conversion to a solid crystal form may often be effected by treatment with a lower alcohol, such as isopropanol or ethanol, after which purification may be effected by recrystallization from such solvent. The iminodicarboxylates obtained by following the above described method for their manufacture are usually white or light-colored solids, sometimes with a slight yellowish tinge. They may be somewhat hygroscopic but are sufficiently free-flowing to be employed, either by themselves or with other materials, such as the present inorganic builder salt, in surface active materials such as detergent-softeners for textiles.

In the preferred heavy duty synthetic detergent compositions of this invention, N-(2-hydroxyhydrocarbyl)iminodicarboxylates or the corresponding acids are formulated with suitable builder materials. The builders are highly preferably in the forms of inorganic water soluble salts but other builder materials may also be employed, including insoluble inorganics and soluble organic compounds. Materials of these types are well known and have been described in various textbooks on detergency. The soluble inorganic salts are most often salts of alkali metals but suitable salts of other metals, such as alkaline earth metals, magnesium and aluminum, and non-metals and radicals, e.g., ammonium and organic cations, such as mono-, di-, and tri-alkylamines and alkanolamines wherein the alkyl and alkanol groups are of about 1 to 4 carbon atoms, preferably of 2 carbon atoms, are also useful. The builder salts are preferably phosphates, including orthophosphates, pyrophosphates and tripolyphosphates, but the usual builder silicates, borates, carbonates, or bicarbonates, may be used instead of or in conjunction with the phosphates. It will be noted that the builder salts are usually of alkaline pH in dilute solution and this also often increases the detergency of the built compound. However, in some circumstances it is desirable to maintain a lower pH and at such times more neutral builders, such as the alkali metal salts, both complete and partial, of sequestrants such as nitrilotri-

acetic acid or ethylene diamine tetraacetic acid may be employed. Examples of the builders that may be used include sodium tripolyphosphates, tetrapotassium pyrophosphate, pentapotassium tripolyphosphate, sodium pyrophosphate, sodium hexametaphosphate, sodium carbonate, potassium carbonate, sodium tetraborate, sodium silicate ( $\text{Na}_2\text{O}/\text{SiO}_2$  ratios of about 0.5 to 0.3), potassium bicarbonate, potassium sesquicarbonate, sodium sesquicarbonate, trisodium nitrilotriacetate, tetrasodium salt of ethylenediamine tetraacetic acid, and the sodium salt of methylene diphosphonic acid. In place of the specific compounds, the suitable corresponding alkaline earth metal, ammonium, lower alkanolamine or lower alkyl amine salts are also employable, either in complete or partial substitution therefor. Of course, mixtures are also useful.

The water soluble inorganic salt builders and the water soluble or organic builders mentioned above are those which are most frequently employed in the present detergent compositions. However, in addition to the preferred condensed phosphates or in replacement of them, similar dispersing, peptizing, sequestering and alkalizing actions may be obtained from various other compounds, which have been suggested as builders for synthetic detergents. Mixed sodium and potassium salts of the condensed phosphates, including the glassy phosphates, may be employed, as may be mixed salts of silicates or tetraborates. Insoluble inorganic builders, such as clays, including kaolin, montmorillonite and bentonite can be used for certain applications, as may be synthetic colloidal magnesium and aluminum silicates, silica sols and diatomaceous earths. Among other suggested builders are sodium zincate, ammonium carbonate, dicyandiamide, sodium fluosilicate, and guanidine salts, such as guanidine carbonate. Various organic builders of known types may be used to obtain special effects. Some of these are listed hereafter in the recital of various adjuvants that may be employed with the present compositions.

With the built detergent-softener compositions there may be included for additional effects other detergents and softening compounds. For example, although it is preferred to utilize anionic synthetic organic detergents, other detergent materials, such as compatible cations, amphoteric and nonionic surface active agents and detergents may be used, too, in suitable formulations. The anionic compounds include higher alkane sulfonates, higher fatty acid monoglyceride sulfates, linear higher alkyl benzene sulfonates, higher fatty acid soaps, polyoxyethylene sulfates, hydroxyalkane sulfonates, higher alcohol sulfates, salts of lower alcohol esters of sulfofatty acids, aromatic polyethoxyether sulfates, acyl sarcosinates, acyl esters of isethionates, acyl N-methyl taurides and others of the commercially available, well-known anionic surface active agents and detergents. In such compounds the aromatic group will usually be benzene, the polyethoxy group will usually be from 3 to 30 ethoxys or other lower alkoxys, the lower alkyl will normally be of 1 to 6 carbon atoms and the higher alkyl will be of 8 to 22 carbon atoms, preferably from 12 to 18. The salt-forming metals or other suitable radicals are preferably alkali metal, such as potassium and sodium but alkaline earth metals, e.g., calcium, ammonium, lower alkyl amine, lower alkanolamine, and magnesium may also be employed. Specific examples of the anionic detergents include sodium lauryl sulfate; sodium linear tridecyl benzene sulfonate; triethanolamine lauryl sulfate; sodium and potassium coconut oil-tallow soaps; sodium lauryl sulfonate; potassium hexadecyl naphthalene sulfonate; lauryl alcohol ethylene oxide sulfate comprising 4 ethoxy groups per molecule; potassium stearyl glyceryl ether sulfonate; sodium lauroyl sarcosinate; and magnesium N-methyl tauride. These are only a few of the well-known anionic surface active agents and to those of skill in the art identification of other members of this class will be obvious.

Among the nonionic surface active agents are the condensation products of alkylated phenols with ethylene oxide, alkyl thiophenols with ethylene oxide, higher fatty alcohols with ethylene oxide and polyalkylene glycols or other polyols with lower alkylene oxides. Specific compounds within this class are phenols condensed with from 6 to 30 moles of ethylene oxide; condensation products of polymers of propylene oxide with polymers of ethylene oxide; and ethers from higher fatty alcohols, such as lauryl alcohol, and polyethylene oxide.

Representative of the cationic surface active agents that are usable are N-aminoethyl higher alkyl amine; N-2 aminoethyl higher fatty acid amides; quaternary ammonium compounds wherein an alkyl group is of about 12 to 18 carbon atoms and the other groups attached to the nitrogen are alkyls of 1 to 3 carbon atoms. Typical of the preferred quaternary ammonium detergents are ethyl dimethylstearyl ammonium chloride; benzyl dimethylstearyl ammonium chloride; trimethylstearyl ammonium chloride; and trimethylacetyl ammonium bromide. Of course, others of these well-known cationic detergents may be used instead. The quaternary surface active materials also function as softening agents. The amphoteric detergents, which contain both anionic and cationic groups, include the N-higher alkyl betaines, N-alkyl-beta-amino propionic acid; and N-alkyl-beta iminodipropionic acid. It will be noted that these compounds bear a superficial resemblance to the softeners of the present compositions. The suitable amphoteric detergents include the fatty imidazolines and betaines containing a sulfonic group instead of a carboxylic group.

To impart their particular effects to the materials being treated, other adjuvants may also be employed in the present detergent compositions. These include filler salts; solvents; soil-suspending agents or anti-redeposition agents; such as sodium carboxymethyl cellulose and polyvinyl alcohol; perfumes; dyes; optical brighteners; antioxidants; preservatives; hydrotropes; bactericides; anti-tarnish agents; opacifiers; bleachers; bluing; abrasives; enzymes; thickeners; foam-enhancing agents; foam-destructive agents; sequestrants; and various other adjuvants. Examples of such materials include 2,6-di-tertiary butylphenol (antioxidant); sodium 2-sulfo-4-(2-naphtho-1,2-triazole) stilbene (an optical brightener); lower alkyl aryl sulfonates such as sodium toluene sulfonate, sodium cumene sulfonate, and potassium xylene sulfonate (hydrotropes); trichlorocarbanilide and hexachlorophene (bactericides); sodium perborate and potassium dichloroisocyanurate (bleaches); pepsin, keratinase and papain (enzymes); water, ethanol, propylene glycol, isopropanol (solvents); sodium sulfate (anhydrous), Glauber's salt, potassium sulfate, sodium chloride, ammonium sulfate (filler salts); lauric diethanolamide (foam enhancer and thickener) and dimethyl siloxane (foam destroyer).

The detergent-softener compositions of this invention may be in either a solid or liquid form, including pastes, gels, free-flowing liquids, emulsions, lotions, thick liquids, bars, cakes, tablets, capsules, powders, granules, spray-dried beads and other suitable forms. These may be produced by usual formulating and processing techniques. To make solids, it is possible merely to blend the various constituents of the desired composition and mix carefully. The powders resulting may be packaged in paperboard cartons or in water soluble polyvinyl alcohol packets. Alternatively, after mixing, these may be tableted, milled, plodded and pressed, dried, agglomerated or subjected to other process steps. Often to make gels, emulsions solutions or other liquid or semi-solid forms of these compositions and sometimes to make solids of a particular type, such as spherical beads or granules, the constituents of the composition are first dissolved or suspended in a

liquid medium, such as water or other suitable solvent. They may then be treated in any of various suitable ways to convert them to desired forms. In one case, a crutcher mix or solution of the iminodicarboxylate and a builder salt, either with or without adjuvants, is spray-dried in a conventional spray tower to produce particles or beads instead of mechanically blended powder. The filler salts, hydrotropes, other detergents and other adjuvants may be added after spray drying or, in suitable cases, may be blended in with the crutcher mix and dried with it.

If the product is to be a liquid, it is preferred that it be a free flowing liquid, of a viscosity between that of water and a syrup, such as maple syrup. If produced as a powder, it is preferred that the particle sizes be from 6 mesh to 200 mesh, preferably being from 12 to 100 mesh (U.S. Standard Sieve Series). However, as indicated previously, other physical forms of the composition may be employed.

Whatever the form of the product, it is important that it contain sufficient of the detergent-softener compound to be effective in use. Thus, usually less than 2% of such material in a solid or liquid product is found to be so low a concentration that when utilized as an additive to wash water or rinse water in an automatic washing machine or when employed as a pre-soak, the concentration of active materials in the final solution is such as to be comparatively ineffective. Therefore, it is considered to be important that at least 2% of the present active detergent-softener be present in the compositions. Similarly, at least 5% of builder salt should be present to have its effect obtained. Maxima of such materials are considered to be 50% and 98%, respectively. Preferred ranges of proportions of the active compound and builder salt, respectively, are 3 to 30% and 10 to 70% of the composition. If a solid product is made, it will normally be most desirable to include from 10 to 20% of the active compound in it, together with 20 to 45% of a builder, such as pentasodium tripolyphosphates. Similarly, when solutions are marketed, they should contain from 5 to 20% of the active compound, 10 to 30% of builder salt, such as tetrapotassium pyrophosphate, and 35 to 85% water. At such concentrations and with such materials, the deterative effects of the softening composition are not adversely affected by the builder salt or other synthetic surface active agents or fillers. Rather, detergency is improved by the builder and anti-static action may often be noted on the washed textiles.

Of course, other liquid or solid adjuvants may also be employed. This term includes other synthetic detergents, softeners, hydrotropes, solvents, fillers, etc., as well as other more minor additives. Generally, from 0.1 to 25% of an adjuvant may be included in the present composition, depending upon the nature thereof. A supplemental synthetic detergent, surface active agent or filler salt may be used in comparatively large proportion, e.g., 10 to 25%, whereas a fluorescent dye or perfume will usually be present only to a very minor extent, e.g., 0.1 to 2%. Preferred ranges for most of the various adjuvants are from 0.5 to 5% of each, with a total adjuvant content of no more than 50% of the composition. However, as much as 50% inorganic filler salt can be used. Such salts, including sodium sulfate, potassium sulfate, and sodium chloride, are often added to aid in improving the physical properties of particulate solid compositions of this invention. They may also be present as byproducts of reaction or as fillers in the starting materials. A preferred concentration thereof in the present products is from 5 to 35%. In cases where some adjuvants may be incompatible upon storage with other constituents of the present compositions, their effects may be obtained by adding them to the wash water together with the present compositions. Except for those cases of incompatibility, the various constituents of these compositions may be mixed together at any suitable stage of manufacture, in some cases even being added during the chemical manufacturing

process whereby the present iminocarboxylates are produced. In such a situation, a synthetic detergent or hydrotrope might be employed during the reaction of olefin oxide with iminodicarboxylic acid to make the precursor of the present compounds. The surface active material can then be carried over with the active ingredient and have its effects utilized in the final product, as well as in the manufacturing procedure. Thus, it is seen that variations in processing conditions may be used. Processing temperatures may be from 20° C. to over 400° C. but are usually from room temperature to ordinary spray drying temperature, such as 25° C. to 300° C.

In use, the present compositions are diluted with about 10 to 100,000 parts of solvent, such as water, per part of the iminocarboxylate detergent-softener compound, to make an effective softening solution. Preferably, the dilution will be with from about 500 to 25,000 parts and most preferably, with about 2,000 to 10,000 parts of water. On a product basis, adjustment will be made for the generally lesser proportion of active material in the liquid preparation but it can be said that usually there will be used from about 100 to 4,000 times as much water as composition. Generally, for a solid product, the amount of water employed will be from about 400 to 2,000 times the weight of the solid, whereas in the case of the liquid preparations, the ratio will be from about 200 to 1,000.

Textiles washable with the present compositions include those made from cotton, wool, rayon, nylon, polyesters, cellulose acetate, and other natural and synthetic fibers. Human and animal hair, including "living" hair may be treated with the iminodicarboxylate, but usually compositions for treating living hair will contain little or no alkaline builder salt.

The detergent-softener composition is normally added as the active detergent ingredient to an automatic washing machine before beginning of washing. It may provide the entire detergent and softening actions or it may be supplemented by other preparations for such purposes. In either case, by adding before the final rinse it is possible to have a softened wash without the necessity for special equipment on the automatic washing machine or the need for the housewife to keep watch over the machine so that she may add softener in the rinse. A similar effect may be obtained by using approximately the same proportions of detergent-softener composition as a pre-soak, before washing. Such pre-soaking may be combined with an enzyme treatment. If considered desirable under the circumstances, the compositions may be added to the rinse water, although this is not usually necessary to obtain the desired softening effect.

The present products have been found to be effective in both hard and soft waters and when washing at either high or low temperatures. Thus, they are useful detergent-softeners over a hardness range from soft water, e.g., of 0 to 50 p.p.m. hardness, to as much as 300 p.p.m. of hardness, calculated as calcium carbonate. Such hardness may be due to calcium, magnesium or other hardness ions or mixtures of such ions in the water. The invented compositions are useful at washing temperatures ranging from 20 to 100° C. but most often the temperature of the wash water is in the range from 30 to 70° C.

The builders employed in the present compositions are usually alkaline and therefore the wash water or soak or rinse water containing such compositions will usually be of pH in the range of 8 to 10, with 9 to 10 being preferred. Nevertheless, it is possible to operate at other pH's with useful effect. In fact, a method of this invention for washing and softening textiles may also be followed in the absence of builder salt, in which case it is easy to obtain an acid pH, e.g., 4 to 7. Although it is most highly desirable to employ present iminodicarboxylates in conjunction with inorganic builder salt, the present invented method extends to utilizing the active compounds alone or with adjuvants other than the builder salt. Thus, where only a softening effect or anti-static action is wanted or when material being treated is not badly soiled, so that

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detergent action is unnecessary, the amount of inorganic builder salt present may be diminished and even reduced to zero. In many cases, as where delicate or fine laundry items are being washed, it may be desirable to avoid contact with inorganic builder salt solutions and in such cases the gentler action of the present composition, without builder or with insoluble or non-alkaline builder, may be preferred. The useful detergency of the present iminodicarboxylates allows their employment without builder in many such situations. The methods of use of such compositions, without builder salt, are the same as those previously described herein.

The soaking, washing and rinsing times employed are those ordinarily followed in treatments of textiles. Thus, soaking may be for a period from about 5 minutes to overnight, washing may take about 2 to 25 minutes and rinsing may take about 2 to 10 minutes, in the usual machine washing operation. Nevertheless, other times and other obvious modifications of the preceding conditions may be used within the invention.

To illustrate the invention the following examples are given. They are not to be interpreted as limiting the invention to the specific embodiments set forth herein, since it is clear that the working examples show only certain preferred embodiments of the invention. Where a single active compound or builder or other material is indicated in the examples or in the specification, it is clear that mixtures of the equivalent materials, within the invention may be employed instead. All temperatures are in degrees centigrade and all parts are by weight, unless otherwise noted.

## EXAMPLE 1

|                                                         | Percent |
|---------------------------------------------------------|---------|
| N-(2-hydroxyhexadecyl)-iminodiacetic acid disodium salt | 23      |
| Pentasodium tripolyphosphate                            | 77      |

The above formulation, in particulate form, wherein the particles are within the size range of 12 to 100 mesh, U.S. Standard Sieve Series, is made by mixing N-(2-hydroxyhexadecyl)-iminodiacetic acid, disodium salt and pentasodium tripolyphosphate powders in a mechanical blend. The N-(2-hydroxyhexadecyl)-iminodiacetic acid, disodium salt is made reacting 1,2-hexadecane epoxide with iminodiacetic acid, disodium salt, according to the method described in this specification and more specifically, in accordance with the method of our patent application entitled N-(2-Hydroxyhydrocarbyl) Iminodicarboxylates, filed on the same day as the present application.

The built composition described above is tested for efficacy as a fabric softener and is found, by standard test, to obtain an exceptionally high rating (10+), indicating an excellent softening effect. The test is conducted on cotton materials but softening is also noted on other natural and synthetic organic textiles, e.g., rayon, wool, polyester blends, nylon. The test utilizes one-half of a terrycloth towel in three gallons of water, having an approximate hardness of 100 parts per million, as calcium carbonate. The water used is at 120° F. and contains 8.6 grams of the composition of this example in the three gallons used. The towel is washed in a Mini-basket of a General Electric Company automatic electric washing machine, using the conventional washing and rinsing cycles. Washing lasts for approximately 10 minutes and rinsing takes about the same time. After rinsing, the towel is essentially freed of water and is dried, after which softness is rated on a scale of 1 to 10, with 1 indicating a towel that is not soft and 10 indicating excellent softness.

In a similar manner, such testing of other iminodiacetates, e.g., N-(2-hydroxydocosyl)-iminodiacetic acid, dipotassium salt; N-(2-hydroxyhexadecenyl)-iminodipropionic acid, magnesium salt; N-(2-hydroxyoctadecyl)-imino-acetic-propionic acid, disodium salt and N-(2-hydroxyhexadecyl)-iminodiacetic acid, di-triethanolamine salt; result in findings of good softening properties for tex-

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tiles, especially for cotton. The results obtained for the N-(2-hydroxyhexadecyl)-iminodiacetic acid, disodium salt, reported above, are considered to be representative of those for the compounds of this invention which are disodium or dialkali metal salts of iminodiacetic acid or comparable iminodi-lower carboxylic acids and in which the R<sup>1</sup> groups are of 14 to 22 carbon atoms. When R<sup>1</sup> is of 12 carbon atoms, the softening obtained is not as good as that with R<sup>1</sup> of greater carbon content. Also, as the carbon content is lowered, softening effect diminishes.

## EXAMPLE 2

|                                                        | Percent |
|--------------------------------------------------------|---------|
| N-(2-hydroxydodecyl)-iminodiacetic acid, disodium salt | 15      |
| Sodium tripolyphosphate                                | 35      |
| Sodium sulfate                                         | 50      |

A detergent powder formula of the above composition is made, in which the particles are in the range of 6 to 120 mesh, U.S. Standard Sieve Series. The composition is made by mechanically blending of solid particles of various ingredients but may also be made by spray drying an aqueous crutcher mix thereof.

The composition is tested for detergency by the preparation of a 0.15% solution of the product in water, followed by the washing of the three cotton percale swatches, each three inches by six inches. The 0.15% concentration corresponds to that normally recommended for use in a home automatic washing machine. The cotton percale swatches are first soiled with a mixture of airborne and sebum soils so that the degree of soil removal can be utilized as a measure of detergency. The swatches are washed in a Tergotometer evaluating washing machine, using waters of two different hardnesses, at two different temperatures, as indicated in the accompanying table. After washing, the swatches are rinsed and then tested for whiteness, using a color difference meter. The time of washing is about 12 minutes and rising is effected in about 10 minutes. After washing, rinsing and drying, the swatches are tested for whiteness, using a color difference meter. A comparison of readings, using the Rd scale, between the materials before and after washing, is made and the delta Rd is calculated. The greater the delta Rd, the more efficient the soil removal and the better is the detergency obtained. Linear tridecyl benzene sulfonate, as the sodium salt thereof, is employed as a standard of comparison for detergency in this test. The test is also run using N-(2-hydroxyhexadecyl)-iminodiacetic acid, disodium salt instead of the N-(2-hydroxydodecyl)-iminodiacetic acid, disodium salt.

The results of this detergency testing are reported in Table 1. From the data and comparison with the control, it is apparent that the compositions tested, which are considered to be representative of those made in accordance with this invention, as described above, are useful detergents. They are effective in hard water and in water of medium hardness and are good for both hot and cold water washing. It is seen that they are most effective in ordinary city water of medium hardness, such as New Brunswick, N.J. tap water. They wash better in hot water than in cold water. Similar results are obtained by the use of other iminodicarboxylates wherein the hydroxy-alkyl is of 8, 10, 14, 18 or 20 carbon atoms. Such results are also obtained when the hydroxyhydrocarbyl is octadecenyl and are also achieved with various other salts of these compounds, e.g., potassium, ammonium, magnesium and triethanolamine salts, and when other builders, e.g., sodium silicate, potassium pyrophosphate, sodium carbonate or borax are employed and other fillers, e.g., sodium chloride, potassium sulfate, are substituted for all or part of the sodium sulfate. Proportions of the constituents of the composition are variable within the ranges given earlier in the specification, with the obtaining of similar results.

An additional benefit resulting from application of the process of this invention is that the cloths washed, whether cotton or the more static-prone nylon, polyester, or blend of synthetic fibers, are observed to be free of static after several washings. The diminution of static charge on the washed materials is apparent after one washing but appears to be increased by repeated washings, apparently indicating that with additional washings, more of the treating iminodicarboxylate is absorbed onto the washed fibers, with consequent decrease in the ability of the fiber to hold an electric charge.

TABLE 1.—SPANGLER SOIL DETERGENCY TESTS

| Composition tested (35% sodium tripolyphosphate, 50% sodium sulfate and 15% A or B)..... | Δ Rd (soil removal) |            |          |            |
|------------------------------------------------------------------------------------------|---------------------|------------|----------|------------|
|                                                                                          | 120° F.             |            | 70° C.   |            |
|                                                                                          | N.B. tap            | 300 p.p.m. | N.B. tap | 300 p.p.m. |
| (A) N-(2-hydroxydodecyl)-iminodiacetic acid, disodium salt.....                          | 16.6                | 12.2       | 15.2     | 9.1        |
| (B) N-(2-hydroxyhexadecyl)-iminodiacetic acid, disodium salt.....                        | 15.5                | 11.8       | 13.1     | 9.3        |

## EXAMPLE 3

|                                                                   | Percent |
|-------------------------------------------------------------------|---------|
| N-(2-hydroxyhexadecyl)-iminodiacetic acid, dipotassium salt ..... | 13.3    |
| Sodium cumene sulfonate .....                                     | 14.4    |
| Dye (Polar brilliant blue, RAW), 1% aqueous solution .....        | 1.7     |
| Water .....                                                       | 70.7    |

The above composition is made by dissolving the solid materials in the aqueous phase, at room temperature, to produce a clear, single phase, low viscosity liquid.

The liquid composition is tested for utility as a softener in the wash cycle of an automatic washing machine by adding 60 grams of the solution to 17 gallons (a tub-full) of New Brunswick, N.J. tap water at 120° F., together with ¾ cup of commercial, low-foaming, built synthetic detergent (Ad). A terrycloth hand towel is washed in such solution and in other tests, a full load of mixed and soiled wash is used. In both situations, the towel and the wash exhibit notable increases in softness, despite being washed in the presence of a commercial heavy duty synthetic organic detergent. Of course, the wash is also satisfactorily cleaned.

When, instead of the above formula, sodium xylene sulfonate is substituted for the sodium cumene sulfonate, comparable results are obtained. Also, when instead of the N-(2-hydroxyhexadecyl)-iminodiacetic acid, potassium salt, other salts thereof, such as the sodium and ammonium salts are used, satisfactory softening results. This is also the case when the hexadecyl group of the softening compound, R<sup>1</sup>, is replaced with a mixture of higher alkyls, such as 1.5% C<sub>14</sub>, 28.0% C<sub>15</sub>, 28.0% C<sub>16</sub>, 22.9% C<sub>17</sub> and 19.6% C<sub>18</sub>. When, in place of 10 to 20% of water, tetrapotassium pyrophosphate is substituted and the commercial detergent is omitted from use in the wash cycle, adequate cleaning is obtained, together with satisfactory softening of the wash. The softening is observable with cotton textiles and also with those made from polyester blends (Dacron, Banlon), nylon rayon, wool and other natural and synthetic fibers and fabrics and blends thereof.

The composition is also useful as a pre-soak for treatment of stubbornly stained items of clothing. In such cases it is often desirable to add from 1 to 5% of an enzyme to improve stain removal. Such enzyme may be papain, lipase or amylase.

## EXAMPLE 4

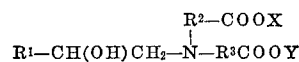
|                                                             | Percent |
|-------------------------------------------------------------|---------|
| N-(2-hydroxyoctadecyl) iminodiacetate (disodium salt) ..... | 12.6    |
| Sodium xylene sulfonate .....                               | 8.0     |
| Dye (1% aqueous solution) .....                             | 1.5     |
| Perfume .....                                               | 0.1     |
| Water .....                                                 | 77.8    |

The above liquid preparation may be made by mixing the ingredients at room temperature. It is a clear, single phase, low viscosity product. The product is evaluated in an automatic washing machine by adding 60 grams thereof to the rinse cycle, following washing of a single towel or an ordinary wash load in New Brunswick, N.J., tap water, at 120° F. The rinse is effected with either warm or cold water, over a period of about 10 minutes. The concentration of the liquid composition in the wash water (the tub holds 17 gallons) is about 0.1%. After completion of the rinsing operation and air drying or machine drying of the articles washed and rinsed, it is noted that they are significantly softer than a control on which no softener had been employed. A similar results is obtained when the composition is used to make a pre-soak solution, wherein the wash is allowed to soak at room temperature in an aqueous solution of the composition at a concentration of about 1%, for a period of about three hours, before washing in a solution of commercial detergent in an automatic washing machine. Such results are also obtainable when builder salt is included with the composition, to the extent of 10 to 50%, e.g., tetrapotassium pyrophosphate, sodium carbonate, or when synthetic detergent, e.g., sodium lauryl sulfate, potassium hexadecyl sulfonate or sodium N-lauroyl sarcoside, is present, in proportion from 5 to 25%. When a supplementary softener is added to the composition, e.g., 5% stearyl dimethyl amine oxide, additional softening is observable. It is also noted that the articles washed, especially those of nylon or polyester, exhibit a diminished tendency to accumulate static charges, with and without the use of the supplementary softener, builder and detergent.

The foregoing examples and specification have described various aspects of the invention and the specific embodiments thereof. The invention is not limited to compositions and methods specifically described but embraces those utilizing equivalent components or steps, as will be clear to one of ordinary skill in the art, reading this specification.

What is claimed is:

1. A composition for the treatment of textiles consisting essentially of from 2-30% of a compound of the formula:



wherein R<sup>1</sup> is alkenyl containing 1 or 2 double bonds or alkyl of 4 to 20 carbon atoms, R<sup>2</sup> and R<sup>3</sup> are divalent alkylene or phenylene radicals of 1 to 9 carbon atoms and X and Y are hydrogen or water-solubilizing salt forming elements or radicals selected from the group consisting of alkali metal, alkaline earth metal, ammonium, mono-alkanolamine, di-alkanolamine, tri-alkanolamine, mono-alkylamine, di-alkylamine and tri-alkylamine in which the alkyl and alkanol group contain from 1 to 4 carbon atoms, the remainder to make up 100% being essentially inorganic or organic salt builder.

2. A composition according to claim 1 additionally containing from 0.1 to 25% of detergent selected from the group consisting of anionic, cationic, amphoteric and nonionic detergents.

3. A composition according to claim 1 wherein the builder is an inorganic salt builder.

4. A composition according to claim 1 wherein R<sup>2</sup> and R<sup>3</sup> are alkylene radicals of 1 to 4 carbon atoms and

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are the same, and X and Y are the same, and the builder salt is an alkali metal salt.

5. A composition according to claim 4 wherein R<sup>1</sup> is a linear alkyl radical, terminally joined to the rest of the molecule and R<sup>2</sup> and R<sup>3</sup> are of 1 to 2 carbon atoms.

6. A composition according to claim 4 wherein said compound is 3 to 30% and the builder salt is from 10 to 70% of the composition.

7. A composition according to claim 6, in said compound of which R<sup>1</sup> is of 12 to 14 carbon atoms, R<sup>2</sup> and R<sup>3</sup> are methylene and X and Y are alkali metal.

8. A composition according to claim 7 wherein the builder salt is an alkali metal phosphate.

9. A composition according to claim 8 which is in particulate solid form and which comprises from 10 to 20% of said compound and 25 to 45% of sodium tri-  
polyphosphate.

10. A composition according to claim 8 which is in liquid form and which comprises from 5 to 20% of said compound, 10 to 30% tetrapotassium pyrophosphate and from 35 to 85% water.

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11. A composition according to claim 9 wherein in said compound R<sup>1</sup> is of about 14 carbon atoms, terminally joined to the rest of the compound.

12. A method for laundering textiles which comprises washing said textiles with a composition as defined in claim 1 and wherein the washing treatment is at a temperature of 30° to 100° C. and at a concentration of one part of said composition to 500 to 25,000 parts of water and at a pH of 8 to 10.

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