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3,684,744

GRANULAR ALKALI METAL NITRILOTRI- ACETATE AND PROCESSES FOR PRODUC- ING SAME

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Ser. No. 61,034

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U.S. Cl. 252—546

4 Claims

ABSTRACT OF THE DISCLOSURE

Caking-resistant granular alkali metal nitrilotriacetate products are prepared by forming a reaction mixture of nitrilotriacetic acid and alkali metal carbonate and water; the molar ratio of nitrilotriacetic acid to the alkali metal content of said carbonate being from about 1:2 to about 1:20, said water comprising from about 5% to about 35% by weight based upon the weight of the total reaction medium and drying the resulting mixture to obtain a detergent additive containing dialkyl metal nitrilotriacetate and having a bulk density of from about 0.4 to about 0.8 g./cc. and having about 60% of its particles smaller than the openings in a U.S. Standard 10 mesh screen and about 60% larger than the openings in a U.S. Standard 60 mesh screen and less than about 8% by weight of water.

This invention is a division of U.S. patent application, Ser. No. 709,875, filed Mar. 4, 1968, issued Dec. 21, 1971 as U.S. Pat. No. 3,629,329 and relates to granular caking-resistant products suitable for dry-blending with other detergent ingredients. More particularly, it relates to a dry, free flowing product containing dialkyl metal nitrilotriacetate and processes for producing same.

The water-soluble salts of nitrilotriacetic acid are desirable detergent additives. Some problems exist with the incorporation of these materials into detergents. For example, essentially all of the commercial production of nitrilotriacetic acid salts is by the alkaline hydrolysis of nitrilotriaminonitrile to yield trisodium or tripotassium nitrilotriacetate. Trisodium or tripotassium nitrilotriacetate is hygroscopic and when it is incorporated into detergent formulations, the detergents tend to cake. The problem with caking is so acute that moisture barriers such as wax coatings, liners of aluminum foil, plastic and the like are used in detergent cartons to prevent caking during storage. While the use of such barriers in the detergent carton is effective to prevent caking during storage, after cartons are open, the contents can be subjected to relatively high humidity conditions, causing the detergent formulation to cake unless it is used relatively soon after opening. It is believed, therefore, that a caking-resistant product which is suitable for dry blending with other detergent ingredients to form a detergent formulation which is equivalent to trisodium nitrilotriacetate as a detergent builder would be an advancement in the art. Furthermore, it is often preferred to use the disodium, dipotassium, or mixtures of these salts in a detergent formulation to improve the detergent functional properties since these salts are less alkaline than the trisodium salts.

In accordance with this invention it has been discovered that a caking-resistant granular product containing dialkali metal nitrilotriacetate having a bulk density of from about 0.4 g./cc. to about 0.8 g./cc. and having greater than about 60% of its particles smaller than the openings in a U.S. Standard 10 mesh screen and larger than the

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openings in a U.S. Standard 60 mesh screen and containing less than about 8% by weight of water has the desirable caking-resistant properties, and detergent building efficiency, and can be dry-blended with other detergent ingredients to form highly desirable detergent formulations that do not cake even under high humidity conditions.

The term "caking resistant" as used herein means that the composition shows no appreciable tendency to cake even when subjected to pressure and stored under relatively high temperatures and high humidity conditions. For example, 50 gram samples after being placed in a cylindrical container and subjected to a pressure of 5 lbs./square inch at the top surface of the sample for 48 hours and at a relatively humidity of 80% and at a temperature of 100° F. with no evidence of caking that is upon screening with conventional screening techniques the particle size distribution is approximately the same as before the material was subjected to the foregoing conditioners of pressure and temperature.

The foregoing desirable detergent additive is produced by forming (1) a relatively uniform reaction mixture comprising (a) nitrilotriacetic acid, (b) alkali metal carbonate and (c) water; said reaction mixture having a molar ratio of nitrilotriacetic acid to the alkali metal from at least 1:2 to about 1:20, said water being from about 5% to about 35% by weight of said reaction mixture and (2) drying the reaction mass to produce a product containing less than about 8% water.

From about 5% to about 35% by weight of water in the reaction mixture is necessary to produce a granular material and for good conversion of the acid. Additionally, a slurry is formed when more than 35% water is used and excessive amounts of material having higher water solubles, and particles smaller than the openings in a 60 mesh U.S. Standard screen are produced at lower water levels than about 5%. The preferred range of water level is from about 10% to about 22.5% by weight of the reaction mixture depending on the type of carbonate.

In the process of this invention order of addition is relatively unimportant; however, it is generally preferred to form a mixture of the acid and the alkali metal carbonate and then add the water. If desired, however, the alkali metal salts can be mixed with water to form a concentrated mixture and this mixture added to the nitrilotriacetic acid. Similarly, the acid and water can be mixed together and added to the alkali metal carbonate. It is essential that the ratio of nitrilotriacetic acid to the alkali metal in the reaction medium is at least 1:2 on a molar equivalent basis in order to convert the acid to its dialkali metal salt since nitrilotriacetic acid is water-insoluble; there must be sufficient alkali metal present to form the dialkali metal salt.

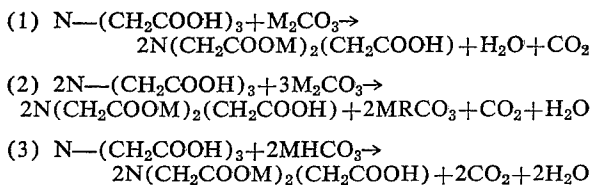
Although any alkali metal carbonate can be used such as the sodium, potassium and lithium carbonates, in most instances, sodium and potassium carbonates are preferred. Both the monoalkali metal carbonates and the dialkali metal carbonates can be used as long as the molar ratio of the nitrilotriacetic acid to the alkali metal is maintained within the ranges specified above.

The molar ratio of nitrilotriacetic acid (NTA) to alkali metal (M) in the reaction mixture can be from 1:2 to about 1:20 and a suitable product is produced. Use of a larger excess of alkali metal that is above a NTA to M molar ratio greater than about 1:20 results in high levels of alkali metal carbonate, thus reducing the metal sequestration capacity. Although in theory if the NTA:M molar ratio exceeds 1:3, that is from about 1:3.1 to 1:20, it would be expected that the nitrilotriacetic acid would be converted to trialkali metal nitrilotriacetate (M_3NTA); however, formation of the trialkali metal salt does not

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occur to an appreciable extent. Molar ratios of NTA:M of from about 1:2.5 to about 1:5 in the reaction medium are preferred for optimum properties of particle size, sequestration rate and density.

In theory the following reactions can occur in the process of this invention, wherein M is an alkali metal:



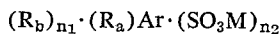
Therefore, under some conditions, it is possible to produce a product containing only the disodium nitrilotriacetate, however, in most instances, it is preferred that an excess of theory of the alkali metal carbonate be used to insure conversion of all of the nitrilotriacetic acid. Therefore, the preferred product will contain a molar ratio of disodium nitrilotriacetate to alkali metal carbonate of from 1:0.25 to about 1:1.5. Particularly preferred are products containing from about 5% to about 30% alkali metal carbonate, about 5% to about 8% water and from about 62% to about 90% disodium nitrilotriacetate.

In most instances, under preferred conditions, a relatively high yield of product having a particle size of smaller than 10 and larger than 100 U.S. Standard mesh screen can be obtained. The foregoing screen size enables the product to be blended with conventional spray-dried or agglomerated type detergents to form a formulated dry detergent having highly desirable properties. Yields of this preferred screen size, up to about 90%, can be obtained by simple screening and followed by reducing the oversized material to -10 mesh. The water-solubility of the products of the present invention is excellent, that is, essentially no water insoluble material is present when 10.0 grams of the product are mixed with 100.0 grams of water at 25° C. If desired, other detergent additives can be incorporated into the reaction mixture prior to the partial neutralization of the nitrilotriacetic acid. For example, the sodium salts of 1-hydroxy ethylidene 1,1-diphosphonic acid can be added to yield a formulated builder material which is reported to have synergistic detergent properties. It is to be noted that the bulk density of the product of this invention ranges from 0.4 g./cc. to 0.8 which enables the product to be dry blended with a conventional spray dried detergent or with other dry detergent ingredients such as dishwashing compounds.

The composition of this invention can be dry blended with any of the anionic, nonionic, zwitterionic or amphoteric type synthetic surface active agents and mixtures of these surface active agents which have been previously formulated and dried by conventional detergent manufacturing methods.

The product can be blended with various spray dried or agglomerated detergent type products containing anionic synthetic surface active agents. Anionic synthetic surface active agents, that is non-soap detergents, are generally described as those compounds which contain hydrophilic and lyophilic groups in their molecular structure and ionize in an aqueous medium to give anions containing both the lyophilic group and hydrophilic group. Any of these compounds or mixtures can be used. The alkyl aryl sulfonates, the alkane sulfates and sulfated oxyethylated alkyl phenols are illustrative of the anionic type of surface active compounds.

The alkyl aryl sulfonates are a class of synthetic anionic surface active agents and can be represented by the formula:



where R_a is hydrogen or a straight or branched chain hydrocarbon group of from 1 to 4 carbon atoms; R_b is a

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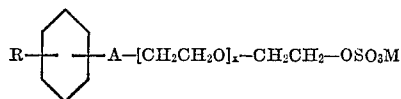
straight or branched chain hydrocarbon radical having from about 1 to about 24 carbon atoms, at least one R_b having at least 8 carbon atoms; n_1 is from 1 to 3; n_2 is from 1 to 2; Ar is a phenyl or a naphthyl radical and M_2 is either hydrogen or an alkali metal, such as sodium, potassium and the like; ammonium, or an organic amine such as ethanol amine, diethanol amine, triethanol amine and hexylamine and the like. R_a can be, for example, methyl, ethyl, propyl, isopropyl, butyl, isobutyl and the like. R_b can be, for example, methyl, ethyl, hexyl, octyl, tertoctyl, iso-octyl, nonyl, decyl, dodecyl, octadecyl and the like.

Compounds illustrative of the alkyl aryl sulfonates include sodium dodecylbenzene sulfonate, sodium decylbenzene sulfonate, ammonium methyl dodecylbenzene sulfonate, ammonium dodecylbenzene sulfonate, sodium octadecylbenzene sulfonate, sodium nonylbenzene sulfonate, sodium dodecyl naphthalene sulfonate, sodium heptadecylbenzene sulfonate, potassium eicosyl naphthalene sulfonate, ethylamine undecyl naphthalene sulfonate and sodium docosyl naphthalene sulfonate.

The alkyl sulfates are a class of synthetic anionic surface active agents and can be represented by the formula RSO_3M , wherein M is either hydrogen, an alkali metal such as sodium, potassium and the like, ammonium or an organic amine, such as ethanolamine, diethanolamine, triethanolamine, ethylenediamine and diethylenetriamine, and the like; and R is a straight or branched chain saturated hydrocarbon radical, such as octyl, decyl, dodecyl, tetradecyl and hexadecyl, as well as the mixed alkyl radicals derived from fatty oils, such as coconut oil, tallow, cottonseed oil and fish oil. R usually has from 8 to 18 carbon atoms.

Compounds illustrative of alkyl sulfate class of anionic surface active agents include sodium octadecyl sulfate, sodium hexadecyl sulfate, sodium dodecyl sulfate, sodium nonyl sulfate, ammonium decyl sulfate, potassium tetradecyl sulfate, diethanolamino octyl sulfate, triethanolamine octadecyl sulfate and ammonium nonyl sulfate.

The sulfated oxyethylated alkylphenols are a class of synthetic anionic surface active agents represented by the general formula



where R is a straight or branched chain saturated hydrocarbon group having from about 8 to about 18 carbon atoms, such as a straight or branched group, such as octyl, nonyl, decyl, dodecyl and the like; A is either oxygen, sulfur, a carbonamide group, thiocarbonamide group, a carboxylic group or thiocarboxylic ester group, x is an integer from 3 to 8 and M is either hydrogen, or an alkali metal such as sodium, potassium and the like, or ammonium, or an organic amine, such as ethanolamine, diethanolamine, triethanolamine, ethylene diamine and the like.

Compounds illustrative of the sulfated oxyethylated alkyl phenol class of anionic surface active agents include ammonium nonylphenoxy tetraethyleneoxy sulfate, sodium dodecylphenoxy triethyleneoxy sulfate, ethanolamine decylphenoxy tetraethyleneoxy sulfate and potassium octylphenoxy triethyleneoxy sulfate.

Nonionic surface active compounds can be broadly described as compounds which do not ionize but acquire hydrophilic characteristics from an oxygenated side chain such as polyoxyethylene and the lyophilic part of the molecule may come from fatty acids, phenol, alcohols, amides or amines. The compounds are usually made by reacting an alkylene oxide such as ethylene oxide, butylene oxide, propylene oxide and the like with fatty acids, a straight or branched chain alcohol, phenols, thiophenols, amides and amines to form polyoxyalkylene glycol ethers and esters, polyoxyalkylene alkyl phenol and poly-

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oxyalkylene thiophenols, and polyoxyalkylene amides and the like. It is generally preferred to react from about 3 to about 30 moles of alkylene oxide per mole of the fatty acids, alcohols, phenols, thiophenols, amides or amines. Additionally, the long chain tertiary amine oxides and the long chain phosphine oxides and the dialkyl sulfoxides can be used.

Illustrative of these synthetic nonionic surface active agents are the products obtained from the reaction of alkylene oxide with an aliphatic alcohol having from 8 to 18 carbon atoms, such as octyl, nonyl, decyl, octadecyl, dodecyl, tetradecyl and the like; with an alkyl phenol in which the alkyl group contains between 4 and 20 carbon atoms, such as butyl, dibutyl, amyl, octyl, dodecyl, tetradecyl and the like; and with an alkyl amine in which the alkyl group contains between 1 to 8 carbon atoms.

Compounds illustrative of synthetic nonionic surface active agents include the products obtained from condensing ethylene oxide or propylene oxide with the following: propylene glycol, ethylene diamine, diethylene glycol, dodecyl phenol, nonyl phenol, tetradecyl alcohol, N-octadecyl diethanolamide, and N-dodecyl monoethanolamide.

Long chain tertiary amine oxides corresponding to the following general formula, $R_1R_2R_3N \rightarrow O$, wherein R_1 is an alkyl radical of from about 8 to 18 carbon atoms, and R_2 and R_3 are each methyl or ethyl radicals. The arrow in the formula is a conventional representation of a semi-polar bond. Examples of amine oxides suitable for use in this invention include dimethyldodecylamine oxide, dimethyloctylamine oxide, dimethyltetradecylamine oxide, dimethylhexadecylamine oxide.

Long chain tertiary phosphine oxides corresponding to the following formula $RR'R''P \rightarrow O$, wherein R is an alkyl, alkenyl or monohydroxyalkyl radical ranging from 10 to 18 carbon atoms in chain length and R' and R'' are each alkyl or monohydroxyalkyl groups containing from 1 to 3 carbon atoms. The arrow in the formula is a conventional representation of a semi-polar bond. Example of suitable phosphine oxides are:

dimethyldodecylphosphine oxide,
dimethyltetradecylphosphine oxide,
ethylmethyltetradecylphosphine oxide,
cetyldimethylphosphine oxide,
dimethylstearylphosphine oxide,
cetyl ethylpropylphosphine oxide,
diethyldodecylphosphine oxide,
diethyltetradecylphosphine oxide,
bis(hydroxymethyl) dodecylphosphine oxide,
bis(2-hydroxyethyl) dodecylphosphine oxide,
2-hydroxypropylmethyltetradecylphosphine oxide,
dimethylolelphosphine oxide, and
dimethyl-2-hydroxydodecylphosphine oxide.

Dialkyl sulfoxides corresponding to the following formula, $RR'S \rightarrow O$, wherein R is an alkyl, alkenyl, beta- or gamma-monohydroxyalkyl radical or an alkyl or beta- or gamma-monohydroxyalkyl radical containing one or two other oxygen atoms in the chain, the R groups ranging from 10 to 18 carbon atoms in chain length, and wherein R' is methyl or ethyl. Examples of suitable sulfoxide compounds are:

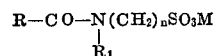
dodecylmethyl sulfoxide
tetradecyl methyl sulfoxide
3-hydroxytridecyl methyl sulfoxide
2-hydroxydodecyl methyl sulfoxide
3-hydroxy-4-decoxybutyl methyl sulfoxide
3-hydroxy-4-dodecoxybutyl methyl sulfoxide
2-hydroxy-3-decoxypropyl methyl sulfoxide
2-hydroxy-3-dodecoxypropyl methyl sulfoxide
dodecyl ethyl sulfoxide
2-hydroxydodecyl ethyl sulfoxide

The 3-hydroxy-4-decoxybutyl methyl sulfoxide has been found to be an especially effective detergent surfactant.

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An outstanding detergent composition contains this sulf-oxide compound in combination with the builder compound of this invention.

Amphoteric surface active compounds can be broadly described as compounds which have both an anionic and cationic group in their structure. Illustrative of the amphoteric surface active agents are the amido alkane sulfonates which are represented by the general formula



where M is either hydrogen, an alkali metal, such as sodium, potassium and the like or ammonium, n is an integer from 1 to 5, R is an alkyl radical with from 8 to 18 carbon atoms, and R_1 is a member selected from the group consisting of hydrogen, alkyl, aryl or alicyclic radicals.

For example, the C-aliphatic substituted, N-aliphatic substituted, amido alkyl sulfonates are illustrative of the amido alkane sulfonates. Compounds illustrative of these include: sodium C-pentadecyl, N-methyl amido ethyl sulfonate; sodium C-tridecyl, N-methyl amido ethyl sulfonate; ammonium C-decyl, N-dodecyl amido pentyl sulfonate; potassium C-hexadecyl, N-propyl amido propyl sulfonate; and potassium C-tridecyl N-hexyl amido methyl sulfonate.

In addition the C-aliphatic substituted, N-aryl substituted, amido alkyl sulfonates are illustrative of the amido alkane sulfonates. Compounds illustrative of these include: sodium C-dodecyl N-benzene amido methyl sulfonate; potassium C-octyl N-naphthalene amido propyl sulfonate; sodium C-hexadecyl N-benzene amido pentyl sulfonate and ammonium C-tetradecyl N-naphthalene amido methyl sulfonate.

Also the C-aliphatic substituted, N-cycloalkyl substituted, amino alkyl sulfonates are illustrative of the amido alkane sulfonates. Compounds illustrative of these include: sodium C-dodecyl, N-cyclopropyl amido methyl sulfonate; potassium C-tetradecyl, N-cyclohexyl amido ethyl sulfonate; ammonium C-decyl, N-cyclopropyl amido butyl sulfonate and sodium C-octyl, N-cyclohexyl amido methyl sulfonate and the like.

Zwitterionic synthetic detergents can be broadly described as derivatives of aliphatic quaternary ammonium compounds in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilizing group. Examples of compounds falling within this definition are 3-(N,N-dimethyl-N-hexadecylammonio)propane - 1 - sulfonate and 3-(N,N-dimethyl-N-hexadecylammonio)2 - hydroxypropane-1-sulfonate which are especially preferred for their excellent cool water detergency characteristics.

The anionic, nonionic, ampholytic and zwitterionic detergent surfactants mentioned above can be used singly or in combination in the practice of the present invention and will be used in weight ratios of surface active agent to the product of this invention of from about 1:10 to 10:1 with weight ratios of from 1:5 to 5:1 being preferred. The above examples are merely specific illustrations of the numerous detergents which can find application within the scope of this invention.

Other illustrative surface active agents can be found in Schwartz and Perry, Interscience Publishers, New York, Surface Active Agents, vol. I (1949) and vol. II (1958), which are incorporated herein by reference.

In addition to the foregoing surface active agents, in most instances other detergent additives will be used, such as the well-known phosphate detergent builders such as sodium tripolyphosphate, tetrasodium pyrophosphate, sodium and potassium sulfates and carbonates, sodium silicate, optical brighteners, corrosion inhibitors, anti-deposition agents, dyes and pigments as well as the organic sequestering agents disclosed in U.S. Pat. 3,368,978. In most instances, the foregoing detergent additives will be used in amounts of from 10% to 80% of the total de-

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tergent formulation. Generally a formulated detergent base containing mixtures of the foregoing detergent additives and surface active agents will be prepared in a conventional manner such as by the conventional spray drying technique or by the preparation of a detergent base utilizing the reaction of sodium hydroxide and sodium trimetaphosphate to produce a material containing the normal detergent additives, a surface active agent and sodium tripolyphosphate hexahydrate as is disclosed in U.S. patent application Ser. No. 460,205, now U.S. Pat. No. 3,390,093.

The foregoing detergent bases will be blended with the composition of this invention to yield a detergent composition having from about 2 to about 55% by weight of nitrilotriacetates calculated on the basis of nitrilotriacetic acid. Preferred ranges are usually from about 5 to about 40% by weight calculated as nitrilotriacetic acid.

To further illustrate this invention, the following non-limiting examples are presented. All parts, proportions and percentages are by weight unless otherwise indicated.

EXAMPLE 1

About 1880 parts by weight of nitrilotriacetic acid and about 1565 parts of sodium carbonate are charged into a ribbon blender. After the mixture is relatively uniformly mixed, about 600 parts of water are added through a nozzle to give a relatively uniform water distribution over the bed of the nitrilotriacetic acid soda ash mixture. After blending for about 15 minutes, the material is dried in a forced-draft oven at 150° F. The dried material was screened through a 10 mesh and the oversize was coarsely milled and rescreened. A sample of the material has particles larger than the openings in a U.S. Standard 60 mesh screen. The bulk density of a sample of the material measured 0.4 g./cc. Utilizing essentially the same procedure only adding 150 parts of water, the material is insufficiently agglomerated and not all of the nitrilotriacetic acid converted to the water-soluble salt. When essentially the same procedure is followed with the exception that 800 parts of water are added, essentially the same results are achieved as when 600 parts of water were added with a slight increase in the desired particle size range. When 1,000 parts of water are added, essentially all of the product is recovered in the -10 to +60 mesh screen size. Adding larger amounts such as 1200 parts of water increases the density of the resulting product to about 0.6 which is desired for incorporation in some denser detergent formulation such as dishwashing compositions. At levels above 1200 parts the product is too wet to handle; thus it is concluded that from about 5% to about 35% of water is required to achieve the product of this invention with from about 15% to about 25% being particularly preferred for this formulation.

EXAMPLE 2

About 150 parts of ultramarine blue is incorporated together with materials prepared in the same manner as described in Example 1. The 0.4 g./cc. density blue beads at a level of 5-10% are blended together with a white, traditionally prepared spray-dried detergent granule. The blue beads do not separate from the spray-dried detergent granules and have low tendency to cake, and help to control the metal ions by forming soluble metal chelates to prevent the precipitation of anionic surface active agents.

EXAMPLE 3

Three hundred and five parts by weight of nitrilotriacetic acid are mixed with 144 parts light soda ash, 149 parts potassium carbonate, 100 parts trisodium salt 1-hydroxyl ethylidene diphosphonate, 78 parts pentasodium tripolyphosphate, and 2 parts alkyl polyoxyethylene ether (a nonionic surfactant) in a twin shell blender. About 670 parts of a 37.5% sodium silicate with an SiO₂ to Na₂O weight ratio of 1.80 (containing about 420 parts of water, or 29% of the total charge) is sprayed through a

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disk-type sprayer located near the center of the blender at a uniform rate over a period of half hour. The blender has a value for venting the CO₂ from the reaction of the carbonates and nitrilotriacetic acid to form the dialkalimetal salts. The sized product contains less than 10% smaller than 60 mesh, and has a bulk density of about 0.65 grams per cubic centimeter. After drying to remove the excess moisture, about 3 parts of a granular potassium chlorine cyanurate are blended together to give a superior automatic dishwashing compound. When a sample is exposed to a relative humidity of 80% at 100° F. and to a pressure of 5 lbs./square inch for a period of 24 hours, the product from the process described above remains free-flowing. If the same composition is slurried so that most of the nitrilotriacetate salt is in the tri-substituted form and spray-dried, the resulting product cakes after exposure to 80% RH at 30° C. for 24 hours. A wax-lined box is required for the latter type of product.

What is claimed is:

1. A caking-resistant granular detergent additive consisting essentially of disodium nitrilotriacetate having a bulk density of from about 0.4 to 0.8 g./cc. having about 60% of its particles smaller than the openings in a U.S. Standard 10 mesh screen and larger than the openings in a U.S. Standard 60 mesh screen, containing an alkali metal carbonate and at most about 8% by weight of water, the molar ratio of disodium nitrilotriacetate to alkali metal carbonate being from 1:0.25 to about 1:1.5.

2. A detergent additive according to claim 1 wherein said alkali metal carbonate is sodium carbonate.

3. A detergent composition consisting essentially of (a) a surfactant containing a surface active agent selected from the group consisting of anionic, nonionic, zwitterionic, amphoteric surface active agents and mixtures thereof, and (b) a detergent additive consisting essentially of dialkali metal nitrilotriacetate having its particles essentially smaller than the openings in a U.S. Standard 10 mesh screen and larger than the openings in a U.S. Standard 60 mesh screen, having a bulk density of from about 0.4 to 0.8 g./cc.; containing an alkali metal carbonate and at most 8% water by weight, the molar ratio of disodium nitrilotriacetate to alkali metal carbonate being from 1:0.25 to 1:1.5; said detergent composition containing from about 2% to about 55% of nitrilotriacetates calculated on the basis of nitrilotriacetic acid the weight ratio of said surface active agent (a) to said detergent additive (b) being from about 1:10 to 10:1.

4. A detergent composition according to claim 3 wherein said detergent additive contains from about 5% to about 30% by weight of alkali metal carbonate.

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U.S. Cl. X.R.

252-180, 383, 384, 385, 527, DIGEST 11

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,684,744 Dated August 15, 1972

Inventor(s) Chung Yu Shen and Norman Earl Stahlheber

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

[In Column 3, line 11, the end of formula reading " $+2\text{MRCO}_3+\text{CO}_2+\text{H}_2\text{O}$ "]
should read $---+2\text{MHCO}_3+\text{CO}_2+\text{H}_2\text{O}---$.

Signed and sealed this 9th day of January 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

UNITED STATES PATENT OFFICE
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