

3,591,630
CAKING-RESISTANT GRANULAR SODIUM NITRILOTRIACETATES AND PROCESSES FOR PRODUCING THE SAME

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5 Claims

ABSTRACT OF THE DISCLOSURE

Caking-resistant granular sodium nitrilotriacetate is prepared by forming a reaction mixture of nitrilotriacetic acid and trisodium nitrilotriacetate and water; the molar ratio of nitrilotriacetic acid to trisodium nitrilotriacetate being from about 1:2 to about 1:10, said water comprising from about 15 to about 25% by weight based upon the weight of the total reaction medium and drying the resulting mixture to obtain a detergent additive containing disodium nitrilotriacetate and trisodium 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 80% larger than the openings in a U.S. Standard 60 mesh screen and less than about 8% by weight of water.

This invention 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 disodium 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 nitrilotriacetonitrile to yield trisodium nitrilotriacetate. Trisodium 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 linings of wax, aluminum foil or plastic, are used in detergent cartons to prevent caking during storage. While the incorporation of moisture barriers into the detergent carton is effective to prevent caking during storage, after the cartons are open and subjected to relatively high humidity conditions, the detergent formulation will 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.

Another problem involved in using trisodium nitrilotriacetate in detergent processing is that detergent slurries which contain trisodium nitrilotriacetate are very difficult to dry. This not only reduces the plant production capacity but also yields a product of very fine particle size. It is believed that a product containing nitrilotriacetates and having a bulk density and large particle size that enables the product to be mixed with the other detergent components to produce a complete detergent formulation will increase the production rate of most plants and will yield an improved quality detergent. The product of the present invention enables the production of an improved detergent at lower costs with a high quality thus constitutes an additional advancement in the art.

In accordance with this invention it has been discovered that a caking-resistant granular product containing disodium nitrilotriacetate and trisodium nitrilotriacetate and

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 about 80% larger than the openings in a U.S. Standard 60 mesh screen and containing less than about 8% by weight of water have the desirable properties of caking-resistance 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 foregoing desirable detergent additive is produced by forming (1) a relatively uniform reaction mixture comprising (a) nitrilotriacetic acid, (b) trisodium nitrilotriacetate and (c) water; said reaction mixture having a nitrilotriacetic acid to trisodium nitrilotriacetate molar ratio of at least 1:2 to about 1:10, said water being from about 15% to about 25% by weight of said reaction mixture and (2) drying the reaction mass to produce a product containing less than about 8% water.

The term "caking resistant" as used herein means that the composition shows no appreciably greater tendency to cake than spray dried detergents which do not contain sodium nitrilotriacetate salts. For example, 50 gram samples of the product of this invention, after being placed in a cylindrical container and subjected to a relative humidity of 80% at 100° F. for 48 hours shows little evidence of caking, that is, upon screening with conventional screening techniques, essentially all of the sample passes through a 6 mesh screen U.S.S. sieve series.

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 sodium salt and then add the water. If desired, however, the sodium 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 sodium salt. It is desirable in some cases to use an excess of the trisodium salt in order to insure that all of the water-insoluble nitrilotriacetic acid is converted to the disodium salt. Hence, the final product may be represented as a granular non-caking, free-flowing mixture of the di- and tri-sodium salts of nitrilotriacetic acid, the mixture containing the trisodium salt in amounts ranging from essentially 0% to about 72% by weight based upon the total weight of nitrilotriacetates present in the product.

The molar ratio of nitrilotriacetic acid to trisodium nitrilotriacetate can be from about 1:2 to about 1:10 and a suitable product is produced. Use of a larger excess of trisodium nitrilotriacetate than a ratio of 1:10 results in a material which fails to granulate when water is added. Although ratios of nitrilotriacetic acid to trisodium nitrilotriacetate from 1:2 to about 1:10 can be used, it is generally preferred to have a molar ratio of from about 1:2 to 1:5.

Additionally, from about 15% to about 25% 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 25% 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. It is preferred to use a water level of from about 17.5% to about 22.5% of the reaction mixture.

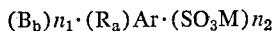
In most instances, under preferred conditions, a relatively high yield of product having a particle size of —12 to +60 (U.S. Standard mesh screen size) can be obtained. The foregoing screen size enables the product to be blended with conventional spray dried detergents to form a formulated dry detergent having highly desirable properties. Yields of this preferred screen size in excess of 60% can

be achieved in a single operation. A higher yield, that is, up to about 90%, can be achieved by reducing the oversized material to -12 mesh. The water-solubility of the products of the present invention is excellent, that is, essentially no water-insoluble material is present when 10 grams of the product are mixed with 100 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 g./cc. which enables the product to be dry-blended with a conventional spray dried detergent or with other dry detergent ingredients.

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. For example, it 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 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 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.

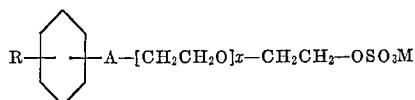
Compounds illustrative of the alkyl aryl sulfonates include sodium dodecylbenzene sulfonate, sodium decylbenzene sulfonate, ammonium methyl dodecylbenzene sulfonate, ammonium dodecylbenzene sulfonate, sodium octadecylbenzene sulfonate, sodium nonylbenzene sulfonate, sodium dodecylnaphthalene sulfonate, sodium heptadecylbenzene sulfonate, potassium eicosyl naphthalene sulfonate, ethylamine undecylnaphthalene sulfonate and sodium docoxylnaphthalene 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 ethanol amine, diethanol amine, triethanol amine, 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 ethanol amine, diethanol amine, 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 polyoxyalkylene 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 dimethylododecylamine oxide, dimethyloctylamine oxide, dimethyldecylamine oxide, dimethyltetradecylamine oxide, and dimethylhexadecylamine oxide.

Long chain tertiary phosphine oxides corresponding to the following formula $RR'P \rightarrow O$, 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.

Examples of suitable phosphine oxides are:

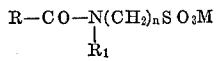
dimethyl dodecylphosphine oxide,
dimethyltetradecylphosphine oxide,
ethylmethyltetradecylphosphine oxide,
cetyl dimethylphosphine oxide,
dimethylstearylphosphine oxide,
cetyl ethylpropylphosphine oxide,
diethyl dodecylphosphine oxide,
diethyltetradecylphosphine oxide,
bis(hydroxymethyl)dodecylphosphine oxide,
bis(2-hydroxyethyl)dodecylphosphine oxide,
2-hydroxypropylmethyltetradecylphosphine oxide,
dimethyloleylphosphine 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. An outstanding detergent composition contains this sulfoxide 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 R₁ 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, amphoteric and zwitterionic detergent surfactants mentioned above can be used singly or in combination in the practice of the present invention. 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, N.Y., 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-redeposition agents, dyes and pigments. 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. 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

One thousand one hundred parts of trisodium nitrilotriacetate powder are blended with 382 parts of nitrilotriacetic acid in a rotary drier. Water is sprayed onto the rolling mixture until granules formed of apparently the desired particle size. The amount of water is about 450 grams and is added in about 5 minutes. The damp granules are dried at 150° F. to remove excess water. X-ray diffraction analysis shows that the resulting product consists predominantly of disodium NTA, with small quantities of NTA acid and trisodium NTA, pH of a 1% water solution is 7.0. The product is screened on a 12 mesh screen U.S. Standard sieve and the oversize is milled and combined with the bulk of the product. Screen analysis of a sample indicates the following.

U.S. Standard screen, mesh:	Percent
+12	1
-12 +60	85
-60	14

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EXAMPLE 2

Eleven hundred parts of trisodium nitrilotriacetate are blended with 255 parts of nitrilotriacetic acid and treated in the same manner as the product of Example 1. X-ray diffraction analysis indicates that the resulting product contains only the disodium and trisodium salts of nitrilotriacetic acid. A water solution of 10 grams of the product in 100 grams of water is clear with no undissolved particles, and the pH of the solution is about 9.6. Screen analysis of a sample indicates the following.

U.S. Standard screen, mesh:	Percent
+12	1
-12 +20	92
-60	7 15

EXAMPLE 3

Preparation A

Twenty parts of the product from Example 2 are blended with 180 parts of a detergent formulation prepared by utilizing the reaction of sodium hydroxide and sodium trimetaphosphate as is disclosed in U.S. patent application Ser. No. 460,205 now U.S. Pat. 3,390,093. The detergent formulation prepared for this test has the following composition and characteristics.

Composition:	Parts per 180 parts by wt.
Sodium alkyl aryl sulfonate	40
Sodium tripolyphosphate	70
Sodium sulfate	30
Sodium silicate solids (Na ₂ O to SiO ₂ ratio=1 to 2-4)	12
Carboxymethylcellulose, dyes, and brighteners	4

Characteristics

Screen analysis, U.S.S. Sieve Series:	
+12	5
-12 +60	75
-60	20

Bulk density, grams per cc. 0.4

Preparation B

Another preparation of the same composition as above-described is prepared in the same manner with the exception that 20 parts of trisodium nitrilotriacetate are incorporated directly in the reaction mixture. The physical properties of the second preparation are as follows:

Characteristics

Screen analysis, U.S.S. Sieve Series:	
+12	8
-12 +60	78
-60	14

Bulk density, grams per cc. 0.42

Preparation C

A third preparation of the same composition as above-described is prepared with the exception that no nitrilotriacetate additive is incorporated. The physical properties of the third preparation are as follows:

Characteristics

Screen analysis, U.S.S. Sieve Series:	
+12	4
-12 +60	80
-60	16

Bulk density, grams per cc. 0.44

Preparation D

A fourth preparation is a spray-dried heavy-duty laundry detergent formulation containing 10% trisodium nitrilotriacetate in a finely divided particle size.

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Preparation E

A fifth preparation is a spray-dried heavy-duty laundry detergent formulation not containing nitrilotriacetate salts.

5 Samples of the five preparations are subjected to an atmosphere of 85% relative humidity at 100° F. in open containers. After 48 hours, the preparations are inspected for cakingness with the following results.

Preparation:	Relative caking
D	Severely caked.
B	Severely caked.
C	Slightly caked.
A	Slightly caked.
E	Slightly caked.

The above results from the caking tests indicate that by the utilization of this invention a detergent containing the beneficial nitrilotriacetates can be prepared. Under similar conditions, a detergent containing trisodium nitrilotriacetate alone caked severely. Essentially all of the particles of Preparations A, C and E upon screening passed through a U.S. Standard 6 mesh screen while over 50% of the particles of Preparations B and D were retained on a 6 mesh screen.

What is claimed is:

1. A process for producing a caking-resistant detergent additive comprising forming a reaction mixture of nitrilotriacetic acid, trisodium nitrilotriacetate and water, the molar ratio of nitrilotriacetic acid to trisodium nitrilotriacetate being from about 1:2 to about 1:10, said water comprising from about 15% to about 25% by weight of the total reaction medium, converting from about 10% to about 100% of said trisodium nitrilotriacetate to disodium nitrilotriacetate, agglomerating and drying the resulting mixture to obtain a detergent additive containing disodium nitrilotriacetate and having a bulk density of from about 0.4 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 80% larger than the openings in a U.S. Standard 60 mesh screen and containing less than 8% by weight of water.

2. A process according to claim 1 wherein the molar ratio of nitrilotriacetic acid to trisodium nitrilotriacetate is from about 1:2 to 1:5.

45 3. A process according to claim 1 wherein the water level is from about 17.5% to about 22.5% by weight of the reaction mixture.

4. A process according to claim 3 wherein the molar ratio of nitrilotriacetic acid to trisodium nitrilotriacetate is from about 1:2 to 1:5.

50 5. A caking-resistant granular detergent additive comprising from about 20% to about 100% by weight disodium nitrilotriacetate and from about 0 to about 72% by weight of trisodium nitrilotriacetate and having a bulk density of from about 0.4 to 0.8 g./cc. having greater than about 60% of its particles smaller than the openings in a U.S. Standard 10 mesh screen and 80% larger than the openings in a U.S. Standard 60 mesh screen, containing less than about 8% by weight of water.

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LEWIS, GOTTS, Primary Examiner

J. L. DAVISON, Assistant Examiner

U.S. Cl. X.R.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,591,630 Dated July 6, 1971

Inventor(s) Chung Yu Shen and Normal 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 39, the beginning of the formula reading "(B_b)", should read---(R_b)---.

In column 8, claim 5, lines 51 and 52, the word "comprising" should be deleted and---consisting essentially of--- inserted therefor.

Signed and sealed this 19th day of September 1972.

(SEAL)

Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents