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SPRAY DRIED CONTROLLED DENSITY DETERGENT COMPOSITION

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U.S. Cl. 252—110 **15 Claims**

ABSTRACT OF THE DISCLOSURE

Soap and a resin which is a copolymer of maleic anhydride and either ethylene or methyl vinyl ether, are used in combination as additives to nonionic detergent crutcher slurries to be spray dried, for the purpose of controlling the bulk density of the spray-dried product within a desirably low range.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to the control of the bulk density of low-density spray-dried nonionic detergent powders. More particularly the present invention relates to a spray-dried detergent composition containing a nonionic detergent, a soap, and a polymer which is a copolymer of maleic anhydride and either ethylene or methyl vinyl ether.

In the commercial production of spray-dried, low-density, built detergent compositions having a nonionic surfactant as the organic detergent component, it has not hitherto been possible to achieve a bulk density within an acceptable low-density range with a countercurrent spray-drying system. As well known, the countercurrent system of spray drying is more efficient and economical than is the co-current system and has been used for spray-drying detergents known in the trade as "concentrated," having a bulk density of about 0.6.

The problem of obtaining a desirably low bulk density in spray-dried nonionic-based detergents was recognized several years ago, and solved in one instance by adding soap to the crutcher slurry.

While soap, when used as the sole density-control agent, has been effective in a spray-drying tower with co-current hot air flow, it has not been effective in countercurrent operations to produce a product having a desirably low bulk density, namely a bulk density of about 0.2 to about 0.35 gram per ml., and at the same time produce a free-flowing powder.

By the present invention, it is now possible to use the more efficient and economical countercurrent system in the spray drying of built nonionic detergent compositions having a bulk density of about 0.2 to about 0.35 gram per ml., and having satisfactory flow properties. Even at slightly higher bulk density levels, the invention is useful to obtain a bulk density lower than otherwise attainable.

A particulate detergent composition is free flowing and has satisfactory flow properties when the particle-to-particle adhesive forces are sufficiently weak to prevent substantially any particle agglomeration which, under conditions wherein the composition is in fluid motion, inhibits or greatly lessens a tendency to cake, or to exhbit a lagging flow, or creep.

The prior art

It is known that copolymers of methyl vinyl ether and maleic anhydride, or of ethylene and maleic anhydride, have been added to aqueous crutcher slurries of nonionic detergent compositions to stabilize the slurry against separation during the holding time between crutching and spray drying, the process being disclosed and claimed in

Canadian Pat. No. 704,074, which issued on Feb. 16, 1965.

The above-mentioned copolymers are also known as stabilizers against phase separation of liquid detergent compositions containing a high concentration of inorganic salts and wherein the active detergent is primarily nonionic, as disclosed and claimed in U.S. Pat. No. 3,060,124, which issued on Oct. 23, 1962, in U.S. Pat. No. 3,235,505, which issued Feb. 15, 1966, and in U.S. Pat. No. 3,301,829, which issued on Jan. 31, 1967, and in U.S. Pat. No. 3,328,309, which issued on June 27, 1967.

The interpolymer of methyl vinyl ether and maleic anhydride is known to provide a higher viscosity and to impart a soapy feel to nonionic detergent compositions in liquid form, as shown in U.S. Pat. No. 2,702,277, which issued on Feb. 15, 1955.

It is known that an ethylene/maleic anhydride copolymer can impart mechanical strength to spray-dried particles of built detergent compositions, thereby lessening attrition and thus allowing better control of bulk density, as disclosed in U.S. Pat. No. 3,380,922, which issued Apr. 30, 1968.

The use of soap to stabilize nonionic detergent crutcher slurries is known where soap is the sole stabilizing agent, as shown in U.S. Pat. No. 2,925,390, which issued on Feb. 16, 1960 and U.S. Pat. No. 2,947,701, which issued on Aug. 2, 1960.

U.S. Pat. No. 3,208,949, which issued Sept. 28, 1965 teaches that nonionic detergent compositions of the liquid type containing electrolyte builders can be stabilized against phase separation by the use of a binary mixture of an alkali metal caprylate and a copolymer of methyl vinyl ether and maleic anhydride, or of ethylene and maleic anhydride.

SUMMARY OF THE INVENTION

It has now been discovered that the bulk density of countercurrently spray-dried nonionic based detergents can be controlled by incorporating into the crutcher slurries a combination of a soap and a polymer which is a copolymer of maleic anhydride with ethylene or methyl vinyl ether.

By the term "bulk density" is meant the density in grams per ml. of loosely packed particles determined in the following manner:

A one-liter container is loosely filled with the spray-dried powder to be tested, the top scraped level, and the net weight determined. The bulk density is defined as the weight in grams of one milliliter of the loosely packed powder. The bulk density figures given in the examples are based on the weight of a one-liter volume of powder obtained by allowing the powder to fall freely from the bottom of the spray-drying tower to the container. The figures given are the average of the bulk densities of several samples taken at intervals during the run.

Accordingly it is an object of the present invention to produce a bulk-density-controlled spray-dried built nonionic-based detergent powder.

It is a further object of the invention to provide a process for controlling the bulk density of a nonionic-based built detergent composition spray-dried in a countercurrent tower.

It is another object of the invention to provide an improvement over known prior methods for controlling bulk density of spray-dried nonionic-based detergent powders.

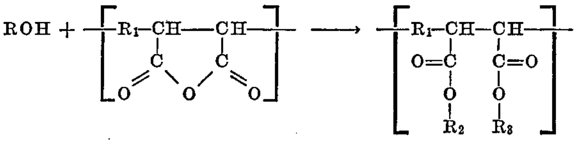
Accordingly, in its broadest aspect, the present invention relates to the control of the bulk density of a built nonionic-based detergent composition spray dried in a countercurrent stream of a hot gas.

In a more specific aspect, the invention relates to a spray-dried built, nonionic based, detergent composition of low bulk density which has been spray-dried in a counter-current stream of hot gas, and which contains a soap and a copolymer of maleic anhydride with ethylene or methyl vinyl ether.

In another aspect the invention concerns a process for controlling the bulk density of a spray-dried built nonionic detergent composition and for obtaining a desirably low bulk density thereof comprising preparing an aqueous slurry of the components to be spray dried, incorporating in said slurry a soap and a copolymer of maleic anhydride and ethylene or maleic anhydride and methyl vinyl ether, and spray drying the slurry countercurrently.

Broadly described, the process comprises charging a mixing vessel with water and adjusting the temperature thereof within the range of about 140° F. to about 210° F., either before or after charging the water to the vessel, adding thereto the desired quantity of a nonionic detergent, thereafter adding the copolymer component and mixing energetically for a period of time from about 15 minutes to about 2 hours.

In this portion of the process the hydroxyl groups of some or all of the nonionic detergent molecules react with at least some of the anhydride groups of the copolymer to form a half-ester in accordance with the following reaction, depicted for simplicity in terms of a single basic monomeric unit:

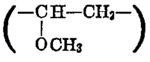


wherein

R_2 and R_3 are either R or H, and only one of R_2 and R_3 is R,

ROH represents the nonionic detergent, and

R_1 represents ethylene (—CH_2CH_2—) or methoxyethylene



$$\left(\begin{array}{c}-\underset{\displaystyle OCH_3}{\underset{|}{C}H}-CH_2-\end{array}\right)$$

To obtain the benefits of the copolymer, only a small proportion of the added copolymer need react as above. The unesterified units of the copolymer are hydrolyzed during the mixing step, the anhydride groups being converted to carboxyl groups.

At this point the reaction medium is on the acid side, the pH being usually from about 2.5 to about 3.2.

If desired, as a variation of the process, the copolymer may be pre-reacted with a small amount of a nonionic detergent in an aqueous medium, and the resulting aqueous system then diluted with water containing the remainder of the desired amount of nonionic detergent. In this case the nonionic detergent which is reacted with the copolymer need not be the same as the nonionic used as the active detergent in the product. This variation can be important as a time-saving device in commercial operations since a large quantity of pre-reacted mixture, sufficient for several crutcher batches, can be prepared at one time and the required amount portioned into each crutcher batch. When pre-reacted, the ratio of the copolymer to the nonionic detergent by weight is conveniently about 2:1 to about 100:1, and preferably about 3:1 to about 10:1.

Following the mixing together of water, nonionic, and copolymer, it is preferred to carry out as the next step the neutralization of the carboxyl groups, suitably to a pH of about 7 to about 11 by adding as the next component an alkali in sufficient quantity at least to react with the carboxyl groups in the above-described half-ester. The alkali may be an alkali metal hydroxide, carbonate, phosphate, borate, etc. The alkali metal hydroxides, particularly the hydroxides of sodium or potassium, are preferred. The soap component is preferably the next component to be added, followed by the detergent builders, and optionally miscellaneous adjuncts, such as optical brighteners, colorants, anticaking agents, suds modifiers, etc. The mixing is continued. The time of mixing following the incorporation of the last ingredient is not critical to the invention, but will be at least sufficient to provide thorough distribution of the solids.

As well known in the art, the aqueous mixture described above is in the form of a suspension or slurry containing undissolved builder or builders. Water comprises about 25% to about 50% of the slurry.

The slurry is spray dried in a conventional manner whereby the slurry is forced through nozzles to form droplets, which are allowed to fall in a tower, which may be of conventional design, through a rising current of an inert hot gas, at about 180° F. to about 750° F., preferably air, thereby forming a free-flowing particulate detergent product. The use of the above-described soap and resin together in the foregoing process permits the production of a powder of which a desirably low bulk density is attainable.

While it is not wished to be held to any theory, it is believed that the polymer and the soap coact, each assisting the other to perform a combined function. It appears that the soap component tends to expand the particle after the slurry leaves the nozzle, but that this is not sufficiently effective unless the polymer is present to maintain the nonionic component uniformly distributed throughout the particle and that it is necessary that the nonionic be uniformly dispersed and distributed throughout the particle in order that the soap may function as an expanding agent.

The compositions of the invention contain four essential components, namely a nonionic detergent, a copolymer, a soap, and a detergent builder, described hereinafter. Water is a fifth essential element of the slurry prepared for spray drying.

The nonionics suitable for use in the present invention are the surfactants which may be broadly described as the condensation products of ethylene oxide and a hydrophobic base having a labile hydrogen or sulfur atom in an alcoholic or phenolic hydroxyl group, or a thio (—SH) group. Specifically the hydrophobic base may be an alkyl phenol having about 6–12 carbon atoms in the alkyl group, alkanols having about 8–22 carbon atoms in the molecule, and the condensates of propylene glycol or ethylenediamine and propylene oxide. Included within the foregoing description are the random condensates of propylene oxide and ethylene oxide as described hereinafter. The hydrophobic base may also be an alkyl thiophenol, a long-chain mercaptan, or oleic nitrile.

When the terms "nonionic detergent" or "nonionic surfactant" are used in the instant specification and claims it is intended that the terms describe compounds falling within the foregoing broad description.

Among the nonionic detergent species suitable for use within the instant invention are the reaction products of long chain mercaptans having about 6 to 18, preferably about 12–18, carbon atoms, with about 5 to 20 moles of ethylene oxide, such as the condensates of ethylene oxide and tertiary mercaptans described in U.S. Pat. No. 2,642,400.

Other nonionics are the Pluronics (trademark of the Wyandotte Chemicals Corp.), formed by condensing propylene oxide with propylene glycol to a molecular weight of about 600–2500 to form a base followed by condensing ethylene oxide to this base to the extent of about 30 to about 90%, total molecule basis, for example those disclosed in U.S. Pats. Nos. 2,674,619 and 2,677,700; compounds formed by the simultaneous polymerization of propylene oxide and ethylene oxide, and containing randomly positioned oxypropylene and oxyethylene groups, and having over 30% ethylene oxide by weight, such as those described in U.S. Pats. Nos. 2,979,528, 3,036,118, 3,022,335, 3,036,130, and 3,048,548, alkyl phenols having 6–12 carbon atoms in the alkyl portion (straight or branched) ethoxylated with 6–25 molar proportions of ethylene oxide; ethoxylates of straight or branched fatty alcohols having 8–22 carbon atoms per molecule and 5 to 30 molar proportions of oxyethylene groups.

Examples of specific nonionic detergent compounds are: branched-chain nonyl phenol condensed with 8–14 molar proportions of ethylene oxide, a condensation product of a secondary alcohol mixture (Tergitol 15–S) having 11–15 carbon atoms and 9–14 molar proportions of ethylene oxide, a mixed C_{14}–C_{15} alcohol made by the Oxo process (Neodol 45) condensed with 9–12 moles ethylene oxide, or a mixture of 65% C_{14} and 35% C_{15} synthetic straight chain primary alcohols condensed with 9–15 molar proportions of ethylene oxide, a polyoxypropylene hydrophobic base having a molecular weight of 1500–1800 condensed with 20%–30% ethylene oxide (Pluronic L–62), and a condensate of a mixed alcohol having 10–14 carbon atoms derived from coconut oil, with about 5 to 30 molar proportions of ethylene oxide.

The choice of a nonionic detergent may vary widely, and it is not critical to the operation of the invention that any particular nonionic be used within the generic types disclosed.

The copolymers useful in accordance with the invention may be described as the linear or cross-linked copolymers of maleic anhydride and either ethylene or methyl vinyl ether. The ethylene/maleic anhydride copolymers are also referred to as EMA resins or DX resins, and the methyl vinyl ether/maleic anhydride copolymers as PVM/MA resins. The linear copolymers of the invention may be characterized by their specific viscosity, and the cross-linked copolymers may be characterized by their viscosity in aqueous solution, measured as described hereinbelow.

The specific viscosity of a substance is defined as the ratio of the viscosity of a solution of the substance at a stated concentration to the viscosity of the solvent.

The specific viscosity of the linear ethylene maleic anhydride copolymers useful in the invention is determined in a 1% solution of the copolymer in dimethyl formamide at 25° C.; that of the PVM/MA resins in a 1% solution in methyl ethyl ketone at 25° C.

The EMA resins suitable for use in the invention may vary over a wide range of molecular weights and viscosities. The specific viscosity, as defined hereinabove, may range from about 0.1 to 1. The specific viscosity of the PVM/MA resins may range from about 0.1 to about 3.5. The cross-linked EMA resins have higher molecular weights than the linear EMA resins, and have viscosities ranging from about 100 cps. to about 8500 cps. as measured at 25° C. on a 2% aqueous solution without pH adjustment, using a Brookfield viscometer, No. 6 spindle at 5 r.p.m. Suitable EMA resins are disclosed in U.S. Pats. Nos. 3,235,505 and 3,328,309, and in Monsanto's Product Information Bulletin No. 1066, "Water-Soluble Copolymers of Ethylene-Maleic Anhydride."

Suitable linear copolymers of ethylene and maleic anhydride are available from the Monsanto Company under the designations "DX-840-21," "DX-840-31," "DX-840-4118," etc. Cross-linked copolymers are available under the designations "DX-840-61," "DX-840-71," "DX-840-81," "DX-840-91" and similar materials in this series. In general, the monomers are polymerized at 1:1 ratio, the resin having molecular weights ranging from about 1500 and upwards. The cross-linked copolymers are generally cross-linked with a diamine, an alkylene polyamine, or a di-olefinic material such as an ether or a hydrocarbon, etc. Examples of polyamine cross-linking agents include diethylene triamine, triethylene tetramine, tetraethylene pentamine, and higher molecular weight polyethylene polyamines. Exemplary di-olefinic cross-linking agents include divinyl benzene, diallyl ether, vinyl crotonate, diallyl esters, and the like. The linear and cross-linked copolymers which can be utilized in preparing the compositions of the invention include the following.

EMA resins, linear:	Specific viscosity
EMA–11 (DX–840–11)	0.1
EMA–21 (DX–840–21)	0.6
EMA–31 (DX–840–31)	1.0
PVM/Ma resins, linear:	
Gantrex AN 119	0.1–0.5
Gantrex AN 139	1.0–1.4
Gantrex AN 149	1.5–2.0
Gantrex AN 169	2.6–3.5

The viscosities in 2% aqueous solution at the unadjusted pH levels of the linear and cross-linked EMA resins suitable for use in the present invention are as follows:

	C.p.s
EMA–11 (DX–840–11)—linear	2
EMA–21 (DX–840–21)—linear	5
EMA–31 (DX–840–31)—linear	7
EMA–61 (DX–840–61)—cross-linked	100
EMA–71 (DX–840–71)—cross-linked	960
EMA–81 (DX–840–81)—cross-linked	1100
EMA–91 (DX–840–91)—cross-linked	8500

The soaps which have utility in the present invention are the well-known alkali-metal salts of fatty (alkanoic or alkenoic) acids, rosin (abietic) acid, tall oil, or synthetic fatty acids having about 8 to about 22 carbon atoms, preferably 12–18 carbon atoms. All contain a hydrophobic hydrocarbon moiety and a hydrophilic carboxyl group, and may be described as alkali-metal carboxylates of an alicyclic or acyclic hydrocarbon having about 8 to about 22 carbon atoms.

The soaps obtained from natural fats and oils have a straight chain hydrocarbon group of about 7 to about 21 carbon atoms, those from rosin have an alicyclic structure wherein the hydrocarbon group has about 20 carbon atoms, those from tall oil are mainly alkenoates and alicyclic carboxylates, and the synthetic soaps may be straight chain, resembling the soaps from the natural fats, or may be branched. The soaps may be used singly, or in admixture. Soaps having the fatty acid distribution of coconut oil may provide the lower end of the broad molecular weight range, while soaps having the fatty acid distribution of peanut or rapeseed oil, or their hydrogenated derivatives, may provide the upper end of the broad molecular weight range. It is preferred to use the soaps having the fatty acid distribution of coconut oil or tallow, or mixtures thereof, since these are among the more readily available fats. The proportion of fatty acids having at least 12 carbon atoms in coconut oil soap is about 84%. This proportion will be greater when there is admixed with coconut or similar oils, the higher molecular weight fats or oils, for example tallow, wherein the principal chain lengths are C_{16} and higher. The preferred soap for use in the present invention then has at least 84% fatty acids having at least 12 carbon atoms.

It will be understood that the coconut oil may be substituted in whole or in part by other "high-lauric" oils, generally exemplified by the tropical nut oils of the coconut oil class, such as palm kernel oil, babassu oil, ouri curi oil, tucum oil, cohune nut oil, murumuru oil, and for present purposes, ucuhuba butter, a vegetable triglyceride high in myristic acid esters.

A suitable soap for use in the present invention is the alkali-metal salt of about equal parts by weight of a mixture of hexadecanoic and octadecanoic acids, namely about equal parts by weight of alkali metal stearate and alkali metal palmitate, or from a mixture of about 45% to about 55% of each.

In addition to the soaps of mixed fatty acids mentioned above, soaps of single chain length may be employed, for example alkali metal caprate (C_{10}), laurate (C_{12}), myristate (C_{14}), palmitate (C_{16}), stearate (C_{18}), arachidate (C_{20}), behenate (C_{22}), oleate (C_{18}), gadoleate (C_{20}), erucate (C_{22}), ricinoleate (C_{18}), etc. The preferred alkali-metal cation is sodium, although the cation may be potassium, rubidium, cesium, or lithium.

If desired, the soaps may be incorporated in the slurry by adding the fatty acid and alkali separately to form the soap in situ.

The soaps may be made by the well-known kettle boiling process from natural fats and oils such as tallow or coconut oil or their equivalents, by boiling with an alkali-metal hydroxide, using procedures well known to those skilled in the art. Alternatively the soaps may be made by neutralizing fatty acids, such as lauric (C_{12}), myristic (C_{14}), palmitic (C_{16}) or stearic (C_{18}) acids with an alkali metal hydroxide or carbonate. Rosin, which is primarily abietic acid, may be converted to rosin soap by neutralization as in the case of fatty acids.

The synthetic acids may be neutralized as in the case of fatty acids.

The proportions of soap expressed herein refer to proportions calculated on the basis of dry, substantially pure soap.

The builder substance employed in the present process may be any one of the water soluble substances known to have a detergency-enhancing effect when used with an organic detergent material. Suitable are alkaline detergent builders such as alkali-metal tripolyphosphate, pyrophosphate, metaphosphate, carbonate, nitrilotriacetate, orthophosphate, silicate, borate, sesquicarbonate, etc.

Also, useful are such substances as alkali-metal oxydisuccinate, oxydiacetate, carboxymethyloxysuccinate, hydrofuran tetracarboxylate, starch maleate, cellulose phthalate, glycogen succinate, semi-cellulose diglycolate, N - (2 - hydroxy-ethyl)-nitrilodiacetate, ethylenediamine tetraacetate, hydroxyethylenediamine tetraacetate, and diethylenetriamino pentaacetate. The alkali metal may be sodium or potassium. Sodium is preferred.

Specific builders are for example sodium carbonate, sodium sesquicarbonate, sodium tripolyphosphate, tetrasodium pyrophosphate, sodium metaphosphate, trisodium orthophosphate, sodium metasilicate, sodium silicate having an SiO_2 to Na_2O ratio of about 2,4, sodium tetraborate, trisodium nitrilotriacetate, etc.

Preferred alkaline electrolyte builders are sodium carbonate, sodium tripolyphosphate, tetrasodium pyrophosphate, trisodium nitrilotriacetate, and sodium carboxymethyloxysuccinate.

When present in the composition, sodium silicate functions as a builder and as a corrosion inhibitor. Suitable sodium silicates are those having ratios of SiO_2 to Na_2O between about 1 and about 3.2. Specific suitable silicates are metasilicate having an SiO_2 to Na_2O ratio of 2.4, and N-silicate having an SiO_2 to Na_2O ratio of 3.2. A potassium silicate may be substituted for sodium silicate. When a silicate is present in the composition as a corrosion inhibitor only, relatively small proportions are required, for example about 2% to about 10%, and usually about 3% to about 6% are employed. When used as a detergent builder, about 20% to about 65% may be used.

The proportions of the essential components of the detergent compositions of the instant invention are tabulated below. The proportions, except for the water content, are based on the dry weight of the product.

	Range, parts by weight, dry basis	
	Broad	Preferred
Nonionic detergent	ca. 4–30	ca. 9–25
Copolymer	ca. 0.1–5.0	ca. 0.2–0.7
Soap	ca. 0.05–5.0	ca. 0.5–1.5
Detergent builder	ca. 20–65	ca. 40–55

The above proportions in parts by weight of dry product are the same in the spray-dried product as in the aqueous slurry before spray drying. The copolymer is in the anhydride form before admixing with the aqueous nonionic solution, and in the hydrolyzed form in the spray-dried product, resulting in a slight increase in the molecular weight, and consequently the proportion by weight of the polymer in the spray-dried product. In addition to the foregoing components, an inert filler may be present, usually in the proportions of about 2 to 35 parts by weight and preferably about 15 to 30 parts by weight. The product will usually contain various adjuvants of the types set forth elsewhere herein. The water content of the spray-dried product may range from about 2 to 20, and preferably from about 10 to 15, parts by weight of the whole composition.

The inert filler may be any water-soluble or water-insoluble substance that is compatible with the components of the composition. This will usually be sodium sulfate but may be for example any other substance having substantially no function in the compositions of the invention other than to dilute or to "fill" the composition to adjust the proportions of the other components to desired levels, such as sodium chloride, magnesium sulfate, magnesium chloride, calcium sulfate, calcium chloride, silica, kieselguhr. The water-soluble non-hygroscopic diluents are preferred, such as sodium sulfate, sodium chloride, magnesium sulfate, and calcium sulfate.

Since a wide variation in water content is permissible, the proportions of the several ingredients in the compositions of the invention are most conveniently expressed on the dry basis. In the examples provided herein, the percentage compositions shown on the dry basis have been calculated from the mixing formulas. It is evident that the percentage compositions on the dry basis of a given formula in an aqueous slurry and in the product spray dried therefrom are identical.

If desired, the product may be formulated with a proportion of one or more ingredients omitted from the composition in slurry form and added to the spray-dried powder in amounts to reduce the proportions of the spray-dried ingredients to the desired levels. Ingredients which may advantageously be omitted from the slurry and added to the spray-dried powder are for example perfumes, amide or alkanol suds modifiers, detergency enhancers, etc. which may exhibit adverse behavior under spray-drying conditions. In some instances it is desirable to withhold some of the anionic detergent from the slurry and add the amount withheld to the spray-dried particles. In such circumstances the proportion of nonionic detergent in the slurry may be as low as about 4%, dry basis. The minimum amount in the spray-dried powder will usually be about 7%, dry basis.

Specific examples are set forth hereinbelow for a better understanding of the products and processes falling within the scope of the invention.

EXAMPLE 1

The following are charged to a mixing vessel.

	Pounds charged to mixer	Percentage basis dry spray-dried product
Water	55.0	
Nonionic detergent / [a]	13.5	16.6
Polymer [b]	0.5	0.6
NaOH (50% aqueous solution)	2.0	1.2
Sodium silicate ,[c] R.U	9.4	5.4
Soap [d]	1.0	1.2
Sodium carboxymethylcellulose [e]	0.46	0.6
Sodium tripolyphosphate—Type I	40.0	49.3
Sodium sulfate	20.34	25.1
Total	142.20	100.0
Water content, percent		12.1

[a] Tergitol 15–S–9, a mixture of secondary aliphatic alcohols having 11–15 carbon atoms condensed with an average of 9 molar proportions of ethylene oxide.

[b] a mixture of equal parts by weight of two ethylene-maleic anhydride resins, i.e., a linear resin identified as EMA–21 (or DX–840–21) having a specific viscosity of 0.6, and a cross-linked resin identified as EMA–61 (or DX–840–61) having a viscosity in 1% aqueous solution of 12,000 cps., said specific viscosity and viscosity being determined as hereinbefore described.

[c] A 47% aqueous solution of sodium silicate having a ratio of SiO_2 to Na_2O of 2.4.

[d] Formed in situ from NaOH and a fatty acid composed of about 45% stearic acid and about 55% palmitic acid.

[e] 65% active matter.

The remainder of the components are then added and the mixing continued for a further half hour. The resulting aqueous slurry is milled through a screen (Rietz mill) and spray dried by pumping through the nozzles of a spray drying tower and allowing the particles to fall through an upward, and counter-current, flow of hot air. The spray drying conditions are as follows:

Diameter of tower	feet	12
Height of tower	do	33
Exhaust flow	c.f.m.	7,000
Slurry temperature	° F.	150
Inlet air temperature	° F.	600
Exhaust air temperature	° F.	265–270
Inlet fan speed	r.p.m.	1350
Slurry moisture	percent	43

The bulk density of the particulate product sampled at the base of the tower is 0.32–0.33 gm. per mil. The powder is free-flowing.

EXAMPLE 2

A detergent slurry is prepared having substantially the same composition as that of Example 1, and spray dried under substantially the same conditions, the only essential difference being that the soap content is 0.5% instead of 1%.

The bulk density of the spray-dried powder is 0.32–0.33 gm. per ml. The powder is crisp and free-flowing.

EXAMPLES 3, 4, AND 5

	Ex. No. 3		Ex. No. 4		Ex. No. 5	
	Pounds	Percent, basis dry spray-dried product	Pounds	Percent, basis dry spray-dried product	Pounds	Percent, basis dry spray-dried product
Water	53.8		35.9		53.8	
Nonionic detergent [a]	15.0	19.27	10.0	19.28	15.0	18.65
Polymer EMA-21 [b]			0.2	00.38	0.3	0.37
Polymer EMA-91 [b]			0.016	0.03	0.025	0.03
NaOH (50% aqueous solution)			1.0	0.96	1.5	0.93
Sodium silicate, R.U.[c]	9.0	5.43	6.0	5.43	9.0	5.26
Soap [d]	0.75	0.96			0.75	0.93
Sodium carboxymethylcellulose [e]	0.46	0.59	0.3	0.58	0.46	0.57
Sodium tripolyphosphate	40.0	51.39	26.7	51.39	40.0	49.75
Sodium sulfate	17.4	22.36	11.4	21.95	18.9	23.51
Total	136.41	100.00	91.516	100.00	139.735	100.00

	Ex. No. 3 [1]	Ex. No. 4 [2]	Ex. No. 5 [3]
Processing conditions:			
Water in spray-dried product, percent	12.1	12.1	12.1
Slurry moisture, percent	43.0	43.0	43.0
Slurry temperature, ° F	155	155	140
Inlet air temperature, ° F	620	620	590–605
Exhaust air temperature, ° F	280	280–290	280–300
Inlet fan speed, r.p.m	1,350	1,350	1,350
Bulk density, g./ml	0.42	0.36–0.38	0.25–0.29

[1] The slurry exhibits considerable separation and is viscous. This composition is not within the invention.

[2] The bulk density of this product after spray drying is higher than desired. This composition is not within the invention.

[3] The bulk density of this product is within the range desired, and the product is free-flowing. This composition is within the invention.

Footnotes a, b, c, d, e—The components are identified as in Example 1.

The direction of the air flow empolyed in the spray-drying step is countercurrent to the fall of powder through the tower. Examples 3 and 4 illustrate the problems encountered in a countercurrent spray-drying operation when either a soap or a polymer of the types described herein are used as the sole bulk-density control agent. Example 5 illustrates the advantages of the instant invention in the use of the soap polymer mixtures.

EXAMPLES 6–9

Examples 6-9 show that the soap-polymer bulk-density control combination functions excellently in carbonate-built compositions.

EXAMPLES 6-9

	Ex. No. 6		Ex. No. 7		Ex. No. 8		Ex. No. 9	
	Mixing formula, pounds	Percent, basis dry spray-dried product	Mixing formula, pounds	Percent, basis dry spray-dried product	Mixing formula, pounds	Percent, basis dry spray-dried product	Mixing formula, pounds	Percent, basis dry spray-dried product
Water	183.5		183.5		183.5		144.0	
Nonionic detergent [a]	75.0	17.8	75.0	17.8	75.0	17.9	75.0	17.8
Polymer [b]	2.0	0.5						
Polymer [bb]			2.0	0.5	2.0	0.5	2.0	0.5
NaOH (50% aqueous solution)	4.0	0.5	4.0	0.5	3.5	0.4	3.7	0.4
Sodium silicate, R.U.[c]	106.0	11.8	106.0	11.8	106.0	11.8	106.0	11.8
Soap [d]	1.7	0.4	1.7	0.4			0.6	0.2
Fluorescent dyes and colorants	0.9	0.2	0.9	0.2	0.9	0.2	0.9	0.2
Sodium carboxymethylcellulose [e]	2.3	0.5	2.3	0.5	2.3	0.5	2.3	0.6
Soda ash [f]	200.0	47.4	200.0	47.4	200.0	47.8	200.0	47.7
Sodium sulfate	88.0	20.9	88.0	20.9	90.0	20.9	89.0	20.8
Total	663.4	100.0	663.4	100.0	663.2	100.0	623.5	100.0

See footnotes at end of table.

EXAMPLES 6-9—Continued

	Ex. No. 6[1]	Ex. No. 7[1]	Ex. No. 8[1]	Ex. No. 9[1]
Processing conditions:				
Slurry water content, percent	34.0	38.0	38.0	34.0
Water in spray-dried product, percent	4-9	9	11-12	10-18.4
Slurry temperature, ° F		140	152	170
Inlet air temperature, ° F	550	525-625	595-620	610-620
Exhaust air temperature, ° F	280	260-280	270-280	270-272
Inlet fan speed, r.p.m	1,300	1,300	1,160	1,330
Bulk density, g./ml	0.23	0.23	0.32	0.29

[1] Mixing formula, pounds.

[b] Gantrex AN139, a linear copolymer of maleic anhydride and methyl vinyl ether having a specific viscosity of 1.0-1.4.

[bb] Gantrex AN149, same as (b) but having a specific viscosity of 1.5-2.0.

[f] About 99% Na_2CO_3.

Footnote a, c, d, e—Same as in Example 1.

The slurry prepared in Example 8 produces an unsatisfactory powder in that the particles are too fine and the flow characteristics are poor. The flow characteristics of the products in Examples 6, 7, and 9 are satisfactory.

EXAMPLES 10-13

In the following experiments wherein the detergent composition is carbonate-built, the counter-current air flow is introduced through multiple inlets.

EXAMPLES 10-13

	Ex. No. 10		Ex. No. 11		Ex. No. 12		Ex. No. 13	
	Pounds	Percent, basis dry spray-dried product	Pounds	Percent, basis dry spray-dried product	Pounds	Percent, basis dry spray-dried product	Pounds	Percent, basis dry spray-dried product
Water	222	------	226.2	------	124.4	------	266.2	------
Nonionic detergent [a]	113	18.02	113	18.06	68	18.33	113	18.05
Polymer [b] (5% aqueous slurry)	60	0.48	------	------	36	0.48	------	------
NaOH, 50% solution	4.4	0.35	------	------	2.6	0.35	------	------
Soap [c]	7.5	1.19	7.5	1.20	------	------	------	------
Fluorescent dyes and colorants	1.3	0.20	1.3	0.21	0.23	0.06	1.3	0.21
Sodium silicate-N [d]	160	9.47	160	9.49	96	9.60	160	9.48
Sodium carboxymethylcellulose [e]	3.5	0.56	3.5	0.56	2.1	0.57	3.5	0.56
Soda ash [f]	300	47.86	300	47.95	180	48.51	300	47.91
Sodium sulfate	137	21.87	141	22.53	82	22.10	149	23.79
Total	1,008.7	100.00	992.5	100.00	591.33	100.00	993.0	100.00

	Ex. No. 10	Ex. No. 11	Ex. No. 12	Ex. No. 13
Processing conditions:				
Slurry water content, percent	37.0	37.0	37.0	37.0
Water in spray-dried product, percent	8-12	4-6.5	10-11	9-13
Slurry temperature, ° F	160	155	160	160
Inlet air temperature, ° F	430-475	390-430	420-430	430
Exhaust air temperature, ° F	182	182-188	180	180-188
Inlet fan speed, r.p.m	1,356	1,300	1,350	1,350
Bulk density, g./ml	0.31	0.41	0.43	0.48

[d] N-silicate is a solution of sodium silicate having 37.1% solids and an $SiO_2:Na_2O$ ratio of 3.2.

Footnote—Components a, b, c, e and f are defined as in Examples 1-9.

Examples 11-13 are outside the invention, the products having a bulk density higher than desired. The density of the product of Example 10 is within desired limits and the flow properties are good.

Having described the invention, modifications within the spirit thereof will be readily apparent to persons skilled in the art. It is not intended that the invention be limited to the best modes exemplified, but limited only within the scope of the appended claims.

What is claimed is:

1. A process for controlling the bulk density of a spray-dried particulate detergent composition containing a nonionic detergent substance and a detergent builder comprising:

(i) preparing a mixture of water and a nonionic detergent;

(ii) adjusting the temperature of said mixture to about 140° F. to about 210° F.;

(iii) incorporating into said mixture of water and nonionic detergent as a coplymer, said copolymer being selected from the group consisting of hydrolyzed linear copolymers of maleic anhydride and ethylene, having a specific viscosity of about 0.1 to about 1, hydrolyzed linear copolymers of maleic anhydride and methyl vinyl ether having a specific viscosity of about 0.1 to about 3.5, and hydrolyzed cross-linked copolymers of maleic anhydride and ethylene having a viscosity of about 100 cps. to about 8500 cps. in 2% aqueous solution;

(iv) mixing said copolymer and said mixture of water and nonionic detergent for a period of time from about 15 minutes to about 20 hours, to form copolymer-nonionic detergent ester and carboxyl groups;

(v) neutralizing said carboxyl groups with an alkali metal hydroxide, carbonate, phosphate or borate;

(vi) introducing into said mixture an alkali-metal soap of a fatty acid having from about 8 to about 22 carbon atoms;

(vii) adding to said mixture a detergent builder, thereby forming a slurry containing undissolved particles of said builder; and

(viii) spray drying said slurry by forming droplets thereof and allowing said droplets to fall in contact with a rising stream of a hot gas at a temperature of about 180° F. to about 750° F., thereby drying said droplets to form a free flowing particulate detergent product having a bulk density of about 0.20 to about 0.35 gram per milliliter;

wherein the essential components are mixed in the following proportions, said proportions being based on the dry weight of the spray-dried product:

Component:	Parts by weight
Nonionic detergent	4-30
Copolymer	0.1-5.0
Soap	0.05-5.0
Detergent builder	20-65

2. A process in accordance with claim 1 wherein said nonionic detergent substance is a condensation product of a secondary alcohol mixture having 11-15 carbon atoms and 9-14 molar proportions of ethylene oxide.

3. A process in accordance with claim 1 wherein said copolymer is a copolymer of ethylene and maleic anhydride, said copolymer being linear and having a specific viscosity of about 0.1 to about 1.0.

4. A process in accordance with claim 1 wherein said copolymer is a copolymer of ethylene and maleic anhydride, said copolymer being cross-linked and having a viscosity in a 2% aqueous solution of about 100 to about 8500 centipoises at 25° C.

5. A process in accordance with claim 1 wherein said copolymer is a copolymer of methyl vinyl ether and maleic anhydride, said copolymer being linear and having a specific viscosity of about 0.1 to about 3.5.

6. A process in accordance with claim 1 wherein said soap is an alkali-metal salt of a mixture of fatty acids at least about 84% by weight of said fatty acids having at least 12 carbon atoms.

7. A process in accordance with claim 1 wherein said alkali-metal soap is a mixture of about equal parts by weight of alkali-metal stearate and alkali-metal palmitate.

8. A process in accordance with claim 1 wherein said alkali-metal soap is formed in situ.

9. A process in accordance with claim 1 wherein said builder is selected from the group consisting of alkali-metal carbonate, sesquicarbonate, tripolyphosphate, pyrophosphate, metaphosphate, orthophosphate, silicate, borate, nitrilotriacetate, N-(2-hydroxyethyl)-nitrilodiacetate, ethylenediamine tetraacetate, hydroxyethylenediamine tetraacetate, diethylenetriamino pentaacetate, oxydisuccinate, oxydiacetate, carboxymethyloxysuccinate, hydrofuran tetracarboxylate, starch maleate, cellulose phthalate, glycogen succinate, semi-cellulose diglycolate, said alkali metal being selected from the group consisting of sodium and potassium.

10. A process in accordance with claim 1 wherein said detergent builder is a substance selected from the group consisting of sodium carbonate, sodium tripolyphosphate, tetrasodium pyrophosphate, trisodium nitrilotriacetate, and sodium carboxymethyloxysuccinate.

11. A process in accordance with claim 1 wherein said detergent builder is sodium tripolyphosphate.

12. A process in accordance with claim 1 wherein said detergent builder is sodium carbonate.

13. A process in accordance with claim 1 wherein said mixture is diluted with a mixture of a nonionic detergent and water subsequent to said formation of ester and carboxyl groups.

14. A process in accordance with claim 1 wherein the step of forming ester and carboxyl groups is carried out in an aqueous medium wherein said copolymer is present in the proportion of about 2 to about 100 parts by weight for each part by weight of said nonionic detergent.

15. A spray-dried detergent composition produced by the process of claim 1.

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