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PROCESS FOR PRODUCTION OF
DETERGENT COMPOSITIONS

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1 Claim. (Cl. 252-121)

The present invention relates to a method for producing particulate detergent compositions of comparatively low bulk density.

Several processes have been utilized to manufacture particulate detergents. Among these may be mentioned spray drying, spray cooling, tray drying, drum drying, blending, and the so-called "floor" process, in which a fluid mixture of components is poured onto a "floor," allowed to crystallize and is then ground to size. Each of these procedures has disadvantages which are overcome by the present invention.

Spray dried products, although of desirable hollow globular shape and low bulk density, require the employment of huge, costly spray towers, dust collecting systems and other costly equipment and result in the production of a detergent which is relatively high in fines that have to be removed therefrom and re-cycled, thereby diminishing tower capacity and adding to drying expense. Spray cooling also requires a tower and yields products which are often of small particle size, dusty and difficult to handle. Also, such process is usually applicable only when the amount of hydratable material is substantial. Tray drying is slow and results in coherent product difficult to break up without generating excessive dust. Drum drying, to be efficient, is carried out at comparatively high temperatures which might decompose some organic detergents. It is sometimes necessary to modify the composition formula, such as by elimination or addition of inorganic salt, plasticizing agents and certain detergents, in order to have a product which can be readily dried by this method. When such composition is size-reduced or blended with additional builder or other material it is often excessively dusty. Mere blending of ingredients results in a composition which might separate during storage and handling. The blending procedure also tends to produce undesirable quantities of dust in the working area as well as in the finished product. The "floor" process requires a great deal of valuable manufacturing space and has the disadvantage of requiring subsequent size-reduction procedures which tend to result in a dusty product.

The present invention avoids many of the difficulties of the prior methods mentioned above and allows the production of substantially dust-free, free-flowing detergent compositions of comparatively low bulk density. This process comprises preparing an aqueous dispersion, paste, slurry or crutcher mix from the materials which comprise a laundering or dish washing detergent composition, with a suitable compound which, in such media, reacts in the presence of heat to yield a gas, preferably a non-flammable, non-toxic gas such as carbon dioxide, forming thin films or ribbons from this paste at a temperature low enough to prevent release of gas, heat drying the ribbons, thereby generating gas internally in the ribbons, expanding their volume and decreasing their density, and mechanically reducing the ribbons to substantially dust-free particles of desired size.

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The synthetic detergent composition which may be converted to particles of low bulk density by the present method may be classified as either a heavy duty product or light duty detergent, the former compositions usually including an alkaline builder salt, such as a phosphate or silicate, which promotes washing action. These detergents are normally employed in the laundering of textiles. The light duty compositions usually contain sodium sulfate or other neutral salt builder or filler and are sufficiently mild to be used on delicate fabrics and for operations in which they contact the hands of the user, such as in dish washing.

In the presence of silicate builders, such as sodium trisilicate and sodium disilicate, or alkaline phosphates, such as sodium tripolyphosphate or tetrasodium pyrophosphate, it is preferred to use a mixture of sodium bicarbonate and magnesium sulfate, preferably 7 parts NaHCO_3 for 8.6 parts $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ per 100 parts finished product. For the more neutral light duty detergents only sodium bicarbonate alone need be used, preferably to the extent of 5 parts per 100 parts finished product. Other materials and combinations thereof may also be employed to generate the gas which reduces the product bulk density. Thus, disodium pyrophosphate and sodium bicarbonate and boric acid and carbonate are useful to generate carbon dioxide gas in both light and heavy duty detergents. Combinations of alkaline earth sulfates and sodium bicarbonate are more useful with heavy duty detergents and replacement of the sulfate with carbonate has been found to give better gas production with the light duty materials.

Although carbon dioxide is the gas most conveniently generated from several readily obtainable materials, other compounds resulting in the production of other gases may also be used. It has been found that nitrosocarbonyl compounds, such as nitrosourea and nitrosourethane, can be controllably decomposed by heat to carbon dioxide and nitrogen, making them suitable as agents for decreasing product density. Similarly, dicarbonic acid salts of nitroso alkylamides such as $\text{N,N}'$ -dinitroso- $\text{N,N}'$ -dimethylterephthalamide, which develop only nitrogen during thermal decomposition, are also useful. It will be noted that these preferred gas generators all produce relatively inert and non-toxic materials which do not interfere with the conduct of ordinary mixing, milling and drying operations.

In addition to the above compositions, other gas generators having an acceptable activity may be used, too. However, those compositions are to be avoided which tend to react in the aqueous slurry of the crutcher or when intimately mixed in the milling or filming processes. Usually relatively strongly acidic agents such as sodium bisulfate will promote premature decomposition of carbonates, bicarbonates and nitrosoureas (in which the bisulfate causes early release of nitrous acid by a sodium nitrite reaction employed). If, on the other hand, disodium pyrophosphate is used, the release of gas proceeds slowly, accelerated by the heat of drying, and the by-product resulting is a builder salt for heavy duty synthetic detergents, tetrasodium pyrophosphate. Care must be taken to assure that the particular combination of materials employed will not prematurely liberate gas. Thus, boric acid is suitable for use with sodium carbonate to slowly release carbon dioxide but cannot be used with sodium bicarbonate because of the production of excessive foam in the crutcher which interferes with mixing and subsequent drying operations and also produces a detergent of unsatisfactory appearance and bulk density.

The carbon dioxide-evolving components are usually employed in equimolar amounts, unbalanced amounts,

however, being not detrimental. Alkali carbonate, alkaline earth carbonate and alkali bicarbonate may be present in an amount from about 3 to 17% and preferably from 3 to 10%, disodium pyrophosphate is suitably used in an amount from 20 to 23%, boric acid from 6 to 12%, and magnesium sulfate monohydrate is employed at from 6 to 16% and preferably from 8 to 10%, based on the dry laundering or dishwashing composition.

The alkali carbonate used may be potassium or sodium carbonate. As alkaline earth carbonate preferably calcium or magnesium carbonate is employed, the calcium carbonate in form of natural chalk or precipitated calcium carbonate, the magnesium in a commercial form such as extra light, medium light or heavy carbonate. Magnesium sulfate is preferably used as monohydrate, e.g., in the form of the natural kieserite.

The synthetic organic detergents which are the active washing ingredients of both the heavy duty and light duty products may be either anionic or nonionic compounds. Among the anionic detergents the most important class is that consisting of sulfuric reaction products, i.e., the sulfates and sulfonates of aliphatic and aromatic compounds having higher aliphatic groups of 9 to 18 carbon atoms. These products are usually employed in the form of their water soluble salts, such as their sodium, potassium, ammonium, triethanolamine or magnesium salts. Among the most important of this group may be mentioned the alkyl aryl sulfonates, e.g., sodium dodecyl benzene sulfonate, sodium alkyl benzene sulfonate in which the alkyl group is a propylene tetramer or pentamer; higher alkyl sulfates, e.g., sodium lauryl sulfate, alcohol sulfates from fatty alcohols obtained from hydrogenation of coconut oil and tallow; monoglyceride sulfate, e.g., hydrogenated coconut oil fatty acid monoglyceride sulfate; higher fatty acyl amides of amino lower alkyl sulfonic acids, e.g., sodium N-methyl taurine; higher alkyl sulfonates; higher alkyl isethionates and so forth. The water soluble salts of higher fatty acids are also useful detergents, although they do tend to be converted to insoluble soap by the hardness in wash water and therefore sometimes are of limited utility. Among the nonionic compounds may be mentioned the block copolymers of ethylene and propylene oxides, referred to as the Pluronic; the higher alkyl ethers and acyl esters of alkylated phenols; the higher alkanolamides, e.g., lauric myristic alkanolamide and higher fatty alcohol esters of polyglycols. Usually the detergent compositions will be based on the anionic detergents with optional addition of some nonionic detergent to improve the activity of the anionic compound. Preferably 20 to 40% organic anionic detergent is present in the finished product.

Other ingredients may be compounded with the detergent, such as builders, already mentioned, anti-redeposition agents, germicides, bleaches, stabilizers, foam improvers, buffers, fillers, optional brighteners, colorants, perfumes, antioxidants and so forth. Generally, and preferably, these are added in the crutcher, usually all before the compound or mixture which releases gas during drying.

The initial step in manufacturing the present low bulk density detergents is that of crutching or mixing together in a high solids content aqueous dispersion or slurry the various detergent composition constituents, together with the compounds which will release a gas during a subsequent drying operation. As has been recited, it is important that the gas generating material should not release a substantial proportion of its gas content before the drying step. Therefore, crutching is effected at temperatures low enough to prevent gas release under the processing conditions employed. While usually conducted at room temperature or the temperature of storage of the various constituents of the crutcher mix, crutching temperature may be lower and may sometimes be as high as 50° C., depending, of course, upon the gas

generating compounds employed and providing that no appreciable gas loss or excessive foaming is encountered.

It is highly preferred to maintain the solids content of the crutcher mix at a comparatively high level. The slurry or paste should be sufficiently mobile to allow adequate mixing and transfer, while still containing a major proportion of solids. With low liquid and water content the possibility of premature liberation of gas is diminished. Additionally, the crutcher mix will form a better film, ribbon or chip and will better retain, in its structure, gas generated in drying, thereby resulting in a more uniform, attractive and lighter product. It has been found by extensive experimentation that a highly preferable moisture content range for crutcher mixes, for both light and heavy duty products, is from about 15 to 25%, although greater but still minor proportions may be present with consequent diminution of processing and product advantages.

After crutching the detergent slurry for a time sufficient to yield a well dispersed mixture of all ingredients, the detergent paste is next converted to film or ribbon form. Despite the fact that an attempt is always made in crutching to produce a very uniform dispersion (the crutching operation sometimes lasting for as long as 15 minutes to 1 hour) it is often observed that particles of constituents are still present in sizes greater than desired and are not sufficiently homogeneously dispersed in the detergent for best distribution of generated gas throughout the product. Therefore, it is highly advantageous to produce a film or thin ribbon of detergent paste by an operation which continuously moves the paste between moving parts, causing it to be repeatedly sheared and assisting in making a very uniform film. Although other machines may be employed, it has been found preferable to use standard multi-roll soap mills with successively reduced clearances between rolls. In the continuous ribbon obtained from these machines the chip thickness can be easily regulated and it has been found that even the insoluble materials used to generate gas in the drying operation are sufficiently well dispersed to avoid over-concentrations and deficiencies of these compounds, which could result in uneven and unsatisfactory puffing of the detergent ribbon in drying.

The films or ribbons of detergent removed from the soap mill or other equivalent machine are mechanically transported to a drier. In the drier a bed of ribbons is formed of a thickness and disposition which will allow the even heating of the ribbons and the removal of moisture vapor. The moving bed of ribbons passes through the drier and, simultaneous with moisture removal, non-condensable gas is produced by the effect of the heating on the gas generating compound present. The non-condensable gas assists in puffing the detergent ribbons and thereby promotes quicker drying.

The drying machine used is preferably of a type employed for the drying of ordinary soap ribbons. In one such drier a wire mesh conveyor carries the said chips slowly through a tunnel where drying air is circulated, counter-current flow being preferred. In another apparatus, a turbine drier, chips are mechanically moved vertically downward from one moving drying tray to another in a heated chamber. In still other processes radiant or infrared heating may be employed. The drying temperature should be determined in large measure by the decomposition or reaction temperature or gas generating materials used, as well as the sensitivity of the detergent to heat and the required production speeds. Normally, the drying air or temperature of the medium surrounding the ribbons will be from about 100° C. to about 250° C., preferably 150° C. to 200° C.

The dried ribbons, which may be partially broken up in transportation after drying, are next cooled and mechanically reduced to the desired particle sizes. Only slight force is needed to break up the light, dried ma-

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terial because of its porous nature. Using only slight force, little fine dust is produced. While the method of size reduction employed may vary, depending upon the machines available and the intended end use of the product, a very satisfactory method is one in which the chips or ribbons are passed through a sieve of correct opening. It has been found that products resulting from passage of the light detergent ribbons through sieves having 16 mesh openings per sq. cm. have particle size distributions approximating those of commercial detergent products on the market and have a lesser proportion of fines than many such other products. They are also of apparent bulk density less than .5, preferably in the .35 to .45 range typical of spray dried materials.

The finished product, while of particle size approximating that of comparable commercial detergents, is of a somewhat different shape from most of those that are spray dried. The particles, being broken ribbons, are more angular, are not glazed on all surfaces and contain a plurality of very fine gas vesicles, rather than a single bubble covered by a thin shell. Thus, they are often structurally stronger than thin-walled spray dried beads and will tend better to retain their original bulk density. The products made according to this invention may also be dried to moisture contents higher than those usually obtainable in spray drying. Thus, moistures of up to 10%, preferably 5 to 8% are obtained with built detergents. For unbuilt or dishwashing compositions a lower moisture content is preferable and often these products are dried to less than 0.5% moisture. Although high in moisture, the flowability of the built detergents is not materially reduced.

In some instances, the product resulting may be of a bulk density greater than desired, due to either the particular materials being used or the specifications on moisture content, particle size or other requirements of the final product. It has been found that the addition to the crutcher mix of a small percentage of potassium stearate, sodium polyacrylate, polyvinyl alcohol, methylcellulose, polyvinyl pyrrolidone or polyacrylamide has a lightening effect on the product produced and often additionally serves as colloidal, soil anti-redeposition agent. Apparently, the polymeric material or potassium stearate assists in entrapping and holding the carbon dioxide generated in the drier. The use of these additives has been found to be especially desirable with the light duty detergent compositions, even the use of very small quantities thereof, such as 0.1% sodium polyacrylate, being capable of decreasing apparent density by as much as 10%. In place of this quantity of polymeric material one should use about 1 to 2% potassium stearate to perform the same function.

If the gas generating compounds of the present process are omitted many difficulties will be encountered in an attempt to produce a satisfactory product by the general method disclosed. It has been found that the gas generators assist in the milling operation, resulting in a less tacky paste which can be satisfactorily milled. Without such constituents it is extremely difficult to transport such detergent pastes from roll to roll and also to chip or film form. As previously stated, the drying rate decreases sharply, as much as 50%, when the amount of gas evolving material is substantially decreased or omitted. The product so made is not easily reduced in size without more severe reduction techniques being employed. It cannot be readily reduced merely by screening and therefore, other processes, producing greater quantities of fines or dust, are used. The detergent resulting, not containing internal gas spaces, will not be as readily soluble in the wash water.

From the above discussion the advantages of the invention, over other manufacturing procedures, are evident. The following examples illustrate, but do not limit the invention. All parts given in the examples, specification and claims are by weight, unless otherwise indicated.

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EXAMPLE 1

	Parts
Sodium tetrapropylene benzene sulfonate paste (54.6% alkyl aryl sulfonate, balance water) ---	64.25
5 Sodium trisilicate -----	7.05
Carboxymethyl cellulose (33% CMC) -----	1.50
Sodium bicarbonate -----	7.00
Magnesium sulfate monohydrate -----	8.65
Sodium tripolyphosphate -----	35.00

EXAMPLE 2

Sodium tetrapropylene benzene sulfonate paste (51.95% alkyl aryl sulfonate, balance water) --	67.30
Sodium disilicate -----	7.35
15 Carboxymethyl cellulose (33% CMC) -----	1.50
Sodium bicarbonate -----	7.00
Magnesium sulfate monohydrate -----	8.00
Sodium tripolyphosphate -----	35.00

EXAMPLE 3

20 Sodium tetrapropylene benzene sulfonate paste (52% alkyl aryl sulfonate, balance water) ----	67.30
Sodium trisilicate -----	7.05
Carboxymethyl cellulose (33% CMC) -----	1.50
Sodium bicarbonate -----	7.00
25 Magnesium sulfate monohydrate -----	8.00
Sodium tripolyphosphate -----	17.50
Sodium pyrophosphate -----	17.50

EXAMPLE 4

30 Sodium tetrapropylene benzene sulfonate paste (52% alkyl aryl sulfonate, balance water) ----	38.50
Sodium coconut oil alcohol sulfate paste (52% fatty alcohol sulfate, 35% water, balance principally sodium sulfate, free alcohol) -----	8.65
35 Water -----	5.00
Sodium disilicate -----	7.35
Carboxymethyl cellulose (33% CMC) -----	1.50
Sodium bicarbonate -----	7.00
Magnesium sulfate monohydrate -----	7.95
40 Sodium tripolyphosphate -----	35.00
Sodium sulfate -----	8.75

EXAMPLE 5

Sodium tetrapropylene benzene sulfonate paste (52% alkyl aryl sulfonate, balance water) ----	48.15
45 Coconut oil fatty acid monoethanolamide (30% active) -----	6.65
Sodium disilicate -----	7.35
Carboxymethyl cellulose (33% CMC) -----	1.50
50 Sodium bicarbonate -----	7.00
Magnesium sulfate monohydrate -----	7.95
Sodium tripolyphosphate -----	35.00
Sodium sulfate -----	10.40

EXAMPLE 6

55 Sodium tetrapropylene benzene sulfonate paste (61.8% alkyl aryl sulfonate, balance water) ---	48.5
Carboxymethyl cellulose, 3% solution -----	16.6
Magnesium silicate -----	5.0
60 Sodium perborate monohydrate -----	12.2
Sodium bicarbonate -----	16.8
Disodium pyrophosphate -----	22.2
Sodium tripolyphosphate -----	6.5
Ethylene diamine tetraacetic acid, sodium salt, 30% solution -----	2.0

EXAMPLE 7

Sodium tetrapropylene benzene sulfonate paste (52.9% alkyl aryl sulfonate, balance water) ---	56.7
70 Potassium stearate, 10% solution -----	6.6
Methyl cellulose, 10% solution -----	4.4
Boric acid -----	6.2
Sodium carbonate -----	5.3
Sodium sulfate -----	49.4
75 Calcium carbonate (natural chalk) -----	7.0

7 EXAMPLE 8

	Parts
Sodium tetrapropylene benzene sulfonate paste (54.6% alkyl aryl sulfonate, balance water) ---	45.9
Sodium bicarbonate -----	7.0
Calcium carbonate (natural chalk) -----	4.2
Sodium sulfate -----	63.7

EXAMPLE 9

Sodium tetrapropylene benzene sulfonate paste (52.9% alkyl aryl sulfonate, balance water) ---	43.5
Potassium stearate, 10% solution -----	10.0
Water -----	3.3
Sodium bicarbonate -----	7.0
Calcium carbonate (natural chalk) -----	2.1
Magnesium carbonate, medium light -----	1.8
Sodium sulfate -----	64.4

EXAMPLE 10

Sodium tetrapropylene benzene sulfonate paste (54.6% alkyl aryl sulfonate, balance water) --	55.00
Sodium bicarbonate -----	7.00
Magnesium carbonate -----	3.55
Sodium sulfate -----	59.00

EXAMPLE 11

Sodium tetrapropylene benzene sulfonate paste (52% alkyl aryl sulfonate, balance water) ---	57.8
Sodium bicarbonate -----	5.0
Sodium sulfate -----	64.6
Rhodamine B, 0.1% solution -----	0.5

Detergent compositions of low bulk density were made from the foregoing formulas by preparing a crutcher mix or paste of the constituents given, milling the paste into thin ribbons, drying the milled material and passing the dry product through a coarse sieve (one having 16 mesh openings per sq. cm.). The listed materials are added to the mixing or kneading machine in the orders given and are stirred or otherwise agitated sufficiently long, preferably between 15 minutes and one hour, to produce a homogeneous solution-dispersion. The mixture is milled to thin ribbon form, between 0.005 and 0.20 inch thickness, dried and size reduced by screening. Table I summarizes the production conditions employed.

Table I

Example	Moisture Content of Detergent Composition Paste (Percent)	Drying Means	Drying Temperature ($^{\circ}$ C.)
1.-----	24.5	Hot Air-----	200
2.-----	25	do-----	200
3.-----	25	do-----	200
4.-----	21.7	do-----	190
5.-----	23.0	do-----	190-200
6.-----	23.4	do-----	150
7.-----	24.5	Infra-Red-----	110
8.-----	16	Hot Air-----	200
9.-----	23	Infra-Red-----	110
10.-----	18.6	Hot Air-----	190
11.-----	20.6	do-----	200

Table II describes physical properties of the products produced by the above processes. All detergent compositions made were substantially dust free, readily soluble, convenient to use and of very good detergency, as well as being of desired low density and readily capable of manufacture on usual soap making equipment.

8 Table II

Example	Moisture Content of Detergent Composition Paste (Percent)	Bulk Density (g./ml.)	Active Oxygen (based on perborate employed)
1.-----	7.7	0.43	(¹)
2.-----	6.4	0.4	(¹)
3.-----	6.4	0.37	(¹)
4.-----	6.0	0.45	(¹)
5.-----	6.0	0.41	(¹)
6.-----	6.5	0.40	95%
7.-----	0.5	0.45	(¹)
8.-----	0.0	0.41	(¹)
9.-----	0.2	0.38	(¹)
10.-----	0.3	0.37	(¹)
11.-----	0.4	0.35	(¹)

¹ Not Applicable.

Sieve tests run on the products of Examples 1 and 10 are tabulated below, in Table III.

Table III

Sieve Opening (mm.)	Example 1 Residue on Sieve (Percent)	Example 2 Residue on Sieve (Percent)
1.68.-----	0.6	0.25
0.8.-----	46.9	21.2
0.43.-----	33.8	30.20
0.25.-----	11.9	29.60
0.117.-----	3.5	11.00
0.15.-----	0.9	2.35
Through 0.15.-----	2.4	5.40

What is claimed is:

A method for producing a detergent composition of low bulk density which comprises mixing at a temperature up to about 50 $^{\circ}$ C. an aqueous slurry comprising a water-soluble higher alkyl benzene sulfonate detergent and a compound substantially non-reactive therein and which releases carbon dioxide when heated, said compound being selected from the group consisting of sodium carbonate and bicarbonate, said slurry containing about 0.1 to 2% of a material selected from the group consisting of potassium stearate, methylcellulose, sodium polyacrylate, polyvinyl alcohol, polyvinylpyrrolidone and polyacrylamide which assists in producing a product of decreased density, to form a substantially homogeneous aqueous mixture having a solids content between about 75 to 85%, milling said slurry and forming solid films thereof in thin ribbon form, the mixing and milling being effected at a temperature insufficient to substantially release the carbon dioxide content from said films, drying the ribbons in hot air at a drying temperature from about 100 $^{\circ}$ C. to 250 $^{\circ}$ C. and sufficient to cause the substantial generation of the carbon dioxide content from the ribbons thereby decreasing their density, and reducing the ribbons to a substantially dust-free particulate form having a bulk density of about 0.35-0.45 and a moisture content of less than 10%.

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