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COMPOSITION AND PROCESS FOR LIGHT-WEIGHT SURFACTANT PRODUCTS

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ABSTRACT OF THE DISCLOSURE

Discrete, hollow detergent particles are produced by subjecting a mass of finely divided solid alkali carbonate particles to a tumbling action by a continuously moving surface such as a rotating pan tilted at an angle. During the tumbling on the moving surface, the alkali carbonate particles are sprayed with an acid reacting surface active agent material whereby said carbonate reacts with the surface active agent material neutralizing same and releasing carbon dioxide gas. The release of the gas results in the formation of discrete, hollow particles of the detergent material.

This invention relates to a process for producing discrete, hollow detergent particles.

In the prior art it has been customary to produce lightweight detergent material by spray drying a slurry of the detergent material whereby discrete, hollow detergent particles are produced. The product in this form is particularly desirable due to the fact that it dissolves rapidly in water when used for washing or other applications.

It is well known to produce this type of product from alkyl, aryl or alkylaryl sulfonic acids or sulfuric acid esters made from alcohols or olefins which are neutralized with alkalis. According to prior art practice, the sulfonic acids or sulfuric acid esters are dissolved in water and neutralized with aqueous alkalis. After neutralization the added water and water formed during the reaction is removed by evaporation or atomization in a spray dryer whereby the desired discrete, hollow bead-like detergent particles are formed.

Such practice possesses certain inherent disadvantages due to the necessity of evaporating large quantities of water by heated air which involves substantial heating expense. In addition, the spray drying apparatus is very large and involves a substantial capital investment for a given capacity. This practice has the further disadvantage that relatively expensive alkali hydroxides must be employed since the less expensive alkali carbonates lead to the formation of a disturbing foam. Also, as a result of the drying process, discoloration and partial decomposition of the product may occur, and a substantial yield loss may result.

A procedure is known in the prior art according to which a sulfonic acid is neutralized by admixture with an alkali carbonate in the presence of a small amount of water wherein the reactants are intimately contacted by kneading or stirring them together. However, a lightweight detergent product characterized by discrete, hollow, bead-like particles cannot be produced by this method.

Accordingly, it is a purpose of this invention to provide a process for producing discrete, hollow detergent particles without applying an excessive amount of heat, wherein expensive space consuming, spray-drying equipment is not required, wherein less expensive alkali carbonates may be employed and wherein discoloration and decomposition of the product is eliminated or substantially reduced.

In accordance with the instant invention, discrete, hol-

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low detergent particles are produced by subjecting a mass of finely divided solid alkali carbonate particles to a tumbling action by a continuously moving surface such as the inner surface of a rotating cylinder or drum or a rotating pan or disc tilted at an angle. During the tumbling on the moving surface, the alkali carbonate particles are sprayed with an acid reacting surface active agent material whereby said carbonate reacts with the surface active agent material neutralizing same and releasing carbon dioxide gas. The release of the gas results in the formation of discrete, hollow particles of the detergent material very similar to the particles produced by spray drying. As a result of the tumbling action, a low bulk density is obtained which permits the formation of bubbles or individual beads of the final product whereas stirring or mixing in a kneading machine or similar devices does not permit such formation due to a comparatively high bulk density. Further, the tumbling action permits quick release of the heat of reaction, thereby preventing discoloration due to excessive heat which is characteristic of prior art processes employing an alkali carbonate.

While the product produced in the tumbling apparatus may be completely dried by the heat of reaction requiring no additional heating or drying operation, in many instances it may be desirable to provide an additional drying step to completely dry the particles. However, such drying may be carried out in a conventional rotary drum-type dryer and even where a drying step is employed, less added heat is required to completely dry the product with the process of the instant invention as compared with a spray drying process.

In general, the weight ratio of surface active agent material to alkali carbonate should not exceed 2/1 since above that point a thick pasty material is obtained rather than hollow particles. On the other hand, there is no actual minimum ratio since where amounts of surface active agent material are less than stoichiometric, you merely have a mixture of the particles of detergent plus alkali carbonate. Since many detergent formulations include alkali carbonates, such smaller ratios, e.g., as low as 1/100 surface active agent to carbonate, may be employed for many purposes and a suitable product obtained.

In many cases it may be desirable to include in admixture with the acid reacting surface active material an additional acid material which is not a surface active agent material in order to react with the carbonate to produce greater quantities of CO₂ than would be produced by the reaction with the surface active agent material alone. Where these are employed, it is preferred to have a weight ratio of the additional acid material to the alkali carbonate of not greater than about 9/1.

It has been found desirable to maintain the temperature of the material being sprayed below 140° F. to avoid discoloration of the product due to heat. Where the acid reacting base stock is mixed with an additional acid, generally the action is exothermic which would tend to drive the temperature above the 140° F. maximum. Accordingly, in one preferred embodiment of this invention the additional acid and the surface active agent material are mixed in a jacketed container such as a conventional reaction kettle, etc., whereby the temperature is maintained below 140° F. by controlling the rate of addition of the acid to the surface active agent material or vice versa and by the use of cooling water or other cooling material flowing through the jacket of the kettle. This may also be accomplished by spraying the surface active agent material and additional acid in two separate streams whereby they may contact in the air. In such instance the droplets of the reactants are surrounded by large volumes of air, thus preventing excessive temperature rise. In addition, they may be mixed in the conduit by means of a pipe mixing type apparatus provided

immediately ahead of the spraying device. This may comprise a simple venturi nozzle within the pipe for introducing the added liquid or a jacketed perforated tube or sparger may be employed wherein one liquid goes through the perforated tube and the other liquid or liquids are introduced directly into the jacket surrounding the perforated tube. By mixing immediately ahead of the spraying device, the materials are sprayed and contact the alkali carbonate particles in the pan before the reaction between the surface active agent and additional acid proceeds far enough to release a substantial amount of the heat of the reaction whereby most of this heat of reaction is released in the pan to assist in drying the product in the pan.

Where desirable, the dry particles either coming directly from the tumbling apparatus or from a subsequent dryer, such as a conventional drum-type rotary dryer, may be cooled by passage through a conventional cooling device, such as a rotating cylinder of drum wherein cooling air passes over the material passing through the drum.

The liquid material may be sprayed onto the alkali carbonate particles by any conventional spraying opening or device such as a nozzle, preferably a pneumatic type spray nozzle employing air under pressure.

The alkali carbonates suitable for use in the process of this invention are preferably the carbonates, bicarbonates and sesquicarbonates of sodium, potassium, and lithium. These carbonates may be used in commercial purity.

Where desired, alkali hydroxides such as sodium hydroxide, potassium hydroxide, and lithium hydroxide may be included in the reaction mixture in lieu of a portion of the alkali carbonate to assist in neutralizing the surface active agent material. However, there should always be enough alkali carbonate to provide a sufficient amount of CO_2 gas to form the desired hollow particles of the detergent. As previously stated, the weight ratio of surface active agent material to alkali carbonate should not exceed 2/1 and, accordingly, there must be a sufficient amount of alkali carbonate present to maintain an alkali carbonate to surface active agent weight ratio of at least 1 to 2. The alkali hydroxide may be added in many ways. For example, solid alkali hydroxide particles may be mixed with the alkali carbonate particles, alkali hydroxide solution may be mixed with the surface active agent and/or additional acid prior to spraying or alkali hydroxide in liquid form or solution may be added to or sprayed onto the alkali carbonate.

The process of the present invention is applicable, for instance, to produce alkyl sulfates, alkyl sulfonates, alkylaryl sulfonates, sulfonated esters of fatty acids, sulfonated amides of fatty acids, and the like.

Such detergents may be produced in the form of discrete, hollow detergent particles from a variety of sulfonic acids or sulfuric acid esters. The alkylaryl sulfonic acids, which may be processed in accordance with the instant invention, preferably contain 4 to 20 carbon atoms in their aliphatic side chains. The sulfonic acids may contain 1 to 2 aromatic rings which, as the case may be, contain hydroxyl groups as additional substituents. In the same way sulfuric acid esters may be processed which have been prepared from alcohols or olefins having preferably 12 to 18 carbon atoms. Also, alcohols or olefins of any carbon number may be used for the preparation of the sulfuric acid esters. The sulfonic acids or sulfuric acid esters can include, for instance, the sulfuric acid esters of lauryl, cetyl or tallow alcohol and, in general, any primary or secondary alcohol containing more than 8 carbon atoms in its molecule. The sulfuric acid esters or sulfonic acids to be used in this invention may be obtained from the corresponding alcohols or alkylaryl compounds by methods known to the art. These may include the reaction with sulfuric acid, chlorosulfonic acid, SO_3 , or other sulfonating agents. Typical sulfonic acids which may be employed are dodecyl

benzene sulfonic acid, biologically soft linear alkyl benzene sulfonic acid, straight chain dodecyl benzene sulfonic acid, tridecyl benzene sulfonic acid, linear alkylate sulfonic acid, linear alkyl benzene sulfonic acid, linear dodecyl benzene sulfonic acid, toluene sulfonic acid, xylene sulfonic acid, alkylaryl sulfonic acid, alkyl naphthalene sulfonic acid.

In addition to sulfonic acids or sulfuric acid esters, other acid reacting surface active agent materials may be employed, such as phosphate acids, e.g., complex organic (aliphatic) phosphate esters in free acid form, complex phosphate acids, alkylaryl phosphate acids; fatty acids including high molecular weight saturated fatty acids, e.g., polyoxyethylated fatty acid, coconut oil fatty acid, low polyunsaturated oleic acid, acetic acid salts of n-alkyl amines, oxyethylated fatty acid, α -sulfonated fatty acid, lanolin fatty acid, sulfated tall oil fatty acid, and pure lauric acid. Also, unsaturated organic acids such as oleic acid, nonylphenoxy acetic acid, sulfated ricinoleic acid, low polyunsaturated oleic acid, organic amino-carboxylic acid may be employed. In addition, chelating acids may be employed, e.g., ethylene diamine tetraacetic acid, 1,2-diaminocyclohexane tetraacetic acid, ethylene glycol bis-(aminoethylether)tetraacetic acid, hydroxyethyl ethylene diamine triacetic acid, ethylene diamine di(o-hydroxyphenyl)acetic acid, diethylene triamine pentaacetic acid, diaminoethyl ether tetraacetic acid, and nitrolo triacetic acid.

The additional acid materials which may be employed for reaction with the carbonate in order to produce additional CO_2 include the common mineral acids such as sulfuric acid and phosphoric acid. In this connection it should be noted that often the readily available sulfonic acid and sulfuric acid ester materials generally include some free sulfuric acid. Other acids which may be employed are dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, and suberic acid; saturated monocarboxylic acids such as formic acid, acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, capric acid, lauric acid, palmitic acid, stearic acid, orthoacetic acid, orthoformic acid, and enanthic acid; hydroxy acids such as glycolic acid, D-gluconic acid, lactic acid, glyceric acid, D-galactic acid, citric acid, and pyruvic acid; unsaturated monocarboxylic acids such as oleic acid, linoleic acid, and ricinoleic acid; aromatic acids such as anthranilic acid, benzene sulfonic acid, benzoic acid, benzilic acid, 1-naphthalene-8-sulfonic acid, naphthoic acid, and toluic acid; and unsaturated dicarboxylic acids such as maleic acid and fumaric acid.

The sulfonic acids, sulfuric acid esters or any of the other above-mentioned acid reacting surface active agent materials being processed may be diluted with water.

The detergent material of the invention is readily formulated with alkaline, acid or neutral builder salts and auxiliary additives such as absorbent siliceous compounds including calcium silicate, fuller's earth, silica gel, divided silica, diatomaceous earth, and mixtures thereof, optical brighteners, anti-soil redeposition agents, for example, carboxymethylcellulose, anti-tarnishing agents such as mercaptobenzothiazole, benzotriazole, ethylene thiourea, and the like, agents to supply higher or smaller proportions of foam or suds as desired, plasticizers, inert fillers, bleaches, solvents, dyes, perfumes, etc., in formulations in which those who practice the art of compounding cleaning compositions are very well versed.

The alkaline builder salts which can be employed in conjunction with the detergent compositions of the present invention include, for example, alkali metasilicates, phosphates, including the molecularly dehydrated phosphates, carbonates and borates and, to a lesser extent, alkali metal hydroxide. Typical alkaline builder salts are sodium orthosilicate, sodium metasilicate, sodium carbonate, trisodium phosphate, sodium tripolyphosphate, tetrasodium pyrophosphate, sodium hexametaphosphate, and sodium tetraborate. In most instances the above-described

auxiliary materials may be added either directly to the inclined pan or rotating drum for agglomeration with the reactants or mixed with the liquid being sprayed onto the carbonate particles.

This invention has the advantage of producing products as lightweight as those made by spray drying with the added advantages of less dustiness, better storage characteristics, greater range of composition and simpler, less costly equipment and process. The products made are particularly suited for detergent applications like hand dishwashing, laundry, metal cleaning, and as intermediates for detergent formulations.

The process of the instant invention has several advantages over producing the product by spray drying. In the spray tower operation, essentially all of the product ingredients have to be added in the slurry, requiring elaborate mixing equipment for preparation and cumbersome equipment for spraying. This requirement greatly limits the chemical composition. Another advantage over spray drying is that an elaborate dust handling system is not required. It is estimated that the installed cost of the equipment for carrying out the process of the instant invention is only about one-fifth to one-tenth of an equivalent spray tower installation. The process of this invention also has the advantage of being more suitable for small scale production.

The following examples further illustrate the invention:

Examples

In the examples illustrated in the table below, the alkali carbonate material in the indicated amounts is introduced into a tumbling apparatus. In Example 10 this is a conventional rotating cylinder or drum, 2 feet in diameter and 8 feet long, rotated by means of an electric motor through a conventional drive mechanism. In the remaining examples, the apparatus is a 3-foot diameter, 1½-foot deep inclined pan, similar to that illustrated in FIGURE 5, page 92 of Chemical Engineering for Feb. 5, 1962. The axis of the shaft on which the pan is mounted is tilted at an angle of 72° to the horizontal. The pan is rotated at 18 r.p.m. by means of a conventional electric motor and drive means driving the shaft, and the tumbling bed of alkali carbonate material is sprayed with a blend of the surface active agent material and additional acid material, where employed, in the amounts indicated in the table below. With the exception of the sodium silicate in Examples

25-27, the ingredients indicated as "Other Materials" in the table are introduced into the inclined pan with the alkali carbonate material. Where sodium silicate is introduced with the alkali carbonate, it is in the form of anhydrous sodium metasilicate fines. The sodium silicate in Examples 25-27 is 1:3.25 Na₂O:SiO₂ ratio by weight and is added as an aqueous solution containing by weight 8.9 percent Na₂O, 29.0 percent SiO₂ and 62.1 percent water.

In Examples 1-22, the additional acid and the surface active agent material are mixed together in a conventional, jacketed mixing tank. Due to the heat liberated during mixing, cooling water is circulated in the jacket whereby the temperature of the mixture of surface active agent and additional acid is kept from rising above 140° F. Stainless steel type 316 is suitable for such mixing tank and for any piping or conduits employed for conducting the material from the mixing tank to the spray nozzle as well as for the spray nozzle itself. Monel metal may also be employed, however, this is considerably more expensive.

In Examples 24-27, the liquid materials are piped directly to the spray nozzle through separate pipes. The fluids are then mixed immediately preceding the spray nozzle in a pipe mixer or sparger type apparatus which, as previously described, is simply a perforated tube surrounded by an outer jacket. The additional acid material is injected through the perforated pipe while the sodium silicate solution and the surface active agent base stock are introduced directly into the jacket surrounding the perforated pipe or tube.

The agglomerated particles discharged from the continuously moving surface of the tumbling apparatus of all examples, except 10 and 19, are dried by one pass through a direct fired rotary dryer, 8 feet long and 22 inches in diameter, rotating at 3 r.p.m. and having a slope of ¼ inch per foot, the inlet air at 310° F. entering the dryer with the product in parallel current flow. The product is then cooled to room temperature in a conventional rotating drum cooler, 2 feet in diameter, 8 feet long and rotating at 3 r.p.m. The agglomerated particles produced in Examples 10 and 19 are not dried or cooled. The finished product comprises small beads of detergent material having a bulk density of about 35 pounds per cubic foot and resembles a spray dried product. However, it is superior to a spray dried product in that it is less dusty, more free flowing and less sensitive to pressure compaction which provides better storage properties.

TABLE

Ex. No.	Alkali carbonate		Surface active agent, base stock			Additional acid		Other materials, parts by weight				
	Kind	Parts by weight	Designation	Parts by weight	Percent surface active agent in H ₂ O slurry	Kind	Parts by weight	NaCl	STPP	Sodium silicate	CITSP	TSP
1.....	Soda ash.....	57.5	1	22.2	12.8	H ₂ SO ₄ (98%)	20.3					
2.....	do.....	34.0	2	71.7	41.6	H ₂ SO ₄ (98%)	31.5	9.5				
3.....	do.....	47.6	2	30.3	17.6	H ₂ SO ₄ (98%)	50.0		5.2	3.7		
4.....	do.....	14.8	2	18.7	10.8	H ₂ SO ₄ (98%)	19.1		51.7	6.2		
5.....	do.....	34.0	2	30.3	17.6	H ₂ SO ₄ (98%)	35.1			3.7		22.5
6.....	Sodium bicarbonate.....	97.7	2	30.0	17.4	H ₂ SO ₄ (98%)	56.9					
7.....	Potassium carbonate.....	66.4	2	27.7	16.1	H ₂ SO ₄ (98%)	47.2					
8.....	Lithium carbonate.....	55.6	2	30.0	17.4	H ₂ SO ₄ (98%)	73.6					
9.....	Soda ash.....	21.0	3	10.0	5.8	H ₂ SO ₄ (98%)	29.1			10.0	22.0	37.0
10.....	do.....	33.2	4	32.0	18.6	H ₂ SO ₄ (98%)	30.7					36.8
11.....	do.....	57.5	5	22.3	12.9	H ₂ SO ₄ (98%)	53.3	10.0				
12.....	do.....	27.7	6	40.5	23.5	H ₂ SO ₄ (98%)	30.8		7.2	6.5		
13.....	do.....	42.7	7	35.4	20.5	H ₂ SO ₄ (98%)	43.5		18.0	4.2		
14.....	do.....	54.1	8	12.6	7.3	H ₂ SO ₄ (98%)	56.6			8.1	12.0	
15.....	do.....	27.6	9	12.0	6.9	H ₂ SO ₄ (98%)	27.4		30.0	6.1	20.0	
16.....	do.....	51.0	10	30.0	17.4	H ₂ SO ₄ (98%)	47.2					14.2
17.....	do.....	48.4	2	72.5	42.0	H ₃ PO ₄	29.1					
18.....	do.....	45.8	2	72.5	42.0	Oxalic acid.....	54.5					
19.....	do.....	37.5	2	72.5	42.0	Acetic acid.....	42.5					
20.....	do.....	42.7	2	36.3	21.0	Citric acid.....	79.0					
21.....	do.....	13.8	2	36.3	21.0	Oleic acid.....	73.3					
22.....	do.....	29.0	2	36.3	21.0	Benzoic acid.....	66.9					
23.....	do.....	48.0	2	72.0	42.0							
24.....	do.....	34.3	2	71.7	41.6	H ₂ SO ₄ (98%)	32.3	9.5				
25.....	do.....	47.8	2	31.2	18.1	H ₂ SO ₄ (98%)	48.2		5.15	7.9		
26.....	do.....	15.1	2	18.7	10.8	H ₂ SO ₄ (98%)	19.3		51.7	13.2		
27.....	do.....	34.2	2	30.3	17.6	H ₂ SO ₄ (98%)	35.3			7.9		
28.....	do.....	24.2	2	72.5	42.0	H ₂ SO ₄ (98%)	52.3					
								24.2 sodium hydroxide				

The surface active agent materials indicated by the numbers ranging from 1 to 10, under the heading "Designation", in the above table are as follows:

- (1) A dodecyl benzene sulfonic acid having the formula $C_{16}H_{30}O_3S$.
- (2) A linear alkyl benzene sulfonic acid having 12 to 13 carbon atoms in the alkyl group.
- (3) An alkylaryl ether.
- (4) A tridecyl benzene sulfonic acid having the formula $C_{19}H_{32}O_3S$.
- (5) A toluene sulfonic acid having the formula $C_7H_8O_3S$.
- (6) An alkyl naphthalene sulfonic acid having the formula $C_{10}H_8O_3S$.
- (7) An octyl diphenyl phosphoric acid having the formula $C_{20}H_{27}O_4P$.
- (8) A coconut oil fatty acid having the formula $C_{15}H_{30}O_6S$.
- (9) A sulfated ricinoleic acid having the formula $C_{18}H_{34}O_7S$.
- (10) An ethylene diamine tetraacetic acid having the formula $C_{10}H_{12}N_2Na_4O_8$.

In the table above, the "Other Materials" designated by abbreviated notation are as follows:

STPP----- Sodium tripolyphosphate.
CITSP----- Chlorinated trisodium phosphate.
TSP----- Tetrasodium pyrophosphate.

It is to be understood that various changes and modification may be made in the foregoing invention without departing from the spirit of the invention and scope of the appended claims.

What is claimed is:

1. A process for producing discrete, hollow detergent particles comprising the steps of subjecting a mass of finely divided solid alkali metal carbonate particles to a tumbling action by a continuously moving surface and spraying said particles with acid reacting surface active agent material wherein said acid reacting surface active agent material is selected from the group consisting of alkylaryl sulfonic acids which contain from 4 to 20 carbon atoms in their aliphatic side chains and one or two aromatic rings, sulfuric acid esters prepared from alcohols or olefins having from 12 to 18 carbon atoms, organic phosphate esters, organic phosphate acids, higher molecular weight saturated fatty acids, unsaturated fatty acids, sulfated and amino unsaturated fatty acids, and chelating acids, whereby said carbonate reacts with said surface active agent material releasing carbon dioxide gas, the release of said gas resulting in the formation of said hollow particles of the detergent material.
2. The process of claim 1 wherein alkali metal hydroxide is included with the reaction components.
3. The process of claim 1 wherein the weight ratio of said surface active agent material to alkali metal carbonate is not greater than about 2/1.
4. A process for producing discrete, hollow detergent particles comprising the steps of subjecting a mass of finely divided solid alkali metal carbonate particles to

a tumbling action by a continuously moving surface and spraying said particles with acid reacting surface active agent material and additional acid material wherein said acid reacting surface active agent material is selected from the group consisting of alkylaryl sulfonic acids which contain from 4 to 20 carbon atoms in their aliphatic side chains and one or two aromatic rings, sulfuric acid esters, prepared from alcohols or olefins having from 12 to 18 carbon atoms, organic phosphate esters, organic phosphate acids, higher molecular weight saturated fatty acids, unsaturated fatty acids, sulfated and amino unsaturated fatty acids, and chelating acids, and said additional acid material is selected from the group consisting of sulfuric acid, phosphoric acid, unsubstituted aromatic dicarboxylic acid having from 2 to 10 carbon atoms, unsubstituted aliphatic monocarboxylic acids having from 1 to 18 carbon atoms, aliphatic and aromatic hydroxy acids, and unsaturated carboxylic and sulfonic aromatic acids, whereby said carbonate reacts with said surface active agent material and with said additional acid material releasing carbon dioxide gas, the release of said gas resulting in the formation of said hollow particles of the detergent material.

5. The process of claim 4 wherein the weight ratio of said surface active agent material to said alkali metal carbonate is not greater than about 2/1 and the weight ratio of said additional acid to said alkali metal carbonate is not greater than about 9/1.

6. The process of claim 5 wherein said surface active agent material is a sulfonic acid and said additional acid is a mineral acid.

7. The process of claim 5 wherein said surface active agent material is a sulfonic acid and said additional acid is sulfuric acid.

8. The process of claim 5 wherein said carbonate is sodium carbonate.

9. The process of claim 5 wherein said carbonate is sodium bicarbonate.

10. The process of claim 5 wherein said carbonate is potassium carbonate.

11. The process of claim 5 wherein said surface active agent material and said additional acid are mixed in a mixing vessel prior to spraying.

12. The process of claim 5 wherein said surface active agent material and said additional acid are mixed in a conduit immediately prior to spraying.

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