1 579 262

# PATENT SPECIFICATION

(11) 1 579 262

(21) Application No. 29836/79 (22) Filed 25 Feb. 1977
(62) Divided out of No. 1579261
(31) Convention Application No. 661471
(32) Filed 26 Feb. 1976 in
(33) United States of America (US)
(44) Complete Specification published 19 Nov. 1980
(51) INT CL³ C11D 7/60 (C11D 7/60 7/14 7/16)
(52) Index at acceptance
C5D 6A5B 6A5D2 6A5E 6B7 6C6 6D

(19)


## (54) BUILDER COMPONENTS FOR DETERGENT COMPOSITIONS

(71) We, COLGATE-PALMOLIVE COMPANY, a Corporation organised under the laws of the State of Delaware, United States of America, of 300 Park Avenue, New York, New York 10022, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to builder components for detergent compositions. In particular, the invention pertains to the manufacture of free flowing detergent builder beads (hereinafter referred to also as base builder beads) capable of carrying relatively large amounts of various liquid or liquefiable detergents and other liquid or liquefiable organic materials, suitable for incorporation into detergent compositions.

The invention provides a method for producing spray dried base builder beads that can be oversprayed with synthetic detergents such as nonionics, anionics and cationics or combinations thereof to produce particulate detergent compositions of improved detergency and solubility and that contain relatively large amounts of the synthetic detergent component while retaining free flowing properties.

Such detergent compositions and a method for manufacturing them are the subject of our British Patent application No. 8123/77 (Serial No. 1579261) from which the present application has been divided.

As used herein the terms "overspray" and "post spray" are synonymous and include any suitable means for applying a liquid or liquefiable substance to the base builder beads, such as spraying the liquid through a nozzle in the form of fine droplets.

Typically, nonionic synthetic detergents having the desired detergency properties for incorporation into commercial particulate detergent products, such as laundry powders, are thick, viscous, sticky liquids or semi-solid or waxy materials. The presence of these materials in a detergent slurry (crutcher mix) prior to spray drying in amounts greater than about 3 percent by weight is impracticable since the nonionic synthetic detergent will "plume" during spray drying and a significant portion can be lost through the gaseous exhaust of the spray drying tower.

The art has recognized the application of nonionic synthetic detergents of this type to various particulate carrier bases to produce relatively free flowing particulate products that can be used for household laundry. Representative patents containing teachings and disclosures of methods for producing particulate free flowing laundry detergents by post spraying a nonionic synthetic organic detergent onto a spray dried particulate product containing detergent builders include, among others: U.S. Patents 3,538,004, 3,849,327, 3,888,098 and 3,888,781, and British Patent 918,499. The prior art is typified by post spraying from about 1 to a maximum of 10 percent by weight of a nonionic synthetic detergent onto a spray dried bead that contains a substantial proportion of a surface active agent such as an anionic detergent, filler materials, and detergent builders.

Further, certain desirable ingredients for detergent compositions, such as cationic surface active agents that provide fabric softening properties, and optical brighteners, bluing agents and enzymatic materials, cannot be spray dried because of thermal decomposition. Such materials can be incorporated into particulate detergent composition by post spraying them onto spray dried base builder beads

embodying the present invention, either alone or in addition to a nonionic detergent or other suitable ingredients.

According to one aspect of the invention a method for producing free flowing detergent builder beads comprises hydrating a first quantity of anhydrous phosphate builder salt in the presence of a second quantity of alkali metal silicate to form a hydrated aqueous slurry; adding a third quantity of anhydrous phosphate builder salt to the hydrated slurry to form a crutcher mix; and spray drying the crutcher mix to form a particulate material; the weight ratio of the first quantity to the second quantity being in the range from 1:5:1 to 5:1 and the weight ratio of the first quantity to the third quantity being in the range from 0.3:1 to 0.7:1.

The resulting base builder beads are suitable for carrying relatively large amounts, e.g. from 2 to 40 percent by weight, preferably from 12 to 40 percent, of various materials suitable for incorporation into detergent compositions, such as anionic, nonionic, and cationic surface active agents, optical brighteners, bluing agents, soil release agents, antiredeposition agents, and mixtures thereof. The post added detergent ingredients may be applied in liquid form onto the base builder beads by any suitable means, preferably by spraying in the form of fine droplets from a spray nozzle while the beads are being agitated. Any liquid or liquefiable organic material suitable for incorporation into a laundry detergent formulation can be post sprayed onto the spray dried base builder beads.

The base builder beads made by the method of the invention are normally spherical or irregularly shaped beads comprising from 45 to 90 percent phosphate builder salt, from 5 to 15 percent alkali metal silicate solids and from 5 to 15 percent water. From 30 to 60 percent by weight of the phosphate component is hydrated in the presence of the alkali metal silicate component and the remainder is in anhydrous form. The beads have a porous, sponge-like outer surface and a skeletal internal structure, in contrast to the hollow beads typical of spray dried powders.

Thus, according to another aspect of the invention, free flowing detergent builder beads comprise, by weight from 45 to 90 percent of a phosphate builder salt, from 5 to 15 percent of alkali metal silicate and from 5 to 15 percent of water, the phosphate builder salt comprising a hydrated portion and an anhydrous portion, the weight ratio of the hydrated portion or an anhydrous basis to the anhydrous portion being in the range from 0.3:1 to 0.7:1, and the beads having a porous outer surface and a skeletal internal structure.

The free flowing ability of a particulate substance can be measured in relation to the flowability of clean dry sand under predetermined conditions, such as inclination with the horizontal plane, the sand being assigned a flowability value of 100. Typical spray dried detergent powders as presently available on the market having a flowability of about 60 in relation to sand, i.e. 60 percent of the flowability of sand under the same conditions.

The base builder beads according to the invention can usually be further characterised as follows:

Particle size distribution: at least about 90% by weight passing through a 20 mesh screen (U.S. series) and being retained on a 200 mesh screen (U.S. series)

Specific Gravity: 0.5—0.8.

Flowability: 70—100.

The base builder beads of the invention can be produced as follows:

A first quantity of a hydratable alkali metal phosphate builder salt is hydrated at a temperature in the range from 140°F to 170°F in the presence of a second quantity of an alkali metal silicate to form a hydrated slurry: the weight ratio of the first quantity to the second quantity generally being in the range from 1.5:1 to 5:1. The hydrated phosphate and silicate are mixed in an aqueous medium, at a temperature which is normally at least 170°F, with a third quantity of anhydrous alkali metal phosphate builder salt to form a crutcher mix, the weight ratio of the first quantity to the third quantity generally being in the range from 0.3:1 to 0.7:1. Various other detergent ingredients, e.g. builders such as carbonates, citrates, silicates for example up to 10 percent by weight thereof based on the weight of solids in the crutcher mix, and organic builders, and surface active agents can be added to the crutcher mix after the hydration step. It is preferred that organic surface active agents in the crutcher mix be limited to less than 2 percent by weight of the solids present and most preferably that the crutcher mix be free from organic surface active agents. The crutcher mix is agitated and maintained at a temperature in the range from 170°F to 200°F to prevent any significant hydration of the third quantity of anhydrous phosphate builder salt. Water is usually present in the slurry

in an amount such that the crutcher mix contains from 40 to 55 percent by weight of solids. Adjuvants such as brighteners, bluing, or other minor ingredients may be present in the crutcher mix if necessary or desirable, or may be added to the spray dried beads.

The crutcher mix is then pumped to a spray tower where it is spray dried in the conventional manner. The spray drying may be performed in a countercurrent or co-current spray drying tower using an air inlet temperature in the range from 500 to 700°F and a spray pressure in the range from 200 psig (lbs./sq. in gauge) to about 1000 psig. The spray dried product comprises numerous base builder beads having the structure already described, in contrast to the hollow structure that typically results from spray drying a detergent crutcher mix.

The accompanying illustrations are photomicrographs of a spray dried base builder bead according to the invention prior to being post sprayed.

Figure 1 shows a major portion of the bead, the magnification being ascertainable by reference to the line below the photomicrograph which represents a length of 1/200 inch. If the illustration were enlarged to have a side of 20 cm the magnification would be 200×.

Figure 2 shows a portion of the bead of Figure 1 at a magnification ten times that of Figure 1.

As shown in the illustrations the base builder beads are solid particles of irregular configuration that have a sponge-like, porous outer surface and a skeletal internal structure. In contrast, conventional spray dried detergent beads such as those currently available on the consumer market typically comprise spherical beads with a substantially non-porous outer surface and a hollow core.

The base builder beads will generally comprise, by weight, from 45 to 90 percent phosphate builder salt, preferably from 50 to 70 percent; from 5 to 15 percent alkali metal silicate solids, and 5 to 15 percent water. However, although the product will not usually be as free flowing, lesser amounts of phosphate may be employed, such as 20 to 25%.

According to a preferred aspect of the invention, a substantial portion of the builder salt component of the base beads is the product of hydrating to a maximum degree, typically to the hexahydrate form, from 30 to 60 percent by weight of the phosphate builder salt in the presence of the alkali metal silicate. The weight ratio of the hydrated phosphate builder salt to the alkali metal silicate in both the crutcher mix and the base beads is in the range from 1.5:1 to 5:1 preferably 2:1 to 4:1, and the weight ratio of the hydrated phosphate builder salt on an anhydrous basis to the anhydrous builder salt in the crutcher mix and the base beads is in the range from 0.3:1 to 0.7:1, preferably 0.4:1 to 0.6:1.

In the presently preferred form of the invention, the crutcher mix contains only inorganic detergent builders and water and is free from organic surface active agents. Most preferably the crutcher mix is also free from filler materials such as sodium sulphate.

The phosphate builder salt component of the base builder beads is chosen from phosphate salts having detergent building properties. Examples of phosphate builder salts having detergent building properties are the alkali metal tripolyphophates and pyrophosphates, of which the sodium and potassium compounds are most commonly used. These phosphates are well known in the detergent art as builders and can either be used alone or as mixtures of different phosphates. More specific examples of phosphate builder salts are: sodium tripolyphosphate; tetrasodium pyrophosphate; dibasic sodium phosphate; tribasic sodium phosphate; monobasic sodium phosphate; dibasic sodium pyrophosphate; and monobasic sodium pyrophosphate. The corresponding potassium salts are also examples, as are mixtures of the potassium and sodium salts.

The alkali metal silicate component of the crutcher mix may be supplied in the form of an aqueous solution, preferably containing from 40 to 60 percent by weight, typically about 50 percent by weight, of silicate solids. Preferably the silicate component is sodium silicate with an $Na_2O:SiO_2$ ratio in the range from 1:1.6 to 1:3.4, preferably from 1:2 to 1:3, and most preferably about 1:2.4.

The following Examples are illustrative of the invention (all percentages are by weight unless otherwise specified).

EXAMPLE 1

An aqueous slurry of the following ingredients is prepared.

| Ingredients | Amount Percent (based on total crutcher mix) |
|---|---|
| Sodium tripolyphosphate powder (anhydrous) | 14.5 |
| Sodium silicate solids ($Na_2O/SiO_2$=2.4) | 7.6 |
| Water | 28.6 |

The slurry is brought to a temperature of about 140°F and mixed well to form the hexahydrate phosphate salt and is subsequently heated to 190°F and maintained between 190°F and 200°F to prevent hydration of the next to be added phosphate ingredients.

The following ingredients are then added to the aqueous slurry at 190° to 200°F to form a crutcher mix.

| Ingredients | Amount Percent (based on total crutcher mix) |
|---|---|
| Sodium tripolyphosphate powder (anhydrous) | 28.3 |
| Water | 21.0 |

The crutcher mix contains from about 45 to about 50 percent solids.

The crutcher mix is supplied to a countercurrent 8 feet high spray drying tower and is sprayed at a manifold temperature of 180°F and a pressure of 600—900 psig using a "Whirljet 15-1" or "Fulljet 3007" spray nozzle.

An air inlet temperature ($T_1$) of about 600°F is used in the spray tower.

The spray dried base beads produced have the following properties and are similar in internal structure and outer surface characteristics to the bead shown in the accompanying photomicrographs.

| Base Bead Properties | | |
|---|---|---|
| Moisture | | 10% |
| Tripolyphosphate (Sodium salt) | | 77% |
| Silicate solids | | 13% |
| Cup Weight | 130 g | (Apparent specific |
| Flow | 86 | gravity=0.55 or bulk |
| Tack | 0 | density=0.55 g/ml) |

| Size Analysis: | |
|---|---|
| On U.S. 20 Mesh | 1% |
| On U.S. 40 Mesh | 19% |
| On U.S. 60 Mesh | 50% |
| On U.S. 80 Mesh | 20% |
| On U.S. 100 Mesh | 6% |
| On U.S. 200 Mesh | 3% |
| Through On U.S. 200 Mesh | 1% |
| | 100% |

EXAMPLE 2

An aqueous slurry of the following ingredients is prepared.

| Ingredients (In order of addition) | Amount, Percent (based on total crutcher mix) |
|---|---|
| Hot Water (140°F) | 25.0 |
| Sodium silicate solids ($Na_2O/SiO_2$=2.4) | 3.5 |
| Sodium tripolyphosphate powder (anhydrous) | 13.0 |

The aqueous slurry is mixed well in a steam jacketed vessel to hydrate the phosphate ingredient and then heated to 200°F with steam.

The following ingredients are then added to the aqueous slurry to form a crutcher mix. The temperature is maintained higher than 180°F to prevent hydration of subsequently added anhydrous phosphate builder salt.

| Ingredients (In order of addition) | Amount, Percent (based on total crutcher mix) |
|---|---|
| Sodium tripolyphosphate (anhydrous) | 13.0 |
| Water | 25.0 |
| Sodium tripolyphosphate (anhydrous) | 13.0 |
| Sodium carbonate | 7.5 |

The crutcher mix is supplied to a countercurrent spray drying tower at a temperature of about 170°F and sprayed at a pressure of 800 psig. The tower conditions include a $T_1$ (inlet) air temperature of 650°F and a $T_1$ (outlet) air temperature of about 235°F.

The spray dried builder beads have a particle size distribution such that 90 percent pass through a 20 mesh screen (U.S. series) and 90 percent are retained on a 200 mesh screen (U.S. series).

## EXAMPLE 3

The procedures of Example 2 are followed with a crutcher mix (about 50 percent solids) of the following composition:

| Ingredient | Amount Percent |
|---|---|
| Sodium tripolyphosphate (hexahydrate) | 13.0 |
| Sodium tripolyphosphate (anhydrous) | 26.0 |
| Water | 47.0 |
| Organic Builder "M" (Monsanto Chemical Co.) | 7.5 |
| Sodium Silicate (solids) | 6.5 |
| | 100.0 |

## EXAMPLE 4

Crutcher mixes having the following compositions are prepared according to the procedures of Example 1.

| | Amount, Percent | | | |
|---|---|---|---|---|
| Ingredient | I | II | III | IV |
| Sodium tripolyphosphate (hexahydrate) | 10 | 12 | 18 | 20 |
| Sodium silicate solids ($Na_2O/SiO_2$=2.4) | 3 | 8 | 6 | 4 |
| Sodium tripolyphosphate (anhydrous) | 30 | 30 | 26 | 28 |
| Water | 57 | 50 | 50 | 48 |

Crutcher mixes I, II, III and IV are spray dried according to the procedures outlined in Example I.

## EXAMPLE 5

The procedure of Example 1 is followed to produce spray dried base beads having the following composition:

| Ingredient | % by weight |
|---|---|
| Sodium tripolyphosphate | 86.031 |
| Sodium silicate ($Na_2O/SiO_2$=2) | 5.111 |
| Stilbene 4 high conc. | 0.852 |
| Moisture | 8.007 |
| | 100.000 |

The stilbene brightener is added to the crutcher mix after the initial phosphate hydration step. The crutcher mix can have a solids content from 40 to 50 percent.

The invention provides builder beads which allow the production of free-flowing detergent beads by a method which does not produce pollution (fuming or pluming) and which is economically feasible, with high throughputs, utilizing conventional plant equipment. In addition to being free-flowing, the detergent product is non-tacky and has improved water solubility relative to prior art detergent powders. Lengthy aging periods are not necessary for the spray dried builder beads before they can be treated with the overspray ingredients, and such aging periods are not needed before filling into containers.

WHAT WE CLAIM IS:—

1. A method for producing free flowing detergent builder beads: comprising hydrating a first quantity of anhydrous phosphate builder salt in the presence of a second quantity of alkali metal silicate to form a hydrated aqueous slurry; adding a third quantity of anhydrous phosphate builder salt to the hydrated slurry to form a crutcher mix; and spray drying the crutcher mix to form a particulate material; the weight ratio of the first quantity to the second quantity being in the range from 1.5:1 to 5:1 and the weight ratio of the first quantity to the third quantity being in the range from 0.3:1 to 0.7:1.

2. A method according to Claim 1 including adding water to the hydrated slurry.

3. A method according to Claim 1 or Claim 2 wherein the hydrating step is performed at a temperature suitable for hydrating the first quantity of phosphate builder salt and the hydrated aqueous slurry is raised to a temperature at which hydration of the third quantity of phosphate builder salt is inhibited.

4. A method according to Claim 3 wherein the temperature to which the hydrated aqueous slurry is raised is in the range from 170°F to 200°F.

5. A method according to any of the preceding Claims wherein the crutcher mix contains from 40 to 55 percent by weight of solids, the weight ratio of the first quantity to the third quantity is about 0.5:1 and the spray drying takes place in a countercurrent spray tower at a spray pressure in the range from 200 psig to 1000 psig and an inlet air temperature in the range from 500°F to 700°F.

6. A method according to any of the preceding Claims which includes the addition to the crutcher mix of up to 10 percent by weight, based on the weight of solids in the crutcher mix, of builder salts chosen from carbonates, citrates and silicates having detergent building properties, and mixtures thereof.

7. A method of producing free flowing detergent builder beads: comprising

a) hydrating a first quantity of anhydrous sodium tripolyphosphate builder salt in the presence of a second quantity of sodium silicate to form a hydrated slurry, the hydration being performed in an aqueous medium and at a temperature in the range from 140°F to 170°F, and the weight ratio of the first quantity to the second quantity being in the range from 1.5:1 to 5:1;

b) raising the temperature of the hydrated slurry into the range from 170°F to 200°F;

c) adding a third quantity of anhydrous sodium tripolyphosphate to the heated hydrated slurry to form a crutcher mix;

d) supplying the crutcher mix to a spray drying tower, the hydrated slurry and the crutcher mix being maintained at temperatures of at least 170°F through the steps (c) and (d); and

e) spraying the crutcher mix in the spray drying tower to produce spray dried builder beads.

8. A method for producing free flowing detergent builder beads substantially as described in any of the Examples.

9. Free flowing detergent builder beads which have been produced by a method according to any of the preceding Claims.

10. Free flowing detergent builder beads comprising, by weight, from 45 to 90 percent of a phosphate builder salt, from 5 to 15 percent of alkali metal silicate and from 5 to 15 percent of water, the phosphate builder salt comprising a hydrated portion and an anhydrous portion, the weight ratio of the hydrated portion on an anhydrous bases to the anhydrous portion being in the range from 0.3:1 to 0.7:1, and the beads having a porous outer surface and a skeletal internal structure.

11. Detergent builder beads according to Claim 10 wherein the phosphate builder salt comprises sodium triphosphate.

12. Detergent builder beads according to any of Claims 9 to 11 which have a

particle size distribution such that at least 90 percent by weight of the beads pass through a 20 mesh screen (U.S. series) and at least 90 percent by weight are retained on a 200 mesh screen (U.S. series).

13. Detergent builder beads according to any of Claims 9 to 12 wherein from 30 to 60 percent by weight of the alkali metal phosphate component is hydrated in the presence of the alkali metal silicate component and the remainder is in anhydrous form.

14. Detergent builder beads according to any of Claims 9 to 13 having a porous sponge like outer surface and a skeletal structure.

15. Detergent builder beads according to any of Claims 9 to 14 which are substantially free from organic surface active agents.

KILBURN & STRODE,
Chartered Patent Agents,
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1980
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

1579262 COMPLETE SPECIFICATION
2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*
Sheet 1


FIG. 1

1579262 COMPLETE SPECIFICATION

2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*
Sheet 2

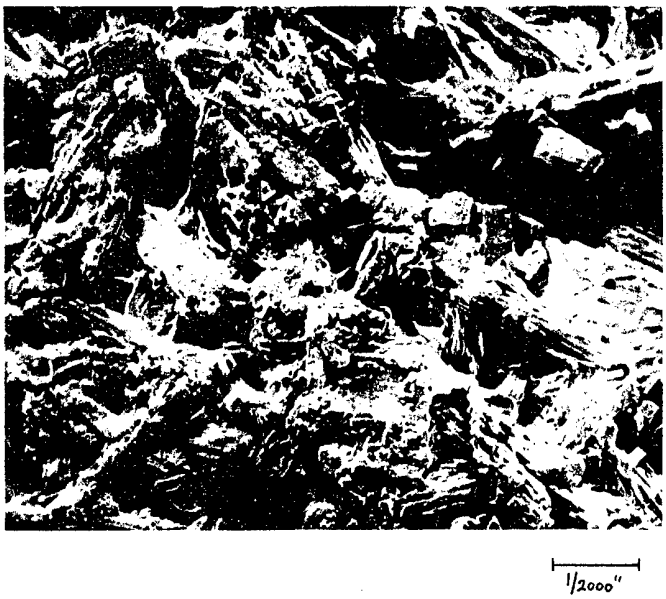


FIG. 2