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DETERGENT BARS

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Continuation of abandoned application Ser. No. 682,411, Nov. 13, 1967. This application Nov. 2, 1970, Ser. No. 86,372

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U.S. Cl. 252—89 14 Claims

ABSTRACT OF THE DISCLOSURE

Detergent bar made by working a detergent such as soap or alkylbenzenesulfonate with puffed borax. Other ingredients such as tripolyphosphates may also be present.

This application is a continuation of Ser. No. 682,411, filed Nov. 13, 1967, now abandoned.

This invention relates to the production of detergent bars.

Detergent bars, which are well known in the art, include ordinary toilet soap bars, synthetic detergent toilet bars, usually made from selected anionic detergents (such as cocomonoglyceryl sulfates) or from mixtures of synthetic detergents with soap, and laundry bars containing a large amount of a builder salt (e.g. an amount at least about equal to the amount of detergent in the bar). Aerated detergent bars, including floating soap bars, are also known.

In accordance with one aspect of this invention, there is provided a novel detergent bar made from a mixture of detergent and puffed borax. Puffed borax, and methods for manufacturing it, are described in Soap and Chemical Specialties, January 1966, pages 58–61, 118–20, which points out that the puffed borax may be made by heating a hydrated sodium tetraborate (such as borax, having 10 molecules of water of hydration, or a crystalline hydrate having five molecules of water per molecule of sodium tetraborate).

Our invention makes it possible to produce detergent bars of great utility and unexpected properties. It is found that the use of the puffed borax imparts desirable qualities with respect to the feel of the bar, its performance in use, its slough behavior and its drying characteristics, among others. For example, a low density bar can be obtained by the incorporation of the puffed borax even though the mixture of detergent and easily crushed puffed borax particles is subjected to pressure and shearing which occur during the blending and extrusion thereof. Furthermore, the invention makes it possible to make bars which, surprisingly, have a highly desirable soap-like feel, even when the detergent therein is of the type (like alkylbenzenesulfonate detergents) which ordinarily yields bars of tacky, uncomfortable feel. Another unexpected result is that the invention makes possible the production of bars which have such features as a longer use life, better slough performance, and quicker drying after use, than comparable bars not containing the highly soluble puffed borax.

In a particularly suitable process for making the detergent bars of this invention, the ingredients of the bar are fed continuously to an intensive shearing and extruding

device such as the mating paddle device described in the applications of Fischer Ser. No. 509,803 of Nov. 26, 1965 is now Pat. No. 3,497,912 (Mar. 3, 1970) and Ser. No. 581,330 of Sept. 22, 1966 is now Pat. No. 3,579,537 (May 18, 1971). For example, in the manufacture of a toilet soap bar, a dry blend of finely divided detergent (e.g. soap chips) and the puffed borax may be fed to the hopper of the device while water is continuously fed to its interior; to produce bars of still lower density, air under superatmospheric pressure may also be fed to the interior of the device, preferably in such manner that the air is injected directly into the pasty mass being sheared in the device. In the manufacture of a built detergent laundry bar, the dry blend fed to the hopper may be modified so as to include also the finely divided builder salt. The detergent may be omitted from the dry feed to the hopper and formed in situe instead, by supplying detergent acid (such as a long chain sulfonic acid) in liquid state to the interior of the mixing device while a neutralizing agent therefor is supplied either in liquid state (e.g. as an aqueous NaOH solution), to the interior, or in solid state (e.g. as solid sodium carbonate) as a component of the dry blend fed to the hopper.

In the preferred embodiments of the invention the puffed borax has a bulk specific gravity of at most about 0.3 (corresponding to a bulk density of at most about 20 lbs./ft.^{3}); the use of puffed borax of such low bulk density yields bars of which feel especially smooth. The bulk density of the puffed borax may be, for example, 3 lbs./cu. ft. or 10 lbs./cu. ft.; a preferred range is about 10–18 lbs./cu. ft. The water contents of the puffed borax materials may be, for instance, within the range of about 0–25%, e.g. about 10%.

The proportion of puffed borax in the bar may vary considerably. It may, for example, be in the range of about 5 to 60%; especially good results have been obtained when the proportion of puffed borax is about 30–40% of the weight of the bar. The ratio of the amount of detergent to the amount of puffed borax may, for instance, be in the range of about 1:3 to 4:1.

The bar may also contain a phosphate builder salt such as pentasodium tripolyphosphate or other alkali metal condensed phosphate, or a carbonate builder salt such as sodium bicarbonate, or a silicate builder salt, such as sodium silicate. Organic builder salts, such as nitrilotriacetates (e.g. trisodium nitrilotriacetate) may be present. Mixtures of two, three or more of these materials may be used. The total proportion of builder salt (including the borax as a builder salt in this calculation) may be, for example, in the range of about 20 to 70% of the total weight of the bar; preferably the total amount of builder salt is greater than the amount of detergent, in bars intended for laundry use.

Another ingredient which may be included, particularly in highly built synthetic laundry detergent bars, is starch in amounts, for example, of about 3 to 20%.

The bars of this invention generally contain water or similar material serving as a plasticizer for the solid composition, e.g., acting to plasticize the detergent. Some water is, of course, also present, in bound form, in the puffed borax which has the capacity to take on additional water of hydration. When an additional hydratable salt, such as anhydrous pentasodium tripolyphosphate, is used as an ingredient, some of the unbound water present in the composition is taken up as water of hydration of that

salt; under appropriate circumstances, this contributes desirably to the hardening of the bar.

As previously indicated, the detergent used in the bar may be a soap or an alkylbenzenesulfonate or a combination of the two. Other deteregnts may be employed in place of, or in admixture with, either of these. The soap used in the bar is preferably one of the well known soaps used for bar manufacture, e.g. a sodium salt of a higher fatty acid (generally a mixture of higher fatty acids) of about 10 to 20 carbon atoms. The alkylbenzenesulfonate may be of the well known branched chain type (e.g. tetrapropylenebenzenesulfonate) or, where biodegradability is important, of the linear alkyl type (e.g. tridecylbenzenesulfonate of high 2-phenyl content as described, for example, in U.S. Pat. No. 3,320,174, May 16, 1967, of J. Rubinfeld); the alkyl group may have about 8–16, preferably 11–15 carbon atoms.

Examples of other detergents are the higher olefin sulfonates, which can be produced by the reaction of SO_3 and a higher olefin of the formula $RCH{=}CHR_1$, where R is alkyl and R_1 is hydrogen (preferably) or alkyl, to produce a sultone-containing product followed by conversion of sultones to sulfonates. The average number of carbon atoms in the olefin (and in the resulting sulfonate) may be within the range of about 10–30, preferably 15–20. The olefin sulfonate generally comprises alkenesulfonate or hydroxyalkanesulfonate, usually a mixture of both, with the alkenesulfonate preferably in major proportion. Typical olefin sulfonates are described in British Pats. 983,056; 1,030,648 and 1,042,854. A preferred olefin sulfonate is produced by treatment of the SO_3-olefin reaction product ("Acid Mix") with strong sulfuric acid under substantially non-hydrolyzing conditions prior to neutralization with base; in one example of such a treatment 1 part of 98% H_2SO_4 is added to about 10 parts of the Acid Mix made from about equimolar proportions of SO_3 (highly diluted with air) and C15–C20 alpha olefin, and the blend is maintained at about 90–100° C. for about 5 minutes, then made strongly alkaline with aqueous NaOH (e.g. using about 20% excess NaOH) and heated at a temperature of about 80–200° C. (e.g. at 90° C. for ½ hour).

Other detergents which may be present in the bar are the alkane sulfonates (such as the primary paraffin sulfonates, e.g. of about 10–20, preferably about 15–20, carbon atoms), or the salts of alkyl esters of α-sulfofatty acid (e.g. of about 10–20 carbon atoms, such as methyl α-sulfomyristic or methyl α-sulfotallow acid). Sulfates of higher alcohols may also be added. Examples of these are sodium lauryl sulfate, Turkey Red Oil or other sulfated oils, or sulfates of mono- or di-glycerides of fatty acids (e.g. stearic monoglyceride monosulfate), alkyl poly (ethenoxy) ether sulfates such as the sulfates of the condensation products (usually having 1 to 5 ethenoxy groups per molecule) of ethylene oxide and a higher fatty alcohol, e.g. lauryl alcohol; lauryl or other higher alkyl glyceryl ether sulfonates; poly (ethenoxy) ether sulfates such as the sulfates of the condensation products of ethylene oxide and nonyl phenol (usually having 1 to 6 oxyethylene groups per molecule).

Other suitable anionic surface active agents are compounds having acidic groups (e.g. —COOH or —SO_3H) and intermediate linkages, such as the amides or esters of long chain fatty acids and amino- or hydroxy-acid (e.g. the lauric amide of such amino acids as sarcosine, β-aminopropionic acid, polypeptides, or N-methyl tauric acid, or lauric acid ester of isethionic acid and soluble salts of such compounds.

The hydrocarbon radicals of the anionic deteregnt materials preferably contain at least about 10 carbon atoms, long chain hydrophobic aliphatic radicals of about 11–18 carbon atoms being particularly suitable, and the cations of the added anionic detergents are advantageously such as to impart water-solubility to the acidic portion of the molecule or to maintain its water-solubility, e.g. sodium, potassium, triethanolammonium, diethanolammonium, or other alkanolammonium, calcium, magnesium (when the surface active agent forms a water-soluble calcium or magnesium salt) or ammonium. Zinc and aluminum salts may be employed also in desired amounts.

The detergent in the bar may comprise a nonionic or amphoteric deteregnt. Among the nonionic detergents are the lower alkylene oxide condensation products of hydrophobic compounds, e.g. ethylene oxide condensates with higher fatty acids, higher fatty alcohols or alkyl phenols having at least 5 and usually from about 5 to 30 oxyethylene groups per molecule. The corresponding higher alkyl mercaptans of thioalcohols, or polyoxypropylene glycols of at least 900 molecular weight condensed with a sufficient number of ethylene oxide groups as known in the art may be used also. Other nonionics are the alkylolamine condensates of higher fatty acids such as lauric and myristic diethanolamide, and the amine oxides, such as lauryl dimethyl amine oxide, lauryl or hexadecyl dihydroxyethyl amine oxide, N-2-hydroxlauryl morpholine oxide or 2-hydroxyhexadecyl dimethyl amine oxide, and the like. Among the amphoteric detergents, usually having an alkyl group of 10–18 carbons, are fatty or higher alkyl imidazolines, such as 1-coco-5-hydroxyethyl-5-carboxymethyl imidazoline known as Miranol CM; and the N-higher alkyl beta-alanines such as dodecyl beta-alanine or N-dodecyl iminodipropionic acid (e.g. the materials known as Deriphats); the carboxylic group of the amphoteric detergent may be in the acid form or in the form of the water-soluble salt (e.g. Na salt). Further examples are the disodium salt of 1-lauryl cycloimidium-2-ethoxyethionic acid-2-ethionic acid and its corresponding 2-lauryl sulfate derivative.

When soaps are employed the acid portion of the soap may be that of a fatty acid such as lauric, myristic, stearic, oleic, elaidic, isostearic, palmitic, undecylenic, tridecylenic, pentadecylenic or other saturated or unsaturated fatty acid of 11 to 18 carbon atoms. Soaps of dicarboxylic acids may also be used such as the soaps of dimerized linoleic acid. Soaps of such other higher molecular weight acids such as rosin or tall oil acids, e.g. abietic acid, may also be employed.

The following examples are given to illustrate this invention further. In this application all proportions are by weight unless otherwise indicated.

EXAMPLE 1

In this example there is employed a mating paddle intensive shearing and extruding device (as described in the applications of Fischer Ser. No. 509,803 of Nov. 26, 1965 and Ser. No. 581,330 of Sept. 22, 1966 is now abandoned (Dec. 18, 1968), Austin and Lee Ser. No. 529,151 of Feb. 21, 1966 is now Pat. No. 3,434,974 (Mar. 5, 1969) and Fischer and Austin Ser. No. 529,087 of Feb. 21, 1966). The dry blend fed to the hopper of the device contains equal proportions of puffed borax (of 0.25–0.28 specific gravity, made by puffing sodium tetraborate pentahydrate) and toilet soap chips (the soap being a sodium salt of a mixture of 80% tallow fatty acids and 20% of coconut oil fatty acids), which chips have a moisture content of 13%. The dry blend also contains ½% of titanium dioxide pigment and ½% of perfume. The dry blend is taken up continuously by the feed screw section of the device, just below the hopper, and is forwarded continuously, by the action of the intermeshing parallel feed screws, to the mating paddle section. Just before entering the mating paddle section, the dry blend is brought into contact with a stream of water which is fed into the interior of the device, at a port located just downstream of the hopper, at a rate equal to 12 parts of water per 88 parts of dry blend. Compressed air is fed into the resulting plastic mixture in the mating paddle section of the device through two air ports situated down-

stream of the water entry port; the pressure of the air at these two ports is 16 p.s.i.g. The device has a jacket to which saturated steam at a pressure of 12–15 p.s.i.g. is supplied, to maintain the mixture in the desired heated plastic condition. The mixture is extruded as continuous bar of 28 x 50 mm. cross-section through the rectangular die at the outlet of a tapered conical nozzle, which extends horizontally at right angles to the parallel horizontal, rotating shafts of the device at about the same level as said shafts, on that side of the device at which the paddles move upwardly. The extruded rod, which has a temperature of 50–55° C. as it leaves the die, is allowed to cool and is then cut into individual bars, whose specific gravity is well below 1 (e.g. 0.94–0.97); their moisture content is about one fourth of the total weight. The bars are strong, have a pleasant feel and lather well during use, are slough resistant, remain hard, and retain their floating and other characteristics on continued long use.

EXAMPLE 2

Example 1 is repeated except for the following: The weight ratio of soap chips: puffed borax is 2.95:1. The amount of TiO_2 is 1% of the dry blend. As a preservative the dry blend has added thereto 0.2% of an aqueous 50% stannic chloride solution. The material injected into the water entry port is a solution of 0.71 part of sodium silicate (having an $Na_2O:SiO_2$ mol ratio of 1:2.37) in 10.2 parts of water, and the ratio of the amount of dry blend to the amount of this solution is 89:11. The air pressure at the air entry ports ranges from 8 to 32 p.s.i.g. during the run. The jacket of the device is unheated. Instead of a tapered nozzle, there is used, at the same position on the device, a straight nozzle in the form of a rectangular tube, 3 inches long; this nozzle is heated, and the temperature of the rod emerging therefrom is in the range of 50–60° C.

The bars have specific gravities of 0.97–1.03 and moisture contents of about 20–22%.

EXAMPLE 3

Example 1 is repeated with the following changes: The weight ratio of soap chips: puffed borax is 7.8:1. The amount of TiO_2 is 1.1% of the dry blend. The material injected into the water entry port is a solution of 0.7 part of sodium silicate (having an $Na_2O:SiO_2$ ratio of 1:2.35) in 9.8 parts of water, and the ratio of the amount of dry blend to the amount of this solution is 89.5:10.5. The jacket steam is supplied at 18–20 p.s.i.g. The nozzle is externally heated and the bar is extruded therefrom at 55–65° C.

The measured moisture content of the bars is about 11.5%. Their density is 1.05, measured after they have been pressed in a conventional soap stamping press.

EXAMPLE 4

Example 1 is repeated with the following changes: Instead of using soap there is employed a blend thereof with about the same amount of a sodium alkylbenzenesulfonate, the latter being added in the form of spray-dried beads containing a minor proportion (10% of the weight of the beads) of sodium silicate (having an $Na_2O:SiO_2$ mol ratio of 1:2.35). More particularly the dry blend contains 32.2% of the spray dried beads, 35.6% of the soap chips and 32.2% of the puffed borax. The weight ratio of the amount of the dry blend to the amount of added water is 88.5:11.5. In this example, the air-injection ports are closed, and the step of injecting air under pressure is omitted. The specific gravities of the bars are in the range of 1.18–1.29.

The alkylbenzenesulfonate used in this Example 4 is sodium linear tridecyl benezenesulfonate.

EXAMPLE 5

In this example, and in Example 6, there are produced detergent laundry bars containing substantial proportions of pentasodium tripolyphosphate, together with a sulfonate detergent produced by neutralization of the corresponding sulfonic acid in the presence of the solid finely divided builder salt. The apparatus described in Example 2 is employed, but no air is injected (the air-entry ports being closed) and the liquid introduced at the first port is a mixture of water and the sulfonic acid.

More particularly, the dry blend is made up of the following components:

Soda ash, light	11.97
Pentasodium tripolyphosphate powder (anhydrous, Form II)	31.6
Soap chips (as in Ex. 1)	17.38
Puffed borax (as in Ex. 1)	38.56
Titanium dioxide pigment	0.16
Perfume	0.16

63.28 parts of this dry blend are employed together with 36.12 parts of the liquid; the latter is made up of 14.65 parts of water, 0.06 part of ultramarine blue and 22 parts of an acid mix (containing 20.8 parts of linear tridecylbenzenesulfonic acid together with water and 0.44 part of H_2SO_4).

EXAMPLE 6

Example 5 is repeated, using a dry blend containing no soap chips and having the following composition:

Soda ash, light	12.28
Pentasodium tripolyphosphate (as in Ex. 5)	32.41
Puffed borax (as in Ex. 1)	37.00
Titanium dioxide pigment	0.16
Optical brightener	0.16
Tapioca starch powder	17.83
Perfume	0.16

61.71 parts of this dry blend are employed together with 38.29 parts of liquid; the latter is made up of the same ingredients in the same amounts as in Example 5 except that the amount of water is correspondingly increased (to 16.22 parts).

The specific gravities of the bars made according to Examples 5 and 6 are in the range of about 1.3–1.4. Ordinarily the specific gravity of highly built synthetic laundry detergent bars are well above 1.5. Even the soap-free bars of Example 6 have a pleasant soap-like slippery feel in use; this contrasts quite noticeably with the tacky or sticky, and rougher, feel of the usual synthetic laundry detergent bars made with the same sulfonated detergent.

When a typical highly built detergent laundry bar of this invention is sectioned and examined under the microscope, and its microscopic appearance is compared with that of the puffed borax used as the starting material, the bar is found to be generally free of the groups of bubble-like structures which are characteristic of the puffed borax; bubble-like structures are found occasionally in the bar, but in a concentration obviously much lower than that corresponding to the amount of puffed borax used in making the bar. This would indicate that the working of the mixture during the manufacture of the bar breaks down the porous structure of the puffed borax, possibly forming very thin curved sodium tetraborate flakes.

The shearing and extruding device used in the foregoing examples has a pair of parallel horizontal shafts on which there are mounted paired feed screw elements (at the inlet end of the device) and paired paddle elements. Each of the paired feed screw elements is composed of four helical turns extending about 8 inches on its shaft. Downstream of these feed screw elements are the paddles, some of which are of the forwardly pitched ("advancing") type and some of the unpitched ("non-advancing" type), as described in applications Ser. No. 509,803 and 581,330, previously mentioned. Each paddle is of stainless steel, one inch thick, its long axis is 4⅞ inches long, its short axis is 2 inches long and its front and read faces are parallel. The two faces of each of the forwardly pitched

paddles are offset by an angle of 12½° (about the axis of rotation of the paddle) so as to advance the mixture longgitudinally of the shafts. The clearance between the front face of a paddle and the rear face of the next paddle is about 0.03 inch. The clearance between the tips of the paddles and the inner walls of the surrounding stationary housing which are wiped by said tips is also about 0.03 inch, as is the clearance between said tips and the edges of the paired paddles which they wipe. The three ports are situated, respectively, about 9 inches, 18 inches and 24 inches downstream of the downstream end of the feed screw section. The specific arrangements of paddles used in the above examples are as follows, starting just downstream of the feed screw elements and using the designation "A" for each pair of the "advancing" (forwardly pitched) paddles and the designation "N" for each pair of non-advancing" (unpitched) paddles, there being 28 pairs of paddles in all: Examples 1 and 4, A-A-A-A-A-N-N-A-A-N-N-A-A-N-N-A-A-N-N-A-A-A-N-A-A-A - A-A; in Examples 2, 3, 5 and 6, A-A-A-N-A-N-A-N-A-N-A-N-A-N-A-N-A-N-A-N-A-N-A-N-A-N-A-N-A-N-A-N-A-N-A-N. The long axis of each paddle is offset 45° from the long axes of the preceding and succeeding paddles. The speed of each shaft is about 100–160 r.p.m., giving about 600–9000 paddle cuts per minutes.

In each of the foregoing examples, the residence time, from initial mixing to final extrusion, is well below 10 minutes, preferably less than 5 minutes, e.g. about 1 to 2 minutes.

While the use of puffed borax is an important and necessary feature of the most useful presently known form of this invention, it is within the broader scope of the invention to use other puffed water-soluble salts in place of all, or part of, the puffed borax. Such puffed salts may be made in a manner similar to that used for manufacturing the puffed borax, e.g. by subjecting a hydrated crystalline salt to heat (e.g. hot air at a temperature in the range of about 200 to 425° C.), to yield a partially hydrated expanded product, preferably having a bulk density on the same order as that of the puffed borax described above. One salt which may be used for this purpose is a granular sodium silicate whose

$$Na_2O:SiO_2$$

mol ratio is about 1:2 and which contains 18.5% water before puffing. It is also within the scope of this invention to use expanded products obtained by puffing such salts as the fully hydrated pentasodium tripolyphosphate, fully hydrated sodium carbonate or fully hydrated potassium carbonate.

As seen under the electron microscope a typical puffed borax has a highly porous structure having numerous openings or pockets and having extremely thin walls many of which project outwards from the body of the granule. FIGS. 1 and 2 are photographs taken with an electron-microscope at the scale indicated thereon. FIG. 1 shows a whole granule and FIG. 2 is an enlarged view of a portion of a granule.

It is understood that the foregoing detailed description is merely given by way of illustration and that many variations may be made therein without departing from the spirit of the invention.

We claim:

1. Process which comprises mixing a bar forming organic anionic, nonionic or amphoteric detergent and water with a puffed water-soluble hydratable salt to form a pasty extrudable mixture containing about 5 to 60% of said puffed salt the ratio of the amount of detergent to the amount of puffed salt being in the range of about 1:3 to 4:1, the amount of water being sufficient to plasticize said detergent in said mixture, said puffed salt having a bulk density of about 10 to 18 pounds per cubic foot, said puffed salt being a product obtained by subjecting a hydrated crystalline salt selected from the group consisting of sodium tetraborate, sodium silicate, pentasodium tripolyphosphate, sodium carbonate and potassium carbonate to heat to expand said salt and produce a highly porous thin-walled structure having numerous openings or pockets having thin walls, said walls being less than 0.01 mm. in thickness, extruding said mixture as a rod through a die and cutting said extruded rod to form individual detergent bars, said mixture being subjected to pressure and shearing during the mixing and extrusion thereof whereby the porous structure of said salt is broken down so that when said bars are sectioned and examined under the microscope they appear substantially free of the groups of bubble-like structures which are characteristic of the microscopic appearance of said puffed salt used to form said bars.

2. Process as in claim **1** in which said detergent is an anionic detergent.

3. Process as in claim **1** in which said detergent is water-soluble alkylbenzenesulfonate detergent having 11–15 carbon atoms in the alkyl group.

4. Process as in claim **1** in which said detergent is soap.

5. Process as in claim **1** in which said puffed salt is sodium tetraborate.

6. Process as in claim **5** in which said detergent is water-soluble alkylbenzenesulfonate detergent having 11–15 carbon atoms in the alkyl group.

7. Process as in claim **6** in which the content of puffed salt is about 30–40% of the weight of the bar.

8. Process as in claim **7** in which said mixture contains pentasodium tripolyphosphate, the total builder salt content, including sodium tetraborate builder salt, of the bar being about 20–70%.

9. Process as in claim **5** in which said detergent is soap.

10. Process as in claim **5** in which the amount of puffed salt is about equal to the amount of soap.

11. Process as in claim **1** in which the puffed salt is puffed borax.

12. Process as in claim **1** in which the mixture is maintained under superatmospheric air pressure before extrusion.

13. Process as in claim **11** in which the period of time from the initial addition of the water to the puffed salt to the extrusion of the mixture is less than 10 minutes.

14. Process as in claim **13** in which the puffed salt, water and detergent are fed continuously to an enclosed zone where they are mixed together and intensively sheared, and from which they are continuously extruded as a rod.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,708,425 Dated January 2, 1973

Inventor(s) Russell Edward Compa et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Insert the attached sheet as part of the Letters Patent.

Signed and sealed this 13th day of August 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

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Commissioner of Patents

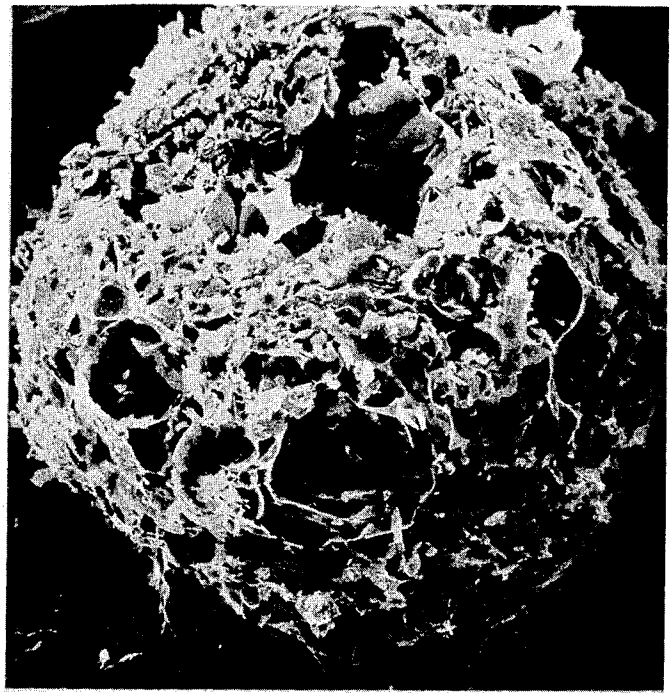
FORM PO-1050 (10-69)

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★ U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334.

DETERGENT BARS

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FIG 1



0.1 mm

FIG 2



0.01 mm

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