March 25, 1969 A. E. AUSTIN ET AL **3,434,974**

CONTINUOUS MANUFACTURE OF DETERGENT LAUNDRY BARS

Filed Feb. 21, 1966 Sheet 1 of 4

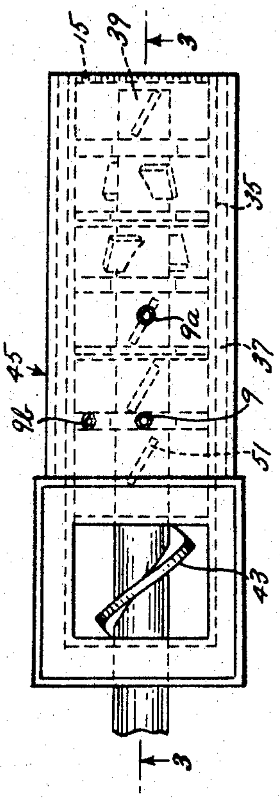

Fig. 2

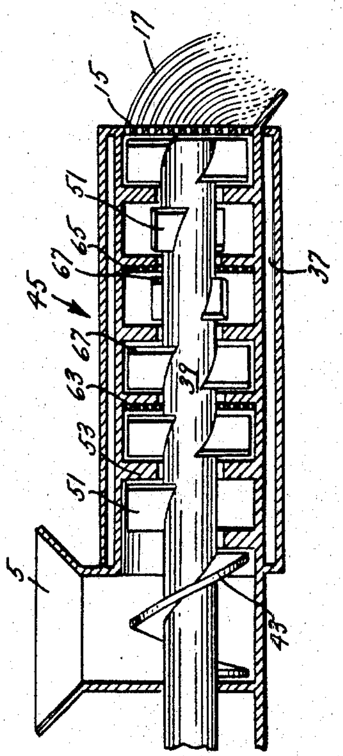

Fig. 3

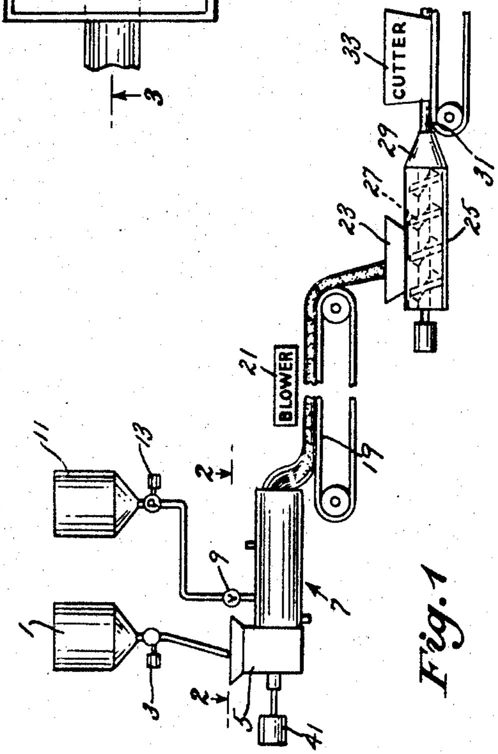

Fig. 1

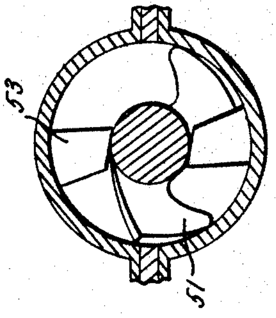

Fig. 4

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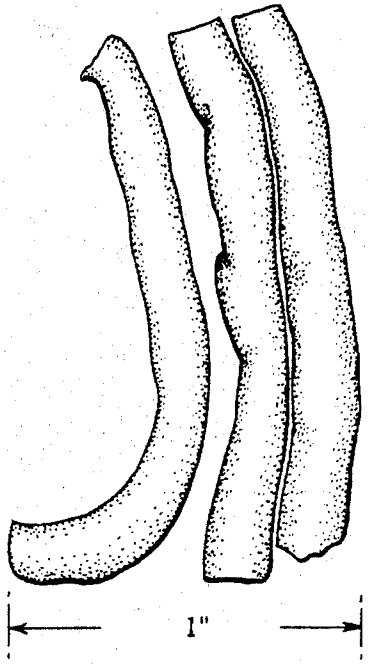

Fig. 5

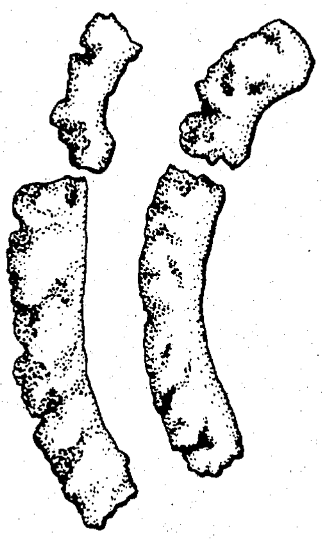

Fig. 6

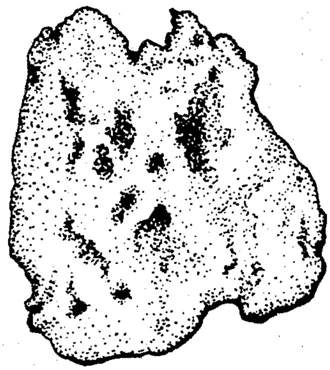

Fig. 7

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CONTINUOUS MANUFACTURE OF DETERGENT LAUNDRY BARS

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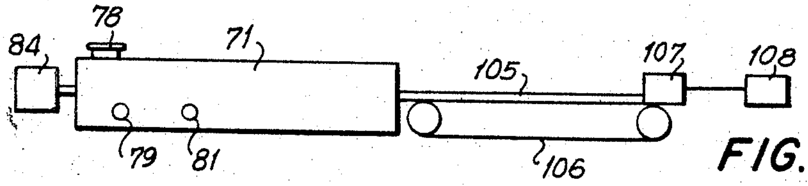


FIG. 8

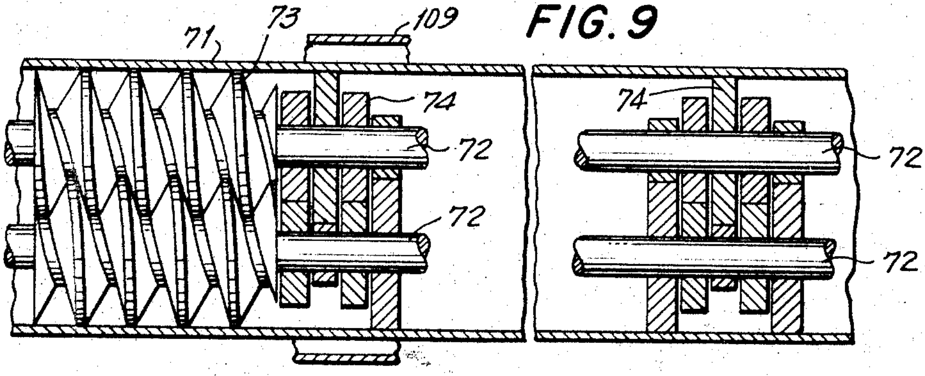


FIG. 9

FIG. 10

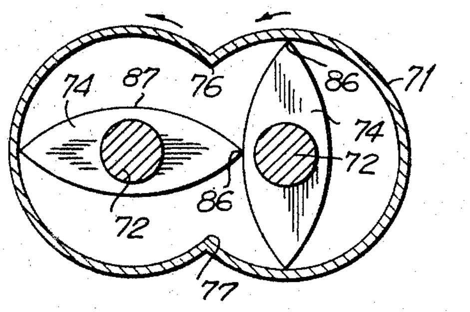


FIG. 11

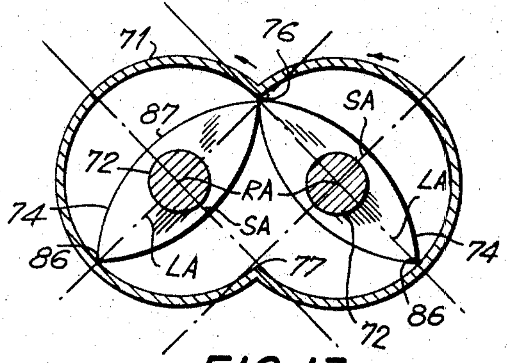


FIG. 12

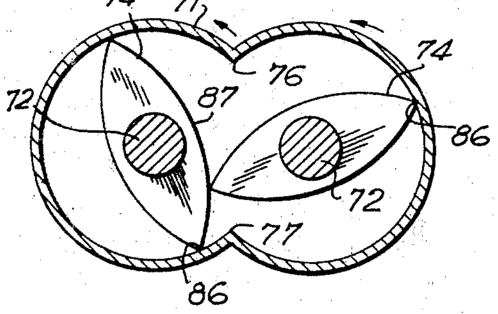
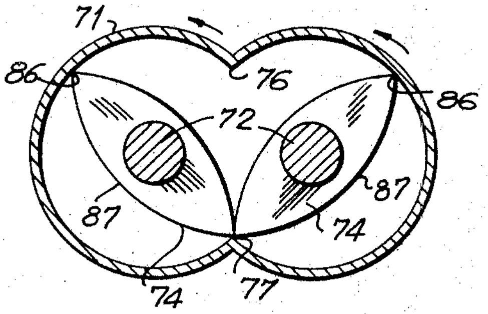


FIG. 13



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CONTINUOUS MANUFACTURE OF DETERGENT LAUNDRY BARS

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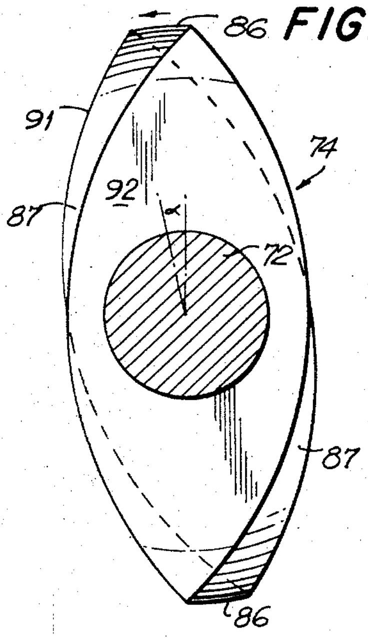


FIG. 14

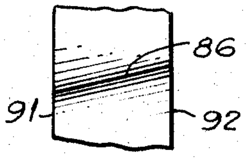


FIG. 15

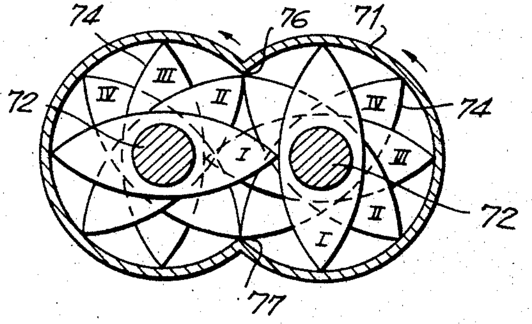


FIG. 16

FIG. 17

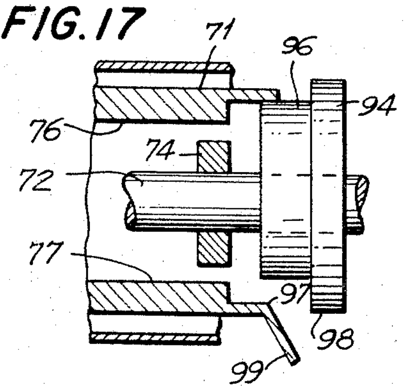


FIG. 18

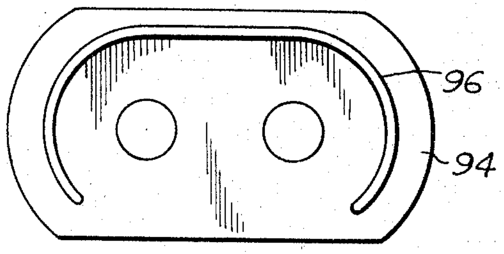
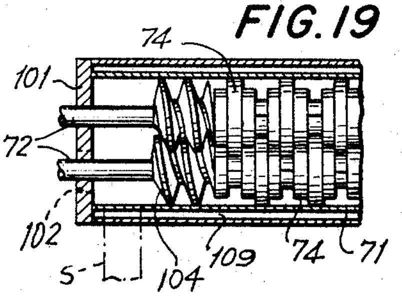


FIG. 19



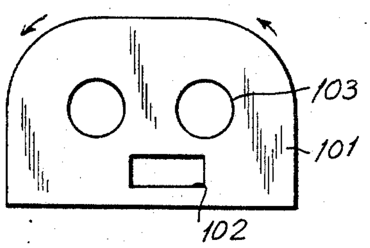


FIG. 20

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CONTINUOUS MANUFACTURE OF DETERGENT LAUNDRY BARS

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Continuation-in-part of application Ser. No. 469,144, July 2, 1965. This application Feb. 21, 1966, Ser. No. 529,151
Int. Cl. C11d *3/065, 11/00;* **B29b** *3/00*
U.S. Cl. 252—138 **24 Claims**

ABSTRACT OF THE DISCLOSURE

Making detergent laundry bars by continuously mixing sodium alkylbenzenesulfonate or other anionic detergent with water and a large amount of solid builder salt such as pentasodium tripolyphosphate and intensively shearing the mix, then (a) extruding strands of the mix, cooling and plodding, or (b) directly extruding a bar. Reaction of the builder salt and the water to form hydrate aids hardening of bar. The sulfonate salt may be formed in situ by reaction of the sulfonic acid and (a) sodium carbonate (in the solid feed) or (b) a stream of NaOH solution.

The present invention relates to a process and apparatus adapted for the continuous manufacture of a laundry bar comprising an anionic synthetic detergent and water-soluble inorganic builder salts and the resulting products, as hereinafter described.

Within the last decade, commercial interest has developed in a laundry bar containing a minor amount of synthetic detergent and a substantial proportion of inorganic salts, particularly due to the commercial success and substantial consumer acceptance from about 1957 of a detregent bar product known in the detergent field under the name of "Limpiol." This product was a mechanically worked plodded detergent bar which contained usually according to analysis about 25–30% sodium higher alkyl benzene sulfonate detergent, about 60–65% inorganic salts and about 10–12% water. The inorganic salt in the product was about 35–40% sodium bicarbonate and about 18–20% sodium tripolyphosphate primarily. It is understood that this product was made by a batch method which usually involved (1) mixing liquid alkyl benzene sulfonic acid and water with the inorganic salts in powdered form in a standard heavy-duty mixer to form a uniform mixture whereby powdered carbonate and bicarbonate "dry" neutralized the sulfonic acid to form the sodium salt with the release of carbon dioxide and water, (2) the mixing was continued until complete neutralization was obtained from the practical standpoint and, (3) the resulting solid mixture was then fed to a soap plodder which further mechanically worked and compressed the mixture, and then extruded it in the form of a continuous bar which was cut into cakes or bars for individual use. It was known also to commercially manufacture laundry bars by equipment consisting of a tilting amalgamator for mixing organic detergent salt and inorganic salts, a mill for further fine mixing as desired, and plodders to form an extruded bar, such as U.S. Patent 2,845,391. Other methods are described in U.S. Patent 2,205,037 and 2,941,948 for example. Subsequently, similar processes have been proposed such as described in U.S. Patent 3,178,370 wherein a fine spray of sulfonic acid is sprayed onto an agitated bed of inorganic salts including carbonate to effect "partial" neutralization of the sulfonic acid with the release of carbon dioxide, and thereafter the mixture is further mechanically worked to make it more homogeneous and to complete the neutralization.

It is an object of this invention to provide an improved method and apparatus for the manufacture of detergent bars.

Another object of this invention is to provision of a rapid and highly economical process for preparing a substantially soap-free solid built synthetic detergent in plastic form.

Other objects of this invention will be apparent from the following detailed description and claims.

In accordance with one aspect of this invention we have discovered that by continuously feeding the inorganic builder salt and an acid form of the synthetic detergent to an intensive shearing zone, in the presence of a neutralizing agent for the acid, the neutralizing reaction is rapid and there is produced continuously a coherent, deformable plastic built detergent which can be extruded and which is suitable for forming into high quality detergent bars. In a preferred form of the invention the neutralization is effected in a single step and the residence time in the intensive shearing zone is very short, e.g. well below ten minutes and preferably less than two minutes; a ½ minute residence time has given excellent results. This short residence time in turn makes it possible to produce large poundages per day of the built detergent bar-forming material using relatively small equipment.

In one preferred embodiment of the invention the blend of detergent and builder salt is discharged from the intensive shearing zone by extruding the blend as a shaped mass of limited thickness, e.g. in noodle-like form. The surface of the extruded material usually is relatively soft and the extruded shapes tend to adhere if pressed together. When such soft-surfaced shapes are fed directly to a conventional single worm bar-forming plodder, difficulties may be encountered unless special attention, and additional labor, is used to forcefully stuff the material continuously into the plodder to bring it into firm contact with the usual extrusion worm or screw of the plodder and prevent blockage of the entrance of the plodder. We have found, however, that the plodder-feeding operation can be greatly facilitated by hardening the surfaces of the discrete shaped masses extruded from the intensive shearing zone. This may be done conveniently by passing these shaped masses, while maintained in discrete form, through a cooling zone, as by passing the extruded noodles onto a conveyor belt while maintaining them in uncoalesced condition, and moving the belt through a zone in which a stream of cool air is blown against the surfaces of the noodles. When the blend contains a hydratable builder salt, such as unhydrated sodium tripolyphosphate, it is believed that part of the surface hardening during the exposure in the cooling zone may be attributed to the hydration reaction of the builder salt with the water formed in, or fed to, the intensive shearing zone. In any event, the surface-hardened shaped masses feed easily into the plodder, and any tendency to coalesce into a large body plugging the entrance to the plodder is reduced or eliminated so that the plodder-feeding operation requires no special attention or additional labor. The thickness of the extruded shaped masses is advantageously well below one inch, preferably below ½ inch, e.g. about 1/32" to ¼".

Feeding into the plodder may also be facilitated by using a double-worm type of plodder, in which there are two counter-rotating worms mounted side-by-side in a single casing and in which both worms simultaneously engage the material being plodded.

In a preferred form of the invention the material is sheared in an elongated zone in which the material is passed between relatively moving shearing surfaces at least one of which includes a moving rotating inclined surface which urges the mixture toward the discharge end of the zone, the distance between the relatively moving shearing surfaces being less than 0.2 inch (e.g. about ⅛" or less; for instance about 1/50–1/16") and the speed of their relative moving being at least about 1 foot per second, the rotational speed of the moving surface being at least 50 r.p.m. The rate of input of shearing energy, as measured by the brake horsepower input to the shearing device, is advantageously at least about 1/20 H.P. per pound of material being processed in the device. Brake horsepower, is, as is well known, the difference between indicated horsepower when the machine is operating as a shearing device and the no-load (or frictional) horsepower measured when the machine is operated empty, at the same rate.

In another aspect of this invention, to be described more fully below, the intensively sheared blend of detergent and builder salt is extruded in the form of a bar (without forming the noodle-like strands and then plodding them), the flowable blend being maintained continuously in a heated flowable condition and continuously under shearing forces from the time of its formation until its passage through the extrusion opening.

Certain embodiments of this invention are illustrated in the accompanying drawings in which

FIGURE 1 illustrates the overall process used in one embodiment of the invention.

FIGURE 2 is a plan view of an intensive shearing apparatus taken along the line **2**—**2** of FIG. 1.

FIGURE 3 is a cross-sectional view of the intensive shearing apparatus taken along the line **3**—**3** of FIG. 2.

FIGURE 4 is a view showing the relationship of the rotating arms, anvil and rotor in the intensive shearing apparatus.

FIGURE 5 is a view of one preferred form of extruded noodles discharged from the intensive treating zone, drawn to scale, with the scale indicated in the figure.

FIGURE 6 is a view of a less preferred form of the extruded noodles, drawn to the same scale as FIG. 5.

FIGURE 7 is a view of a still less preferred form of extruded material which is in the form of a relatively small lump of the blended, neutralized plastic detergent-builder composition, shown on the same scale as FIGS. 6 and 7.

FIGURE 8 illustrates the overall process used in another embodiment of the invention.

FIGURE 9 is a plan view of one form of intensive shearing and extrusion apparatus used in the latter embodiment, with portions in cross-section.

FIGURES 10–13 are end views showing successive positions of the paddles used for mixing and intensive shearing in the apparatus of FIG. 9.

FIGURE 14 is an end view of one type of paddle which acts also to advance the material along the apparatus.

FIGURE 15 is a top view of the tip section of the paddle of FIG. 14.

FIGURE 16 is an end view showing one arrangement of the paddles.

FIGURE 17 is a side view, with parts in cross-section, showing an arrangement at the discharge end of the apparatus of the embodiment illustrated in FIG. 8.

FIGURE 18 is an end view of an end wall shown in FIG. 17, looking downstream.

FIGURE 19 is a top view, with parts in cross-section, showing another extrusion arrangement of the apparatus of the embodiment illustrated in FIG. 8.

FIGURE 20 is an end view of the end wall shown in FIG. 19.

Turning now to FIG. 1, a dry blended mixture of powdered inorganic salts containing a solid neutralizing agent is fed from a bin **1** through a flow measuring and feeding device **3** to the hopper **5** of an intensive shearing apparatus **7** to be described in detail below. A liquid mixture of detergent acid and color is injected continuously into an inlet port **9** of the intensive shearing apparatus **7**, being supplied thereto from a tank **11** by a metering pump **13**. Heat is generated by the neutralization reaction occurring in the intensive shearing zone, as well as by the work of shearing. The substantially neutralized bar-forming blend is continuously discharged in heated condition from the intensive shearing apparatus, through its apertured extrusion plate **15**, in the form of discrete noodle-like generally cylindrical strands **17** which are continuously deposited onto a continuously moving endless conveyor belt **19** serving as a cooling and hardening zone. To aid in the cooling a stream of air (e.g. at room temperature) is blown against the strands **17** on the conveyor belt, by a suitable blower **21**; advantageously the belt is perforated to bring substantially all surfaces of the strands into direct cooling relationship with the air.

The belt transports the strands **17** continuously to the inlet **23** of a plodder **25**, of the usual screw extruder type, where the strands are continuously conglomerated and extruded, by the action of the driven rotating screw **27**, through the die **29** whose opening has substantially the same shape, usually rectangular, as the cross-section of the desired bar. The continuously extruded material **31** is then subdivided into individual bars, by a suitable cutter indicated generally as **33**, after which the individual bars may be stamped, if desired, with various indicia or into other shapes.

The intensive shearing device **7** of the illustrated embodiment comprises a generally cylindrical chamber **35** preferably surrounded by a cooling jacket indicated generaly as **37** and having the usual inlet and outlet for circulating cooling fluid, such as cold water. Within the chamber **35** is a rotor **39** extending the entire length of the device, one end of the rotor being externally journalled and connected to the drive motor **41** (FIG. 1), and the opposite end, which (in the illustrated embodiment) terminates inwardly of the apertured extrusion plate **15**, being free or supported by a spider bearing. Mounted upon the rotor **39** just below the hopper is a feed screw **43**, which serves to bring the powdered material into an intensive shearing zone, indicated generally as **45** at the inlet end of which it makes its initial contact with the liquid material.

In the zone **45** there are rotating arms **51**, integrally welded or otherwise fastened to the rotor **39**, cooperating with stationary anvils **53** secured to and projecting inwardly from the inner wall of the cylindrical chamber **35**. More particularly, in the illustrated embodiment, the arms **51** are arranged in pairs, each arm of a pair being displaced from its mate by 180° and both arms of each pair being situated in the same location axially, on the rotor; the anvils are similarly arranged in pairs, close to the paths of the rotating arms so that the material in the chamber is advanced, by its engagement with the inclined surfaces of the arms, and thereby wiped and mulled against the surfaces of the anvils, there being a small clearance (e.g. 1/16 inch) between the arms and their corresponding anvils. The anvils may have inclined downstream faces to aid in advancing the material through the chamber.

Within the zone **45** there are a pair of spaced multi-apertured plates **63** and **65**, respectively, through which the material is forced by the wiping action of the adjacent inclined arms **51** whose forward edges **67** run close to the apertured plates **63**, **65**, the clearance between the arm edges and these plates being, for example, less than about ⅛ inch (e.g. 1/16 inch).

In a typical installation easily capable of processing 2000 lbs. per hour of material, the diameter of the cylindrical chamber **35** is about 6 inches, the overall length of the zone **45** is about 19½ inches, each plate (**63** and **65**) is about ¼ inch thick and contains a considerable number of round holes each about ¼ to ½ inch in diameter, and the rotor is driven at the rate of about 340 r.p.m. It will be understood that the chamber **35** need not be filled with the detergent bar-forming material but can, if desired, be run only partly full (e.g. ¼, ½ or ¾ full). The material being sheared in the chamber **35** need not be under pressure, except for the localized pressures in the relatively thin shearing areas, as in the areas where the arms **51** wipe against the anvils **53** or against the apertured plates **15**, **63**, **65**, or against the cylindrical inner wall of the chamber **35**.

Another form of useful intensive shearing apparatus is one having a helically threaded rotor rotating rapidly in an internally helically threaded cylinder, there being a very small clearance between the rotor and cylinder for the passage of material being advanced and sheared by the rotation of the rotor.

The extruded noodle-like strands illustrated in FIG. 5 (which were extruded through 3/16 inch diameter circular openings in the apertured discharge plate **15**) have given outstanding results when plodded into bar form. These strands are dense (specific gravity, measured by liquid displacement, in the range of about 1.1–1.7), of substantially uniform cross-section, and relatively smooth and glossy, and can be handled more easily than the rougher and pock-marked forms shown in FIGS. 6 and 7, from which good bars can also be made.

To facilitate the plodding operation the noodle-like strands extruded from the intensive shearing zone are preferably not of indefinite length. Their lengths are advantageously on the order of less than about two feet, preferably less than about 6 inches (e.g. ½–3 inches). The action of the rotating arms just behind the apertured discharge plate **15** of the illustrated intensive shearing device helps in this respect, since the arms have a cutting action on each incipient strand at the inner side of the apertured discharge plate. While the cut end of the incipient strand becomes adhered to material supplied thereto after each such cut, the extruded strand has a weakened portion corresponding to the cut, and therefore tends to break easily, particularly as the strand becomes harder and less plastic on cooling.

The water soluble anionic organic synthetic detergents which may be present in the compositions produced in accordance with this invention contain a sulfo acid solubilizing group joined (directly or indirectly through an intermediate linkage) to a hydrophobic organic group. Thus, such detergents include both organic sulfonates, e.g. $R-SO_3^-$ compounds and organic sulfates, e.g. $R-O-SO_3^-$ compounds, having sufficient water solubility to form detersive aqueous solutions with foaming properties in concentrations which are suitable for use in laundering operations. In the formula, R is a radical having an aliphatic chain of at least six carbons, the radical preferably having about 8–30 carbons. The detergents may be used individually or in any desired combination.

Among the suitable water soluble anionic sulfonated detergents, the higher alkyl aryl sulfonate detergents having about 8 to 15 carbon atoms in the alkyl group are particularly effective. It is preferred to use the higher alkyl benzene sulfonate detergents for optimum effects, though other detergents containing a mononuclear aryl group, such as xylene, toluene or phenol, may be used also. The higher alkyl substituent on the aromatic nucleus may be branched or straight-chained in structure. Examples of straight chain alkyl groups are n-decyl, n-dodecyl and n-tetradecyl groups derived from natural fatty acids and petroleum. Examples of branched chain alkyl derivatives are propylene and butylene polymers such as propylene trimer, tetramer and pentamer. Examples of other suitable water soluble anionic sulfonated detergents which may be satisfactorily used in the compositions of this invention are the alkane sulfonates containing about 8 to 20 carbon atoms in the alkyl group and the alkyl sulfonates wherein the alkyl group of about 8 to 20 carbon atoms is linked to the sulfonic acid group through a $-COOR_1-$ group, e.g. oleic acid isothionate, $-CONHR_1$ group, e.g. lauric acid taurate, or a-OR_1 group, e.g. dodecyl glyceryl ether sulfonate, wherein the R_1 is a lower alkyl or a substituted lower alkyl group containing 2–3 carbon atoms.

Among the suitable water soluble organic sulfated detergents which it is preferred to use in compositions of the invention are alkyl sulfates, e.g. sodium lauryl or coconut fatty alcohol sulfate, and the alkyl ethyleneoxy ether sulfates, e.g. sodium lauryl tri-ethyleneoxy sulfate, said alkyl groups having about 8 to 20 carbon atoms and the ethyleneoxy sulfates containing about 1 to 15, preferably 2 to 10 moles of ethylene oxide. The alkyl groups may be derived from naturally occurring glycerides or synthetically from petroleum, e.g. cracked waxes or ethylene polymerization.

Other suitable organic sulfate detergents include sulfuric acid esters of polyhydric alcohols incompletely esterified with higher fatty acids, e.g. coconut oil monoglyceride monosulfate, and sulfated higher alkyl phenol-ethylene oxide condensates having an average of about 2 to 18 moles of ethylene oxide per phenol group and about 6 to 18 carbons in the alkyl group. The sulfated higher alkyl phenol-ethylene oxide condensates which it is preferred to employ have about 4 to 6 moles of ethylene oxide per phenol group and about 8 to 12 carbon atoms in the alkyl group.

As previously indicated, these sulfate and sulfonate detergents advantageously are supplied to the shearing zone in an acid liquid state and are present in the final product in the form of their alkali metal and alkaline earth metal salts. The preferred alkali metals are sodium and potassium and the preferred alkaline earth metals are calcium and magnesium. Optimum effects are obtained with the sodium salts in general.

The proportion of anionic organic detergent should be suitably selected so as to yield a product having the desired performance and physical characteristics. The detergent action functions as a foaming and cleansing agent as well as a plasticizer in the compositions of the invention. The proportion of said detergent will be minor compared to the inorganic salts, usually in the range of about 10 to 40% by weight, and preferably about 15 to 30% by weight, of the finished bar.

The water soluble inorganic builder salts are known in the art generally and may be any suitable alkali metal, alkaline earth metal, or heavy metal salt or combinations thereof. Ammonium or an ethanolammonium salt in a suitable amount may be added also, but generally, the sodium and potassium salts or similar salts effective to add hardness or strength to the bar are preferred. Examples are the water soluble sodium and potassium phosphates, silicates, carbonates, bicarbonates, borates, sulfates and chlorides. The builder salts contribute detersive efficiency when used in combination with sulfonic acid and/or sulfuric ester organic synthetic detergents. Particularly preferred builder salts are the alkaline builder salts such as polyphosphates, silicates, borates, etc. Inasmuch as the builder effects and processing characteristics of the individual salts vary to some extent, generally mixtures of inorganic builder salts are used in variable, predominating, proportions, e.g. about 45–85% by weight of the finished bar, usually in the range of about 50–75% preferably in proportion of about 50–65% by weight.

In the water soluble inorganic builder salt mixtures used in the detergent laundry bar compositions, it is preferred to have present a mixture of sodium tripolyphosphate and sodium or potassium bicarbonate. The combination or mixture of salts wherein the bicarbonate to tripolyphosphate ratio is selected from the range of about 1:1 to about 3:1, and which when admixed with the particular organic detergent and water in proportions such that this mixture of inorganic salts is at least about 40% of the total weight of the manufactured bar, results in desired processing effects and produce bars having superior physical characteristics. Preferably, the proportion of this particular inorganic salt mixture is within the range of about 45 to about 65% by weight of the manufactured bar.

Both Phase I and Phase II sodium tripolyphosphate and mixtures thereof may be successfully used in the compositions. The usual commercial tripolyphosphate consists mainly of the Phase II material. The commercial tripolyphosphate material is usually essentially tripolyphosphate, e.g. 87–95%, with small amounts, e.g. 4–13% of other phosphates, e.g. pyrophosphate and orthophosphate. Sodium tripolyphosphate in its hydrated form may be used also. While trisodium orthophosphate may be used in the amounts indicated, its presence often results in a bar which tends to "sweat" in hot, humid climates and whose surface tends to slough off more readily in such climates.

The sodium or potassium bicarbonate is an effective pH buffer and is preferred because the particular tripolyphosphate bicarbonate mixture results in plastic detergent compositions which yield superior extruded bars. This material is also desirable in that it is relatively inexpensive, has suitable solubility and does not cause "frosting" on the surface of the bar. The sodium bicarbonate may be incorporated directly as anhydrous bicarbonate or in the form of sesquicarbonate, a hydrate containing both bicarbonate and carbonate.

Other suitable builder salts which may be incorporated in the built synthetic detergent bar compositions include the water soluble sodium and potassium silicates, carbonates, borates, e.g. sodium tetraborate, chlorides and sulfates, e.g. magnesium sulfate. Generally, the total proportion of these additional builder salts will be within the range of from 0.5 to 24% by weight of the manufactured bar. The sodium and potassium silicates having an

$$Na_2O:SiO_2$$

ratio within the range of 1:1 to about 3.5:1 are particularly effective as corrosion inhibitors in proportions of about 1 to 8% by weight of the finished bar. The sodium sulfate content is advantageously kept low, e.g. below ⅓ the weight of the phosphate (on an anhydrous basis); preferably, to avoid frosting, the sodium sulfate content is below about 5% of the weight of the bar.

The final essential ingredient in the built synthetic detergent bar composition is water or similar material. This component is generally present in a proportion within the range of about 2 to 30% by weight of the bar. This material serves as a plasticizer in the solid compositions produced by this invention and also helps promote the neutralization reaction. It will be appreciated that the total amount of water is the sum of the amount added with the other ingredients in the feed (e.g. in the sulfonic acid, or with the salts, or separately) and the amount formed during the neutralization reaction. It is preferred that the water is from about 4% to 25% by weight.

In the previously described embodiment illustrated in the drawing the neutralizing agent was contained, in solid form, in the mixed powder fed to the intensive shearing zone, and the feed water was supplied in the liquid sulfonic acid portion of the feed. With certain detergent acids (such as long chain alkylbenzene sulfonic acids) the presence of the desired quantity of feed water causes partial gelation of the sulfonic acid-water blend, so that there are difficulties in metering the blend accurately to the intensive shearing apparatus. In the practice of our invention we have been able to avoid this difficulty by adding the feed water continuously in a separate stream; advantageously when the powder contains an ingredient (e.g. unhydrated sodium tripolyphosphate) which tends to form hydrated crystals on contact with water, this separate stream of feed water is introduced into the intensive shearing apparatus downstream of the point where the liquid detergent acid is fed, so as to allow intimate prior contact between the acid and the unhydrated material. Preferably this addition is made just slightly downstream of the point of contact of the acid and powder, so that the moving builder salts come into contact with the water less than a second, e.g. only a fraction of a second, after their contact with the acid. Our invention also makes it possible to use a liquid neutralizing agent and to employ alkali metal hydroxides as the neutralizing agents. Thus, an aqueous solution of sodium hydroxide (e.g. of about 20 to 75% concentration) may be used as the neutralizing agent, alone, or in conjunction with a solid neutralizing agent. It is advantageous to add the stream of aqueous alkali metal hydroxide at a stage just upstream of the point where the liquid detergent acid is introduced, particularly when the builder salt mixture contains material (such as solid carbonate and/or bicarbonate) which can act as a neutralizing agent; such upstream addition insures that the detergent acid will react preferentially with the alkali metal hydroxide instead of with the carbonate or bicarbonate, even though the moving builder salts come into contact with the added alkali less than a second, e.g. only a fraction of a second, before the mixture comes into contact with the acid. Highly alkaline silicates such as alkaline sodium silicate may also be used as neutralizing agents, advantageously as aqueous solutions added in the same manner as the sodium hydroxide.

Optionally, a fatty acid alkylolamide may be included in the composition of this invention. Such materials are generally condensation products of higher fatty acids having about 10 to 18, preferably 12, carbon atoms in the acyl group with alkylolamines selected from the group consisting of monoethanolamine, diethanolamine and isopropanolamine. Examples are lauric, capric, myristic and coconut monoethanolamide, diethanolamide and isopropanolamide, and the ethylene oxide adducts of such amides (advantageously with small amounts, e.g. 1 to 2 moles, of ethylene oxide per mole of amide). The alkylolamides which often act as suds builders may be present in proportions within the range of about 0 to 5%, preferably about 2%.

Various other ingredients may be included if desired. The compositions may beneficially include specific chelating agents capable of complexing iron such as the water soluble salts of ethylene diamine tetraacetic acid and the like. Other conventional auxiliary material which may be incorporated in the compositions are soil-suspending agents such as sodium carboxymethylcellulose, tarnish inhibitors such as melamine, fluorescent brightening agents, perfumes, coloring agents, germicides or bacteriostats, other detergent materials such as water-soluble non-ionic, amphoteric and cationic surfactants or water-soluble and insoluble soaps, skin-conditioning agents such as glycerine or lanoline, and the like. These materials may be admixed with the compositions in any suitable manner which does not substantially adversely affect the plasticity or basic properties of the compositions and are preferably present in minor amounts relative to the synthetic anionic detergents.

Other ingredients which may be employed are starches (such as tapioca flour, cornstarch, yucca starch or potato starch); the presence of the starch aids in the processing of the mixture, improves its workability and appears to promote its flow over the inner walls of the bar-forming die of the plodder. Other agents which have related effects, and which may be added together with or in place of the starch, are clays such as bentonite and kaolin, which like starch tend to absorb moisture and swell to form gels in hot aqueous media, zinc oxide and finely divided cellulose (Solka-Floc). These additives may be included in amounts up to about 20%; their effects are marked above about 5% (e.g. 7%); a preferred proportion is about 10–12% of starch. Starch also helps to give the bar a brighter color.

Another processing aid is a wax such as paraffin, which may be added as fine flakes mixed with the builder salts or dissolved or dispersed in heated detergent sulfonic acid. Related waxy materials such as petrolatum may also be used. The wax also helps to increase the life of the bar in ordinary use and to prevent "sweating" of the bar in certain climates, when used in small amounts (e.g. ¼ to 1½%); smaller and larger amounts may be used as desired.

Among the particular detergent acid materials which may be used in the process are the industrially available alkyl aryl sulfonic acids having an average molecular weight in the range of about 270 to 380, preferably from about 300 to 380, prepared by sulfonating the corresponding alkyl aryl hydrocarbon with a sulfonating agent such as sulfur trioxide, oleum or sulfuric acid to yield a liquid composition containing about 65–99% sulfonic acid, about 1–34% sulfuric acid or sulfur trioxide monohydrate, 0.5–2% sulfonation by products and about 0–10% water.

The neutralizing agent used in the process (advantageously alkali metal, preferably sodium or potassium, carbonate, oxide or hydroxide) may, as indicated previously, be employed in solid hydrated or unhydrated form, e.g. as dry finely divided particles pre-mixed with the inorganic builder salt, or they may be supplied as aqueous solutions or slurries. The carbonates and bicarbonates generally are used in solid forms. Advantageously there is present an amount of neutralizing agent at least equal to the amount stoichiometrically necessary for complete neutralization of the detergent acid and any acid constituents (such as sulfuric acid) accompanying the detergent acid. It is preferable to avoid generation of carbon dioxide during the nuetralization reaction; thus, when a carbonate is employed as a neutralizing agent, it is preferable to have present sufficient neutralizing agent to insure that the carbonate does not lose CO_2 but is instead converted to a bicarbonate or sesquicarbonate.

When a gas is released during neutralization, it has been noted that the substantially neutralized homogeneous paste discharged from the mixer has different characteristics. It is lighter in density and somewhat more porous, often tending to break the extended noodle-like strands into grains like those illustrated in FIG. 7.

When the neutralizing agent is a suitable carbonate or bicarbonate, the inorganic builder salt may comprise only the neutralizing salt itself, in which case the neutralizing salt is usually present in excess of the stoichiometric quantity needed to completely neutralize the liquid organic sulfo acid containing material. For best results, however, additional inorganic builder salts (e.g. polyphosphates) should also be present with the particulate neutralizing agent to enhance the performance characteristics of the built detergent product.

It is found that when excess unreacted soda ash is present in the final bar, the product is less advantageous in that it is not as smooth or as free from bloom, particularly in the embodiment, described below and illustrated in FIGS. 8*ff*, in which the bar is extruded directly from the intensive shearing zone.

The amount of water (including water of neutralization) present in the intensive shearing zone will generally be varied in accordance with the type and amount of anionic detergent formed therein. It should, however, be sufficient to impart some plasticity to the anionic detergent at the temperature of the shearing operation. Ordinarily, it is advantageous to supply some water in addition to the water of neutralization. The amount of water present is such that the composition is solid, plastic and ploddable without the need for an intermediate drying step. Water present in salt hydrates which are stable under the conditions prevailing in the shearing zone will generally not be available for plasticization.

The heat liberated by the neutralization reaction raises the temperature of the mixture of builder salt and anionic detergent and makes the mixture more plastic and workable in the intensive shearing zone. The temperature attained in this zone will naturally depend also on the amounts and heat capacities of the builder salt and other ingredients present, as well as the amount of heat generated by the shearing. It is often advantageous to abstract some of the heat from the mixture, as by circulating cooling fluid around the shearing zone. In the process in which the pasty mass of material is extruded from the intensive shearing zone in the form of noodles or other thin shapes, such cooling helps to reduce the tackiness of the surfaces of the extruded shapes and also minimizes the tendency for these shapes to coalesce when in contact with each other on the conveyor belt. However, our process may be operated over a wide range of temperatures of the material being extruded from the intensive shearing zone; for example, temperatures in the range of about 100° to 200° F.

As previously mentioned, the neutralization reaction takes place very rapidly in the zone of intense shearing. In a preferred form of the invention the material emerging from that zone is practically completely neutralized as evidenced by an indicator incorporation test. We have found that with such neutralization, the process can be carried out in a controlled manner more effectively to produce the desired uniform product; which can be plodded without additional mechanical working; also the surface stickiness often characteristic of incompletely neutralized products can be avoided or reduced. A satisfactory test for determination of the completion of the neutralization from the practical standpoint is by the incorporation of a suitable dye as an indicator which normally changes color at a pH of about 3 to 4 in water, such as Pylaklor Detergent Blue S–500 or Bromphenol blue. For example, the Pylaklor dye preferably dissolved in water is added at a suitable inlet in a concentration of about 0.01% of the finished formula weight (for example, with an amount of water corresponding to about 12% of the finished formula weight) with the inorganic salts and sulfonic acid. Where the mixture being discharged is essentially pink in color to the eye, then insufficient neutralization has occurred whereas a non-pinkish color, e.g. bluish, means that the neutralization is practically complete.

In the strand-forming process described above, the thickness of the material extruded from the intensive shearing zone is, as stated previously, advantageously less than about an inch. The cross-section of the extruded material may be substantially circular (as when the discharge plate has circular orifices) but the formation of other shapes, such as rectangular, triangular, dumb-bell shaped, star-shaped, ribbon-shaped, etc. by the use of suitably shaped orifices, is within the broad scope of this invention.

The plodding operation, to which the previously extruded strands, grains, or similar shapes are subjected, may be carried out in a conventional manner. Advantageously the material supplied to the plodder is still in heated condition, although its surface may be in a cooler harder state; this facilitates the screw compaction and extrusion operation in the plodder. As previously indicated, the plodder usually comprises a continuous screw or worm revolving in a closed cylinder. If desired, two stages of plodding may be used, the extruded product from a first plodder being fed, in extruded strand form, directly to the inlet of the second plodder and the outlet of the first plodder may advantageously be maintained at a subatmospheric pressure (e.g. a pressure of about ⅓ atmosphere); this procedure has been found to produce a more deeply colored product (when coloring material has been incorporated in the formulation), helps to eliminate any trapped gases and leads to a final product which is less tacky in heated condition. The cylinders surrounding the worm of the plodder may be heated or cooled as desired to insure maintenance of the material in the desired plastic condition. For that formation of a firm bar, the stock temperature of the material being extruded from the plodder is generally lower than the temperature at which the material is extruded from the intensive shearing zone; it is usually within the range of about 90–130° F., generally in the neighborhood of 95–105° F. The previously described cooling of the noodles or other thin shapes extruded from the intensive shearing zone, prior to their entrance into the plodder, thus facilitates the production of a firm bar. To give the surface of the bar a smoother finish it is often desirable to heat that portion of the material which is in contact with the bar-forming die or nozzle at the discharge end of the plodder, as by heating the walls of the nozzle, e.g. to a temperature about 10 to 20° F. higher than the temperature of the material in the plodder.

It is within the broad scope of this invention to subject the material, after its discharge from the intensive shearing device and before the plodding step, to an additional milling treatment if desired, for the purpose of cooling and/or for mixing in or dispersing certain special ingredients, such as paraffin wax or titanium dioxide.

In another aspect of the invention the operations of bar-forming and neutralization with intensive shearing are directly connected, as by fitting a bar-forming extrusion zone directly to the exit end of the intensive shearing device. For this purpose the rotor of the intensive shearing device may have an extension carrying an extrusion screw or worm (in certain cases, the extrusion zone may be cooled to reduce the temperature of the blend to a level facilitating the direct extrusion of a firm bar). This type of process constitutes one aspect of another preferred form of this invention. Here the flowable blend formed by the intensive shearing is extruded directly as a bar through an extrusion opening of relatively large size (large enough to form the bar), the flowable blend being maintained continuously in a heated flowable condition and continuously under shearing forces from the time of formation of the flowable blend until its passage through the extrusion opening. Advantageously, the residence time, from feeding to extrusion, is very short, e.g. well below 10 minutes and preferably less than 5 minutes; a 1 to 2 minute residence time has given excellent results. The blend preferably leaves the extrusion opening within one minute of its exit from the intensive shearing zone. The extruded bar may then be hardened (as by cooling to room temperature) and cut into individual bars and pressed. One advantage of this form of the invention is that it makes possible the formation of a high quality detergent laundry bar without the use of the very heavy and expensive conventional plodders. At the same time, the power required to produce the bars is greatly reduced. For example, the overall power may be decreased by about 50% or more as compared to that needed when the intensively mixed material is fed to a conventional plodder. One particularly suitable type of apparatus for use in carrying out this form of the invention is illustrated in FIGS. 8 to 20.

The apparatus includes a jacketed housing **71** within which there are mounted a pair of parallel rotatable shafts **72**, each extending horizontally the full length of the housing and each having mounted thereon, for rotation therewith, feed screw elements **73** and agitator elements or paddles **74**. The longitudinal cavity within the housing is made up of two intersecting circular cylindrical zones (as can be seen from the end view in FIG. 10) meeting at upper and lower ridges **76** and **77**, respectively, each such cylindrical zone being coaxial with the rotatable shaft situated in said zone, there being a small radial clearance between the inner walls of the cavity and the outer peripheries of the paddles and feed screw elements. There is an opening or hopper **78** at one end of the housing, above the feed scrw elements and a plurality of spaced injection ports **79**, **81**, communicating with the cavity.

The two shafts are adapted to be driven in the same direction by a drive motor and gear arrangement **84** situated at one end of the housing. The feed screw elements on the shafts are of conventional helical type, suitably intermeshing in well-known fashion as the shafts rotate to advance the material, supplied through the hopper **78**, in an axial direction towards the paddles.

The paddles are arranged in matching pairs, the design being such that a tip **86** (FIG. 10) of one paddle of each pair is always moving in wiping relationship to an edge or flank **87** of the other paddle of the pair during the continuous co-rotation of the shafts. In the construction shown, the paddles of any pair are identical with each other and mounted with their long axes LA (FIG. 11) at right angles, the edges **87** of each paddle being defined by equiradial symmetrical arcs whose centers are symmetrically situated on the prolongations of the short axis SA of the paddle. As will be seen from the sequence shown in FIGS. 10 to 13, during the co-rotation of the shafts about their rotational axes RA, one tip **86** of the left-hand paddle follows along an edge **87** of the right-hand paddle, two tips of the paddles then meet, after which a tip of the right-hand paddle follows along an edge of the left-hand paddle. Thus, in a full 360° rotation, each edge of each paddle will be wiped once by a tip of its matching paddle. During this full 360° rotation, the internal walls of the housing will be wiped twice by the tips of the paddles.

Certain paddles are designed to advance the material longitudinally of the shafts. In these paddles (hereinafter called "advancing paddles"), the profile of the rear face **91** (FIGS. 14 and 15) of the paddle **74** is offset by a slight angle α (about the axis of rotation) from the profile of its front face **92**. For example, for a paddle having its long axis 4⅞ inches long and its short axis 2 inches long, and having a thickness of 1 inch, the two faces may be offset by an angle of 12½°. The other paddle of the same pair has the profiles of its faces similarly offset by the identical angle, the design being such that the edge of each paddle will be wiped by the tip of its paired paddle, as previously described. Thus, in any cross-section through the pair of paddles, at right angles to the axis of rotation, the relationship of the cross-sectional profiles will be the same as that shown in FIGS. 10 to 13. To advance the material from the hopper end of the housing toward its opposite end, the profile at the rear face of the paddle (that is, the face nearest the hopper end) is preferably offset (from the profile at its front face) in the same direction as the direction of rotation of the paddles illustrated by the arrow in FIG. 14. It will be appreciated that while the tips are shown as being relatively sharp in the drawings, they may be relatively blunt, as indicated by the dotted lines on FIG. 14, the dimensions being adjusted so that the tips, though blunt, still are in close wiping relationship with the inner walls of the housing and with the edges of the matching paddle.

To continue the longitudinal advance of the material, in a more or less helical path, the long axes of each successive pair of paddles may be offset, by an acute angle, from the long axes of the pair previously engaged by the material being treated. FIG. 16 (in which the arrows indicate the direction of rotation of the shaft) illustrates various positions of the front faces of successive paddles, the paddle designated as I being nearer to the discharge end of the machine than the other paddles; the paddle II being next, then the paddle III and then the paddle IV which is furthest from the discharge end, there being a 45° angle between the long axes of successive paddles. This offsetting of the long axes of adjacent paddles also aids in the mixing action of the apparatus. As will be seen from FIG. 15, when the paddles are in the position designated as II, for example, their further movement acts to compress the material between the edges or flanks of the paddles and the walls of the housing, forcing the material into the paths of the movement of adjacent pairs of paddles.

The front and rear faces **92**, **91** of the paddles are advantageously flat and, when the paddles are mounted on the shafts and situated in planes perpendicular to said shafts, the faces of adjacent paddles are preferably close to each other; thus the clearance between the front face of one paddle and the rear face of the next paddle may be on the order of about 0.03 inch. The clearances between the tips of the paddles and the inner walls of the housing may be, for example, about 0.03–0.04 inch. The clearances between the tip of the paddles and the edges of the paired paddles which they wipe may be about the same, e.g about 0.03 inch.

At the discharge end of the apparatus, several arrangements may be employed for extruding the material. In one arrangement (illustrated in FIGS. 17 and 18), there is an adjustably mounted end wall **94** having a rearwardly projecting skirt **96** dimensioned to fit closely within the walls of the housing **71**, whose shape at this point is a symmetrical oval (formed by two spaced opposed vertical semicircles, of the same diameter and aligned with the corresponding inner walls of the main cavity in the housing, joined by tangent horizontal lines). The material leaving the last paddles **74** flows between the lower wall **97** of the housing and the bottom portion **98** of the end wall **94**. The skirt **96** prevents flow of material out of the sides and top of the discharge end. Smooth outward flow is aided by the presence of an inclined apron **99** extended downward from the lower wall **97**. In another extrusion arrangement (illustrated in FIGS. 19 and 20), there is a fixed end wall **101** having a rectangular bar-sized discharge opening **102** therein, but otherwise completely blocking the end of the housing, the discharge opening being eccentrically arranged with respect to the center line of the cavity in the housing and located nearer to the right side of the housing which corresponds to that side where the motion of the paddle tips has a generally upward, rather than downward, component. The end wall **101** has circular holes **103** for receiving the parallel shafts **72**. In one form which has been used with the paddle arrangement previously described, the plate **101** is about 1 inch thick and the discharge passageway is horizontal and rectangular, being about 2 inches wide and 1 inch high, the plate being spaced about an inch from the forward ends of the upper and lower ridges **76**, **77**, the shape of the cavity in the housing adjacent the plate **101** being a symmetrical oval as previously mentioned. There are a series of feed screw elements **104** identical with those at the inlet end of the machine, mounted on the shafts **72** to help force the material through the passageway **102**. Alternatively, discharge may take place from a side discharge tube S shown in dotted lines. The provision of the feed screw elements at the discharge end makes it possible to obtain a much higher discharge pressure.

In the overall process illustrated in FIG. 8, the powdered material is supplied continuously to the hopper **78** while the liquid ingredients are supplied to one or both of the ports **79**, **81**; the extrudate **105** is taken up on a continuously moving endless belt **106**, allowed to harden by cooling and aging, and then cut into individual bars at **107** and pressed in conventional manner at **108**.

A suitable heat transfer medium, such as cooling water, may be supplied to any desired portion of the jacket **109** of the housing **71**.

The preferred extrusion temperature in the process illustrated in FIG. 8 is preferably above 100° F. One suitable range is about 120–140° F.; the periphery of the extrusion opening may be heated to a temperature above (e.g. 10–20° F. above) that of the extrudate to promote the extrusion. It has been found, however, that much higher extrusion temperatures may be employed, yielding special effects. Thus, in runs involving continuous neutralization (an exothermic reaction which tends to heat the product considerably, as previously noted) there was produced an extrudate having a temperature above 140° F. (e.g. 186° F.) which extruded smoothly, as a bar, from the discharge opening, retaining the cross-section of that opening (in this case, a side discharge tube such as that shown at S, rectangular in cross-section). The extruded material at this relatively high temperature was found to be considerably tougher than similar extrudates at lower temperatures; it had sufficient strength so that during the continuous extrusion, the hot bar (about 2 inches wide and about 1 inch in height) leaving the tube supported its own weight over a span, measured horizontally, of over 4 feet, forming a catenary curve whose lowest point was about 2 feet below the level of the two ends of that span.

Typically the extrusion opening may have an area of at least about 2 square inches and a height (at least equivalent to the thickness of the individual bars) in the range of about ¾ to 3 inches, and a width of at least about 2 inches. The width of the extrusion opening may be that of the width of a single bar or may be a multiple of that width, in which case the extrudate may be cut lengthwise before or after it is fully cooled and hardened (e.g. by pulling or pushing it past one or more cutting elements, such as thin vertical wires which may be heated to facilitate the cutting).

It is also within the broad scope of this invention to carry out the processes described herein while at the same time dispersing air or other gas in the mass of material during the intensive shearing thereof to produce a built laundry detergent bar of substantially lower density. This feature is described and claimed in the application of Charles F. Fischer and A. Earl Austin entitled "Detergent Laundry Bars", filed on even date herewith, whose entire disclosure is incorporated herein by reference.

The following examples are additionally illustrative of the nature of the present invention, and it will be understood that the invention is not limited thereto.

Example I

An intensive shearing device (as illustrated in FIGS. 1 to 4 of the drawing) comprising a cylinder 6 inches in diameter having an intensive shearing zone 19½ inches long equipped with a multi-armed rotor turning at 104 r.p.m. is continuously fed with two streams of material. One stream consisting of the following composition is pumped into the device at a rate of 215 lbs./hr.:

	Percent by weight
Tridecylbenzene sulfonic acid (.99 AI) (obtained by sulfonation of a benzene alkylated with a polypropylene in conventional manner)	72.1
"Pylaklor" blue color (Detergent Blue S–500)	1.5
Water	26.4
	100.0

The second stream is a blend of inorganic builder salts in coarse particulate form (100% through a ten mesh screen having the following composition; this stream is fed to the hopper of the intensive shearing device at a rate of 340 lb./hr. using a Vibra Screw feeder:

	Percent by weight
Sodium carbonate (commercial grade anhydrous)	12
Sodium bicarbonate (commercial grade anhydrous)	64
Sodium tripolyphosphate (commercial grade anhydrous)	24
	100

The shearing device includes a cylindrical rotor of 2¾ inch diameter having eleven arms securely welded thereto; each arm is a portion of a helix extending over an angle of about 100° or more, and reaches to within about ⅛ inch of the inner wall of the 6 inch diameter cylinder within which the rotor operates. The thickness of each rotor is about ½ inch. Projecting from the inner wall of the cylinder are a series of spaced anvils each extending radially inwards about 1½ inch and having cross-sections of about ¾ inch x ¾ inch. The paths of the arms come into close proximity (about 1/32–1/16 inch clearance) to the anvils. Within the device are two spaced apertured plates, spaced equally ⅓ and ⅔ of the length of the shearing zone. Upstream of the first apertures plate (which is ¼ inch thick and has 34 spaced ½ inch diameter circular axial holes) there are 3 arms and 3 anvils. Downstream of the first plate and upstream of the second apertured plate (which is ⅛ inch thick and has 62 spaced ⅜ inch diameter circular axial holes) there is another set of pairs of arm and anvils, and there is a similar set between the second plate and the discharge plate (which plate is 3/32 inch thick and has several hundred 3/16 inch diameter circular holes), through which the material is extruded. The clearances between the various plates and the corresponding rotating arms are on the order of 1/16 inch.

The two streams are contacted and mixed upstream of the first plate of the device and the resulting sheared neutralized heated mixture is extruded through the discharge plate in the form of needles having a surface area-to-volume ratio of about 23 in.$^{-1}$.

The discharged material is blue in color, indicating substantially complete neutralization of the acid form organic detergent, and is a homogeneous plastic mass. The noodles, in a layer piled about 1 inch high, are allowed to cool in air for about 20–25 minutes; their average temperature thus drops to about 100–110° F. They are then directly extruded using a plodder having a four inch cylindrical barrel. The plodder barrel is cooled with water and the walls of its nozzle are heated to about 120° F. The rectangular cross-section of the extruded bar is 2½ inches by one inch.

The extruded bar at a temperature of about 100° F. is cut into 4 inch lengths and stamped into a form having a design impressed therein in a suitable press. This stamped bar has a homogeneous appearance and a relatively smooth surface. The resultant laundry detergent bar contains about 28% sodium tridecyl benzene sulfonate, about 9% water (including water of hydration), about 16% sodium tripolyphosphate (on an anhydrous basis) and the balance mainly sodium bicarbonate (over 40% on anhydrous basis) together with minor amounts of sodium sulfate, color and sulfonation by-products.

Examples II and III

Example I is repeated with the exception that the water is not admixed with the alkyl benzene sulfonic acid prior to addition, but is added as a separate stream. Thus, three streams, e.g. the solid inorganic salt stream, the liquid sulfonic acid stream and the water stream, are continuously injected into the intensive shearing device. Rates of addition are: builder salt mixture—340 lb./hr.; tridecylbenzene sulfonic acid stream comprising 96% organic sulfonic acid, 1% sulfonation by-products, 2% sulfur trioxide monohydrate and 1% water—146 lb./hr.; water 41 lb./hr. In Example II the water stream is added just downstream of the first apertured plate through a port (such as port *9a* in FIG. 2), and in Example III the water stream is added upstream of the first plate and in the same vertical plate (transverse to the axis of the rotor) as the tridecylbenzene sulfonic acid through a port 90° subsequent to the point of addition of the acid (such as port *9b* in FIG. 2).

In Example II, the temperature of the substantially completely neutralized blue, homogeneous plastic material discharged from the intensive shearing device is about 136° F. This material is cooled to an average temperature of about 100° F. and is extruded in the same bar form as in Example I.

In Example III, the temperature of the substantially completely neutralized, blue, homogeneous plastic material discharged from the intensive shearing device is about the same as in Example II. After the material is cooled to a temperature of about 100° F., the material is extruded using the same plodder and operating conditions used in Example I. Again, the finished bars have satisfactory physical properties.

Example IV

The apparatus of Example I is continuously fed with three streams of material, at a rate of 600 pounds/hr. 27.2% of the feed is an acid stream of the following composition:

	Percent by weight
Tridecylbenzene sulfonic acid	86.9
Sulfur trioxide monohydrate	9.0
Sulfonation by-products	1.4
Water	2.7
	100.0

The second stream is a blend of inorganic builder salts in particulate form having the following composition and represents 59.6% of the total feed:

	Percent by weight
Sodium tripolyphosphate (as in Ex. I)	33.6
Sodium bicarbonate (as in Ex. I)	47.8
Tapioca starch	18.4
Perfume	0.2
	100.0

The third stream is an aqueous sodium hydroxide solution, containing 73% of 50° Baumé caustic solution together with the coloring material, and represents 13.2% of the total feed. The stream of sodium hydroxide solution is fed to the shearing zone in the same vertical transverse plane as the sulfonic acid containing mixture, through a port slightly upstream of the port through which the acid is added.

The temperature of the material discharged from the intensive shearing device is about 195° F. All the zones are cooled with water. The plastic material is blue in color indicating substantially complete neutralization of the acid form detergent and homogeneity of the paste. The noodles of the plastic paste are cooled and plodded as in Example I.

The extruded plodder bar is cut into 4 inch lengths and stamped in a press. The stamped bar has a smooth surface and a substantially homogeneous appearance. Composition of the resultant laundry bar is approximately:

	Percent by weight
Sodium tridecylbenzene sulfonate	25.0
Sodium sulfate (anhydrous basis)	3.5
Sodium tripolyphosphate (anhydrous basis)	20.0
Starch	11.0
Sodium bicarbonate (anhydrous basis)	28.0
Perfume, color, sulfonation by-products	1.0
Water	11.5
	100.0

Example V

Example IV is repeated with th efollowing exceptions: The total feed rate is 2093 pounds per hour. The rotor speed is 343 r.p.m. The three streams have the following compositions:

	Percent
Powder blend, 75.3% of the total:	
Sodium sesquicarbonate (a hydrate)	56.9
Sodium tripolyphosphate (commercial grade anhydrous)	25.6
Tapioca starch	14.6
Paraffin flakes	1.7
TiO$_2$ (anatase).	
Perfume.	
Caustic solution, 5.2% of total:	
NaOH	48.9
Water	51.1
Plus color.	
Detergent acid, 19.5% of total:	
Tridecyl benzene sulfonic acid	96.0
Sulfuric acid	2.0
Moisture	1.0
Sulfonation by-products	1.0

The temperature of the material discharged from the shearing device, which is ice cooled, is 158° F. The residence time in the shearing device is less than ½ minute, calculated on the basis of a volume of about 290 cubic inches in the device and a density of the material of about 1.5.

Example VI

Example V is repeated with the following exceptions: The total feed rate is 1380 pounds per hour. The powder blend, 71.2% of the total, contains 54.4% of sodium sesquicarbonate, 28.1% of sodium tripolyphosphate, 15.4% of starch, 1.8% of paraffin, together with TiO_2 and perfume. The caustic solution is 9.2% of the total and has an NaOH concentration of 27.6%. The detergent acid is 19.6% of the total. The extruded noodles have a temperature of 158–162° F. and are fed, after 3–5 minutes aging, to the plodder. Bars of excellent appearance are produced, containing 20% sodium tridecylbenzenesulfonate, 38.8% sodium sesquicarbonate, 20% sodium tripolyphosphate, 11% starch, 0.6% sodium sulfate, 1.25% paraffin, 14.4% total water (of which about 6.4% represents water which is part of the sesquicarbonate) as well as minor amounts of TiO_2, perfume, color and sulfonation by-products.

Example VII

Example IV is repeated except that the two intermediate orifice plates are omitted, the total feed is about 560 pounds per hour, the detergent acid used is that of Example V, the sodium hydroxide solution has a concentration of 24.2%, and the powder blend contains 50.3% sodium bicarbonate, 32% sodium tripolyphosphate, 17.6% tapioca starch and perfume. The detergent acid stream is 24.5% of the feed, the sodium hydroxide stream is 13% of the feed and the powder blend stream is 62.5% of the feed.

Examples of a process in which the flowable blend is maintained continuously in a heated flowable condition and continuously under shearing forces from the time of formulation until its passage through the extrusion opening are given below. In these examples the material was subjected to intensive shearing forces in one portion of the apparatus and to lesser, but significant, shearing forces during its subsequent flow through the discharge portions of the apparatus (said shearing forces accompanying the flow of the pasty material under pressure), and there was no stage during its travel through the apparatus that the material was in a quiescent state in which it had an optunity to solidify. Incidentally, in these examples, the pentasodium tripolyphosphate in the heated material emerging from the discharge opening was largely still unhydrated, and the hydration reaction, occurring during the aging period while the material was being allowed to cool at room temperature, aided in and accelerated the hardening of the bar.

Example VIII

In this example, the apparatus used was that of FIGS. 8 to 18, having an internal cavity about 3 feet long, the internal diameter of each of the intersecting circles being about 5 inches, the feed screw flights (four turns on each shaft) extending about 8 inches on each shaft, the long axes of the paddle faces being almost 5 inches long, and the short axes being about 2 inches long, the paddles being 1 inch thick, the offset between faces of the advancing paddles being 12½°. The sequence of paddles (starting from the feed end and using the designation A for the advancing paddles and the designation N for the non-advancing paddles) was: 5A (meaning five successive pairs of advancing paddles), 1N (meaning one pair of non-advancing paddles), 3A, 1N, 4A, 1N, 3A, 1N, 5A, the long axis of each paddle being offset 45° (as previously described) from the long axes of the preceding and succeeding paddles. The apparatus was continuously fed with three streams of material. One stream, having the following composition, was fed to the hopper at the rate of 776 lbs./hr.:

74 parts (12¼%) of sodium carbonate (commercial grade anhydrous);

215 parts (33.8%) of sodium sesquicarbonate (a hydrate);

186 parts (31%) of sodium tripolyphosphate (commercial grade anhydrous);

103 parts (17%) of tapioca starch;

18⅝ parts (3.1%) of sodium toluene sulfonate; plus small amounts of TiO_2 (anatase) and perfume. The foregoing composition was made by dry-blending the ingredients, in finely divided form, followed by pulverizing.

Another stream, containing detergent acid, was pumped into the apparatus through port **79** (leading into the lower portion of the section containing the feed screw flights) at the rate of 294 lb./hr.; this stream had the following composition:

Tridecyl benzene sulfonic acid 96% (branch chain type, from propylene polymers);

	Percent
Sulfuric acid	2
Moisture	1
Sulfonation by-products and impurities	1

The third stream, containing cold water and a blue indicator dye, was pumped into the apparatus through port **81** (leading into the lower portion of the section containing the paddles, about 2 feet from the discharge end of the apparatus) at the rate of 135 lb./hr.; this stream had the following composition:

	Parts
Water	50
Blue color of Example 1	0.05

A slab of plastic pasty material 9½ inches wide and 1½ inches thick was discharged, and taken up, continuously from the apparatus. The average residence time of the material in the apparatus was less than 2 minutes (the free volume of the apparatus, per se, was about 0.4 cu. ft.). The process was run for about ¼ hour continuously to normalize it. The uniformly blended blue slab material thereafter discharged from the apparatus, at a temperature of 135–140° F., was allowed to cool and harden in air and was then cut transversely to a rectangular shpe (bout 4 inches by 2½ inches) to form individual bars which were then pressed (as in Example 1) within ½ to 3 hours after extrusion, using a pressure of about 200 p.s.i.g. The water content of the bars (including water of hydration) was about 17% and the specific gravity of the slab material was 1.57.

In the foregoing example, the speed of the shafts was such that there were about 12,000 paddle cuts per minute; a "paddle cut" occurs between the paddles of successive pairs each time the paddle of one pair, on one shaft, passes in close shearing relationship with a paddle of the other pair, on the other shaft; for example, in FIG. 16 paddle I on the left hand shaft and paddle II on the right hand shaft are just beginning to make a "cut." With all the pairs of paddles offset as shown in FIG. 16 of the drawing, there will be two "cuts" per full rotation; for example, with 26 pairs of paddles the number of paddle cuts per minute will be equal to the r.p.m. of the shaft multiplied by 52.

Example IX

Example VIII was repeated except that the stream of solids, supplied at the rate of 955 lb./hr., had the following composition:

	Percent
Sodium sesquicarbonate (a hydrate)	52.1
Sodium tripolyphosphate (commercial grade anhydrous)	29.5
Tapioca starch	16.2
Paraffin	1.8

plus

TiO_2 and perfume.

The sulfonic acid stream was supplied to port **81** at the rate of 276 lbs./hr. Instead of a simple water-color mixture, there was supplied (to port **79**) 179 lbs./hr. of a caustic-water-color stream containing 59% water and 40.9% of a 48.9% solution of NaOH in water. The moisture content of the product was about 17% (including water of hydration).

Example X

In this example the apparatus used was similar to that described in Example VIII except that the sequence of paddles from the feed end was: 6A, 1N, 3A, 1N, 3A, 1N, 3A, 1N, 9A (the long axis of each paddle being offset, as in Example VIII, 45° from the long axes of the preceding and succeeding paddles, except that for the last five paddles, adjacent the discharge end, this angle of offset was 90°), and the discharge was effected through a horizontal rectangular side discharge tube about 2 inches wide, about 1 inch high and about 6 inches long, whose axis was at right angles to the axes of the shafts and which led from a point on the lower portion of the housing adjacent the last few paddles, being situated on that side of the housing where the paddles had a downward movement. (The end wall of the apparatus in this case was constructed to block completely any discharge of material through said end wall; no discharge screw elements **104** were present.)

A stream of dry-blended, screened (but not pulverized) solid ingredients, of the following composition, was fed to the hopper at the rate of 624 lbs./hr.:

	Lbs.
Sodium carbonate	71¼
Sodium tripolyphosphate	187
Sodium bicarbonate	262
Tapioca starch	103
Perfume, minor amount.	

All the salts were anhydrous.

The same detergent acid stream as used in Example VIII was fed at the same point as in that example, at a rate of 415 lbs./hr.

A stream of cold water and a very small amount of blue dye was fed to the port **81** at the rate of 70⅔ lbs./hr.

No cooling water was employed in the jacket of the apparatus.

The bar emerging continuously from the discharge tube had a temperature of about 186° F. It extruded smoothly, retaining the cross-section of the extrusion opening without significant slump, and was not sticky. After cooling it was cut transversely to form individual bars.

Apparatus like that of Example X (except that the paddle sequence was: 3A, 1N, 3A, 1N, 1A, 1N, after which 1A, 1N sequence was repeated 11 times more) was also used to produce continuously extruded bars of good appearance from the following formulation:

Composition of stream of solid ingredients, all ingredients being anhydrous:

	Percent
Soda ash	16.9
Sodium bicarbonate	40.7
Trisodium phosphate	5.8
Sodium tripolyphosphate	28.6
Sodium sulfate	3.5
Carboxymethylcellulose	.6
Sodium chloride	.3
Lauric-myristic isopropanolamide	3.1
Q.s. perfume.	

Composition of detergent acid stream: same as in Example VIII. Ratio of rates of feed of streams of solid: acid: water=11:4:1.

Similar results were obtained when, instead of a discharge tube of substantially uniform cross-section along its length, there was employed a discharge tube of the tapered, converging type, whose cross-section at its inlet end was larger than that of the extrusion opening.

This invention finds its greatest utility when the neutralization and intensive shearing are carried out together as previously described. In another aspect of the invention, however, preneutralized anionic synthetic detergent and the builder salt are supplied continuously to the continuous intensive shearing device and there intimately blended and extruded, being subjected thereafter to the same process as previously described herein. In this embodiment, the preneutralization of the anionic detergent acid may be effected by blending it with the neutralization agent, and the resulting detergent salt may be dried, as by spray drying, to produce fine particles which are added to the continuous intensive shearing device with the builder salt. In this aspect of the invention, as in the case where the neutralization and intensive shearing are carried out together, the builder salts may be of the common non-plastic type, although it is not outside the broad scope of the invention to employ plastic builder salts.

Examples of the procedure using a previously neutralized material are given below:

Example XI

41.2 parts of spray dried detergent containing 76.2% sodium tridecyl benzene sulfonate, 9.5% sodium silicate, 10.8% sodium sulfate, and moisture was mixed with 22.4 parts of sodium tripolyphosphate, 12.3 parts of tapioca starch and 24 parts of sodium bicarbonate. A stream of this mixture was fed with a stream of water equal to 10.7% of the total feed continuously into the hopper of an intensive shearing device identical with that used in Example I, except that a forming die having a large opening was fitted to the discharge end of the device so that the extruded strands coalesced and were forced from the die in the form of a bar. The temperature of the extrudate was 130° F., as a result of the heat of hydration and the heat added by the intensive shearing; no cooling medium was used.

Example XII

In this example, the apparatus used was that of FIGS. 8, 10–16, 19 and 20, having an internal cavity about 3 feet long, the internal diameter of each of the intersecting circles being about 5 inches, the feed screw flights (two turns) extending about 4 inches on each shaft, the discharge screw flights (two turns) also extending about 4 inches on each shaft, the long axes of the paddle faces being almost 5 inches long, and the short axes being 2 inches long, the paddles being about 1 inch thick, the offset between long axes of successive paddles being 45°, the pattern of paddles being: eight pairs of advancing paddles at the feed end, followed by two pairs of non-advancing paddles and two pairs of advancing paddles, this two-and-two arrangement being repeated three times more, then one pair of non-advancing paddles and the 4 inches of discharge screw flights (104).

The discharge was effected through the off-center 2″ x 1″ rectangular discharge passageway previously described, spaced about 5 inches from the nearest pair of paddles. The speed of rotation of the co-rotating shafts was about 150 r.p.m. The rates of feed were 605 pounds per hour of the dry mixture and 75 pounds per hour of cold water, which was injected continuously into the lower portion of the cavity at a point about 9 inches downstream of the feed screw section. After a normalization period of about 30 minutes, a smooth bar was extruded continuously. The extruded material which, as extruded, had a temperature of about 130° F., was permitted to cool, in a quiescent state, to room temperature and was then cut into individual bars and pressed at a pressure of about 200 p.s.i. The specific gravity of the bars was 1.5–1.6. The dry mixture used in this example was a finely divided blend of 41% sodium tridecyl benzenesulfonate (branched chain type, from sulfonation of a mixture of reaction products of benzene and propylene polymers); 12% of tapioca flour, 24% sodium bicarbonate, 22½% pentasodium tripolyphosphate (commercial grade anhydrous) plus perfume and minor impurities, which had been screened through a standard 40-mesh screen to remove lumps.

The material emerging from the discharge opening retained the shape of the cross-section of that opening without significant slump, the thickness, width and shape of the extruded bar being substantially the same as the height, width and shape of the discharge opening.

It will be understood that it is of course within the broad scope of this invention to fit the apparatus illustrated in FIGS. 9 to 20 with a multi-apertured extrusion plate so that there are produced noodle-like strands which may be further processed in the manner previously described.

This application is a continuation-in-part of our application Ser. No. 469,144, filed July 2, 1965, now abandoned.

Although the present invention has been described with reference to particular embodiments and examples, it will be apparent to those skilled in the art that variations and modifications can be substituted therefor without departing from the principles and true spirit of the invention.

Having thus described our invention, what we claim is:

1. Process for the manufacture of coherent solid built detergent laundry bars which comprises continuously feeding an acid form of a synthetic anionic detergent, solid water-soluble hydratable inorganic builder salt, and an alkaline neutralizing agent for said acid form to a zone in which the feed materials are continuously intensively sheared together and continuously forwarded through said zone, continuously discharging an intimate plastic blend of neutralized synthetic anionic detergent and solid builder salt from said zone, and continuously extruding said plastic blend into the form of a bar, the residence time from feeding to extrusion being less than 10 minutes whereby the extruded blend contains hydratable builder salt and water other than water of hydration so that hydration, contributing to the hardening of the extrudate, occurs in the blend after the extrusion, the proportions of the ingredients being such that the bar contains about 10–40% detergent, an amount of solid builder salt in excess of the amount of detergent and up to about 85% and about 4 to 25% water, said neutralizing agent being selected from the group consisting of sodium and potassium carbonates, bicarbonates, oxides and hydroxides.

2. Process for the manufacture of coherent solid built detergent laundry bars which comprises continuously feeding an acid form of a synthetic anionic detergent, solid water-soluble hydratable inorganic builder salt, and an alkaline neutralizing agent for said acid form to a zone in which the feed materials are continuously intensively sheared together and continuously forwarded through said zone, continuously discharging an intimate plastic blend of neutralized synthetic anionic detergent and solid builder salt from said zone, and continuously plodding said plastic blend into the form of a bar, and including the steps of continuously extruding the blend from said zone in the form of thin shapes, hardening the surfaces of said shapes, compacting said hardened shapes and then extruding the material into the form of a bar, the proportions of the ingredients being such that the bar contains about 10–40% detergent, an amount of solid builder salt in excess of the amount of detergent and up to about 85%, and about 4 to 25% water, said neutralizing agent being selected from the group consisting sodium and potassium carbonates, bicarbonates, oxides and hydroxides.

3. Process as set forth in claim 2 in which the temperature of the mixture in said zone is raised by the heat of neutralization and in which said shapes, having a thickness of up to about ¼ inch, are extruded from said zone in heated plastic condition, said surfaces being hardened by cooling said shapes prior to compacting the material.

4. Process as set forth in claim 2 in which the residence time of the material in said zone in less than two minutes and the energy of shearing in said zone is at least 1/20 brake horsepower per pound.

5. Process as set forth in claim 4 in which said acid form of the anionic detergent is a sulfonic acid having an aliphatic chain of 8 to 20 carbon atoms.

6. Process as set forth in claim 5 in which said acid form contains a minor proportion of sulfuric acid.

7. Process as set forth in claim 5 in which the builder salt in said bar is a mixture of sodium tripolyphosphate and sodium bicarbonate.

8. Process as set forth in claim 5 in which the proportions of the ingredients are such that the bar contains about 45 to 65% of a mixture of sodium tripolyphosphate and sodium bicarbonate or sodium sesquicarbonate, and about 4 to 25% water, and in which the neutralization reaction is practically complete in said zone.

9. Process as set forth in claim 2 in which the feed to the intensive mixing zone contains starch, in amount sufficient to give a proportion in the range of about 5 to 20% in the finished bar.

10. Process as set forth in claim 2 in which the feed to the intensive mixing zone contains paraffin wax, in amount sufficient to give a proportion up to about 1½% in the finished bar.

11. Process as set forth in claim 8 in which the residenec time in the intensive shearing zone is less than two minutes, during which the temperature of the mixture therein is raised by the heat of neutralization, the process including the steps of continuously extruding the mixture in heated condition from said zone in the form of thin elongated strands of thickness up to about ¼ inch, hardening the surfaces of said strands by cooling said strands while maintaining them in essentially discrete form and compacting the cooled strands and then extruding the material in the form of a bar.

12. Process as set forth in claim 11 in which the strands are extruded from said zone at a temperature in the range of up to about 200° F. and extruded in bar form at a low temperature, in the range of about 90 to 130° F.

13. Process for the production of a solid built detergent bar which comprises continuously feeding at substantially a constant rate a stream of an alkylsulfonic acid having 8 to 20 carbon atoms in the alkyl group and a stream of said builder salt which is a mixture of sodium tripolyphosphate and sodium carbonate or bicarbonate at one end of an elongated zone together with a neutralizing agent for said acid and discharging at the opposite end of said elongated zone a practically completely neutralized pasty mass which is a blend of the sodium salt of said alkyl sulfonic acid and a water soluble solid builder salt which is present in said excess, intensively shearing together the materials fed to said zone by passing them between two relatively moving shearing surfaces in said zone, at least one of said surfaces being a moving rotating inclined surface which engages said mixture and urges said mixture toward the discharge end of said zone, said inclined surface being inclined with respect to the longitudinal direction of the flow of the mixture in said zone, the distance between said relatively moving shearing surfaces being less than 0.2 inch and the speed of their relative movement being at least one foot per second, said moving surface rotating at a speed of at least 50 r.p.m., and continuously shaping the mixture discharged from said zone into the form of a bar, the proportions of the ingredients being such that the mixture discharged from said zone contains about 45 to 65% of a mixture of sodium tripolyphosphate and sodium bicarbonate or sodium sesquicarbonate, and about 4 to 25% water, the residence time of the material in said zone being less than two minutes and the energy of shearing in said zone being at least 1/20 brake horsepower per pound, the temperature of the material in said zone being raised by the heat of neutralization reaction, the amount, character and strength of the neutralizing agent being sufficient to cause preferential reaction of said acid with said neutralizing agent without substantial liberation of carbon dioxide, said process including the steps of extruding the material from said zone in plastic heated condition, at a temperature of up to 200° F., in the form of strands having a thickness of up to about ¼ inch and hardening the surfaces of said strands by cooling, while maintaining said extruded strands in substantially discrete form, prior to the shaping of the material into the form of a bar, said bar-shaping being effected by compacting and extruding the material at a lower temperature than the temperature at which it is discharged from said zone, said lower temperature being in the range of

about 90 to 130° F., said neutralizing agent being selected from the group consisting of sodium carbonate, bicarbonate, oxide and hydroxide.

14. Process for the manufacture of coherent solid built detergent laundry bars which comprises continuously feeding finely divided solid water-soluble hydratable inorganic builder salt to a zone in which there is formed a mixture of said salt, a synthetic anionic detergent and water, in amount sufficient to plasticize said detergent and in which the ingredients of said mixture are continuously intensively sheared together to form a heated flowable blend and continuously forwarded through said zone, extruding said heated flowable blend through an extrusion opening of such size that said blend is extruded continuously from said extrusion opening as a mass whose cross-section has a thickness of at least about ¾ inch and an area of at least about 2 square inches, said flowable blend being maintained continuously in a flowable condition and continuously under shearing forces from the time of the formation of said blend until its passage through said extrusion opening, subdividing the extrudate into detergent laundry bars, said blend leaving said extrusion opening within about one minute of leaving the intensive shearing zone, the residence time from feeding to extrusion being so short that the extruded mass contains hydratable builder salt and water other than water of hydration, and hydration of the hydratable salt occurs after extrusion thereby contributing to the hardening of the extrudate, the proportions of the ingredients being such that the bar contains about 10–40% detergent, an amount of solid builder salt in excess of the amount of detergent and up to about 85% and about 4 to 25% water.

15. Process as set forth in claim **14** in which said hydratable salt is pentasodium tripolyphosphate.

16. Process for the manufacture of coherent solid built detergent laundry bars which comprises continuously feeding finely divided solid water-soluble hydratable inorganic builder salt to a zone in which there is formed a mixture of said salt, a synethetic anionic detergent and water, in amount sufficient to plasticize said detergent, and in which the ingredients of said mixture are continuously intensively sheared together to form a heated flowable blend and continuously forwarded through said zone, extruding said heated flowable blend through an extrusion opening of such size that said blend is extruded continuously from said extrusion opening as a mass whose cross-section has a thickness of at least about ¾ inch and an area of at least about 2 square inches, said flowable blend being maintained continuously in a flowable condition and continuously under shearing forces from the time of the formation of said blend until its passage through said extrusion opening, subdividing the extrudate into detergent laundry bars, the residence time from feeding to extrusion being less than 10 minutes and so short that the extruded mass contains hydratable builder salt and water other than water of hydration, and hydration of the hydratable salt occurs after extrusion thereby contributing to the hardening of the extrudate, the proportions of the ingredients being such that the bar contains about 10–40% detergent, an amount of solid builder salt in excess of the amount of detergent and up to about 85% and about 4 to 25% water.

17. Process as in claim **16** in which said synthetic anionic detergent is formed in said zone by reaction of a basic neutralizing agent with the corresponding preformed detergent acid in the presence of said builder salt, said neutralizing agent being selected from the group consisting of sodium and potassium carbonates, bicarbonates, oxides and hydroxides.

18. Process as set forth in claim **17** in which said detergent acid is a higher alkyl benzene sulfonic acid and said finely divided builder salt comprises sodium carbonate, at least a portion of said sodium carbonate acting as a neutralizing agent by reacting with said acid.

19. Process as set forth in claim **17** in which said detergent acid is a higher alkyl benzene sulfonic acid and said neutralizing agent comprises sodium hydroxide, said sodium hydroxide being supplied in aqeous solution to said zone.

20. Process as set forth in claim **17** in which solid preformed synthetic anionic detergent is preblended with said salt before feeding said solid salt to said zone.

21. Process as in claim **18** in which there is fed to said zone a continuous stream of a mixture of the sodium carbonate and anhydrous pentasodium tripolyphosphate and a separate continuous stream of the alkyl benzenesulfonic acid having 10 to 14 carbon atoms in the alkyl, said neutralizing reaction being exothermic thereby raising the temperature of the mixture in said zone and increasing its plasticity, the residence time from feeding to extrusion being less than 10 minutes whereby the extruded blend contains hydratable pentasodium tripolyphosphate and water other than water of hydration so that hydration, contributing to the hardening of the extrudate, occurs in the blend after the extrusion.

22. Process as in claim **21** in which the temperature of the blend being extruded is about 120–186° F.

23. Process as in claim **22** in which the temperature of the blend being extruded is above 140° F., said residence time is less than 5 minutes, and the proportion of the builder salts in the bar is about 45 to 85%.

24. Process as in claim **23** in which the bar consists of essentially of about 50 to 75% of builder salt, about 10 to 40% of detergent, about 10 to 20% of starch, and about 4 to 25% of water.

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