DETERGENT COMPOSITIONS CONTAINING HYDRATED ALKALI METAL TRIPOLYPHOSPHATES

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This application is a continuation-in-part of my co-pending application Ser. No. 200,325, filed June 6, 1962, and now abandoned.

This invention relates to novel methods for manufacturing detergent compositions that contain hydrated alkali metal tripolyphosphates. More specifically, this invention relates to novel processes in which low bulk density detergent compositions containing at least one hydrated alkali metal tripolyphosphate can be manufactured without being spray-dried.

Heretofore, it was believed necessary that when a detergent manufacturer wanted to manufacture a detergent composition having a relatively low bulk density (i.e., less than about 0.8), he had to utilize either very light density raw materials or the process operation known as spray-drying in at least one stage of his overall detergent manufacturing process. The spray-drying operation is, however, a relatively expensive one, requiring, first of all, a considerable investment of capital in the spray-drying equipment (including, for example, such items as high pressure pumps, a very large spraying "tower," and special facilities for heating, and controlling the flow of air for the "tower"). In addition, the actual cost of the heat necessary for the spray-drying operations (to evaporate water from detergent slurries) is high, as compared to the total cost of the raw materials in the final, relatively low bulk density detergent product. As a result, the high cost of spray-drying, many of the smaller detergent manufacturers have not been able to afford to spray-dry their detergent products, and thus have been placed at a competitive disadvantage, because many consumers of detergent products prefer to use the lighter (lower bulk density) products.

The polyphosphate that is presently preferred for use in most detergent compositions is a tripolyphosphate; paratetrapolyphosphate; tripolyphosphate; however, have a decided shortcoming which can presently be overcome (in conventional detergent manufacturing practice) as most only partially, and to that extent only by exercising very stringent precautions during the conventional detergent processing steps. This shortcoming is the result of the tripolyphosphate's susceptibility to hydrolytic degradation. Thus, during the time a slurry is being formulated, and ultimately spray-dried, a significant proportion of the tripolyphosphate is generally hydrolyzed to orthophosphates and pyrophosphates which are nearly as effective (as sequesterants) in "building" detergent products as is tripolyphosphate and generally, therefore, are not nearly as desirable as tripolyphosphate in the final detergent products.

In addition, it is ordinarily preferred that before a detergent slurry is spray-dried, generally at least most of the water or detergent slurry contains at least 80 percent of the concentrate. However, when a slurry containing hydrated tripolyphosphate (derived by simply hydrating anhydrous sodium tripolyphosphate) is spray-dried, a substantial proportion of the tripolyphosphate hydrate degrades (presumably because of the high temperatures the slurry must be subjected to in order to be effectively spray-dried) to yield acidic decomposition products, which also are not nearly as desirable in the final detergent products as is the tripolyphosphate hydrate.

Consequently, it is a primary object of the present invention to provide processes whereby detergent compositions that contain hydrated alkali metal tripolyphosphates and have relatively low bulk densities can be manufactured without the necessity of spray-drying.

It is another object of this invention to provide processes whereby detergent compositions that have relatively low bulk densities and which contain hydrated alkali metal tripolyphosphates, particularly sodium tripolyphosphate hexahydrate, can be manufactured without exposing the hydrated nials to excessively high degrading temperatures.

It is still another object of the present invention to provide processes whereby detergent compositions having widely varying physical properties (including those having widely varying bulk density, particulated solids, and shaped solids that contain a cellular structure, as well as shaped solids that contain compressed particulated solids) can be made utilizing practically the same basic processing equipment for each type of compositions.

The above, as well as other objects of the invention which will become apparent from the following discussion, can be achieved in accordance with this invention by utilizing selected process conditions and raw materials which will result in the formation of a detergent slurry containing hydrated alkali metal trimetaphosphate, (b) the reaction of the trimetaphosphate with a strong base to thereby convert the trimetaphosphate to tripolyphosphate, (c) the hydration of a substantial proportion of the trimetaphosphate while the slurry is in the foamed condition, and (d) removing sufficient water from the slurry while it is in the foamed condition to thereby form a solid (sometimes particulated) porous product. In the present processes, generally (b) and (c) are performed simultaneously in view of the very fast rate of hydration of the tripolyphosphate.

The processes for preparing light (low bulk) density detergent compositions, in accordance with the present invention, require that a "slurry" be utilized in order to achieve several specific advantages, including mainly the achievement of a better uniformity of ingredients through the final detergent product. Detergent " slurries" are well known in the art, and need not be detailed here, except to point out that those which can be used in the processes of this invention must contain at least about enough water to hydrate all of the alkali metal tripolyphosphate in the final detergent compositions that can be manufactured therefrom, and also at least enough water to initially form a fluid properties to the slurry. Thus, useful slurries generally should contain at least about 10 weight percent of water, based on the total weight of the completely formulated slurry. For some of the preferred embodiments of this invention, it is preferred that the slurries be fluid and initially contain at least about 20 weight percent of water (and when sodium tripolyphosphate hydrate is to be formed in these processes, at least about 5 weight percent of water in excess of the amount required to produce said sodium tripolyphosphate hydrate). Because in most of the processes of this invention it will be necessary to evaporate at least part of that water which is present in the slurries (especially that amount which is in excess of the amount that can be utilized to hydrate the tripolyphosphate salt), some of the benefits that can accrue from the use of sodium tripolyphosphate hydrate as lyophilized powder. The sodium tripolyphosphate hydrate is to be used in the invention will be most apparent when slurries containing at most about 50 weight percent of water are utilized. "Slurries" differ from solutions in that the former contain more than enough materials to dissolve in the continuous aqueous phase thereof, even though the materials dispersed through the aqueous phase may have a fairly high solubility in water.

It has been unexpectedly found that when the conver-
sion of an alkali metal trimetaphosphate (to tripolyphosphate) is made to occur during the time in which one of the foregoing slurries is in a "foamed" condition, so that sufficient "free" water is removed from the slurry to result in a thickening and ultimate "setting up" (solidification) of the slurry (by hydration of the tripolyphosphate often accompanied by the evaporation of some of the "free" water); solid, particulated and/or formed or molded products having unexpectedly low bulk densities result therefrom. The term "free" water is herein intended to encompass that water which was initially in the slurry and which is present in the particular composition being referred to in an unbound (i.e., not present as the hydrate of any of the salts in the composition), unevaporated state. It should be noted that the use of the term "free" water with reference to a given composition at any given time does not necessarily imply that the composition referred to is in a fluid or even a semi-solid state, since many apparently solid detergent compositions can contain as much as ten weight percent or more of "free" water without losing substantially all of their soap properties.

It is an advantage of the present invention that practically any water-soluble "hydratable" (that is, one that can be hydrated in an aqueous slurry) alkali metal tripolyphosphate salt that can be formed via the interreaction of a strong base with an alkali metal trimetaphosphate can be utilized in the manufacture of detergent compositions in accordance with the present invention. Particularly preferred, among this group (the "hydratable" alkali metal tripolyphosphates) are sodium tripolyphosphate (Na$_5$P$_3$O$_{10}$), potassium tripolyphosphate (K$_3$P$_3$O$_{10}$), lithium tripolyphosphate (Li$_3$P$_3$O$_{10}$), trisodium diapotassium tripolyphosphate (Na$_5$K$_2$P$_3$O$_{10}$), and the like, while still further preferred is sodium tripolyphosphate, mainly because of their economic advantage over the other hydratable alkali metal polyphosphate salts described above, as well as other considerations, generally those polyphosphate salts having sodium and/or potassium cations are a preferred class for use in the processes of this invention.

The low bulk density detergent compositions that can be made via the processes of this invention are those that contain a significant amount of the hydrated alkali metal tripolyphosphate; that is, usually at least about 10 weight percent and often as much as about 75 weight percent, based on the total weight of the final solid detergent composition. However, generally, it is preferred that the final compositions contain between about 15 and about 60 weight percent of the alkali metal tripolyphosphate salt, at least about 60 and preferably at least about 75 weight percent of which is in the hydrated state.

Although it was pointed out in the objects, above, that in the processes of the present invention, the hydrated tripolyphosphate salts need not be exposed to such high, degrading temperatures as those ordinarily utilized in detergent spray-drying operations, it will nevertheless generally be necessary to apply heat in some manner to the detergent slurries that are utilized herein in order to attain slurry temperatures of at least about 50° C. during some of the latter stages of the present processes. One method which has been discovered whereby both heat and the desirable tripolyphosphate can be introduced into the detergent processes of this invention simultaneously, and whereby several additional advantages can also be attained (including greater ease in controlling the viscosity of the detergent slurries than is ordinarily possible utilizing conventional slurry processes involving the use of tripolyphosphates and a faster overall detergent process as compared with conventional processes for manufacturing comparable detergent products, and others), is by utilizing as one of the major raw materials in the detergent slurry an alkali metal trimetaphosphate, and preferably sodium trimetaphosphate. Consequently, such processes that involve the utilization of the heat of reaction of an alkali metal trimetaphosphate with a strong base constitutes particularly preferred embodiments of the invention. These preferred embodiments make it possible for a detergent manufacturer to make advantageous use of the reaction of alkali metal trimetaphosphates with a base in the presence of alkali metal cations (when a substantial portion of the alkali metal is completely water-soluble; final detergent composition is desired) to produce an alkali metal tripolyphosphate. The reaction, which is accompanied by the evolution of a large amount of heat, is believed to be represented by the following series of steps:

Initially, the trimetaphosphate ring is cleaved by the base, forming the tripolyphosphate anion, as is shown in Equation 1:

\[
\text{(Trimetaphosphate)} \xrightarrow{+ 2OH^-} \text{(Tripolyphosphate)}
\]

Subsequently, the tripolyphosphate crystallizes in the slurry as the hydrate, as shown in Equation 2:

\[
\text{(Tripolyphosphate)} \xrightarrow{+ 5M^+ + yH_2O} M_5P_3O_{10}yH_2O \quad \text{(Hydrate)}
\]

wherein M is an alkali metal cation and y is an integer which is equal to the number of water molecules that are necessary to make an identifiable hydrated salt of the particular alkali metal tripolyphosphate that results from the above-described reaction. Generally, y will be a whole number within the range of from 1 to 15. For the several reasons pointed out above, it is preferred that M represent sodium and, therefore, that y equal 6. Note that initially the trimetaphosphate could be either an acidic alkali metal trimetaphosphate (containing one or two acidic groups), a "common" alkali metal trimetaphosphate (wherein all of its alkali metal cations are the same), or a "mixed cation" alkali metal trimetaphosphate (in which more than one type of alkali metal cation is present therein). Thus, alkali metal trimetaphosphates useful in the successful practice of the present invention are those that are water-soluble and that can be represented by the formula

\[
\text{A-O-P-O-O-P-O-B}
\]

wherein M is an alkali metal cation, A can be either H or an alkali metal cation, and B can be either H or an alkali metal cation; and when A and/or B are alkali metal cations, they can differ or be alike, and they do not necessarily have to be the same as M; although it is preferred that M, A and B be alkali metal cations and that they be the same (and still further preferred that all of M, A and B are sodium). Typical non-limiting examples of the alkali metal trimetaphosphates encompassed by the above formula include Na$_2$PO$_4$, Na$_2$HPO$_4$, Na$_2$H$_2$PO$_4$, KPO$_4$, KH$_2$PO$_4$, K$_2$HPO$_4$, Li$_2$PO$_4$, Li$_2$HPO$_4$, CsPO$_4$, RbH$_2$PO$_4$, K$_2$PO$_4$, Na$_2$LiPO$_4$, Na$_2$RbPO$_4$, K$_2$LiPO$_4$ and the like. Note that when acidic trimetaphosphates are used in the practice of the processes of this invention, the amounts...
of strong base necessary to convert the trimetaphosphate to the desired tripolyphosphate should be adjusted to take into account the necessity first to "neutralize" the acidic hydrogens on the acidic trimetaphosphate molecule.

When alkali metal trimetaphosphate, and particularly sodium trimetaphosphate, is utilized in formulating and manufacturing detergent compositions according to the present invention, particularly any amount of the material up to about 60 weight percent, based on the total weight of the fully formulated slurry, or even more, can be utilized. However, the amount of alkali metal trimetaphosphate that is actually utilized usually depends upon basically two requirements of the detergent manufacturer: the amount of tripolyphosphate which is utilized to provide detergent product, and the proportion of this amount of tripolyphosphate that should be in the hydrated state. Because the products which result from the practice of this invention should generally contain at least about 15 weight percent of hydrated tripolyphosphate (when trimetaphosphate is used as a "raw" material), the slurries contemplated herein will ordinarily contain at least about 5 to 8 weight percent initially (based on the weight of the slurry "solids"), of one of the alkali metal trimetaphosphates. On the other hand, because of the presence of water, strong base, and other detergent ingredients in the fully formulated slurries, generally not more than about 60 weight percent of any of the alkali metal trimetaphosphates can be utilized therein, if relatively complete conversion of the trimetaphosphate to tripolyphosphate in the detergent manufacturing process is desired. It is preferred that the amount of alkali metal trimetaphosphate which is utilized in the aqueous slurries in the practice of this invention be from about 13 to about 60 percent by weight (based on the total weight of the fully formulated slurry just prior to the "hydrating" step of the processes of this invention, which step will be described in greater detail below).

For a more thorough understanding of the overall processes of this invention, reference is now made to FIGURES 1 and 2 of the drawings. FIGURE 1 represents a schematic diagram of one of the preferred processes of the present invention, which preferred process is illustrated in more detail in FIGURE 2. The process illustrated in these drawings can be described as follows: Into a typical detergent cruncher, fitted with an efficient stirrer 3 and a jacket 5 through which steam or hot or cold water can be circulated by means of lines 7 and 8, are charged (all parts being by weight) 355 parts of water, 782 parts of sodium trimetaphosphate, 14 parts of sodium carbonate, 5 parts of sodium hydroxide, and 63 parts of sodium silicate, having a SiO₂/Na₂O ratio of 2.40, 30 parts of lauryl monoisopropanolamide. The resulting precursor slurry is stirred for about 15 minutes during which steam is passed through jacket 5 in order to increase the temperature of the precursor slurry to about 85°C. The hot slurry is then pumped through lines 9 and 11 to a conventional vacuum type deaerator 13. Deaerated slurry then passes through lines 15 and 17, through slurry pump 19, and line 21 to an efficient blender 31 (in this instance line 21 leads to the inlet port of a conventional centrifugal pump). During its passage through line 21 the slurry is monitored by means of a flow meter 25 and a density meter 27. While the precursor slurry is being pumped through line 21, a 50 weight percent aqueous solution of sodium hydroxide is pumped from the caustic storage tank 33 through line 35 and caustic metering pump 37 to heat exchanger 39 where its temperature is brought up to 70°C. From there it is pumped through line 41 into the same entry port of blender 31 as that into which the precursor slurry is being introduced. The speed of caustic metering pump 37 is adjusted (depending upon the data from flow meter 25 and density meter 27) so that for every 100 parts by weight of precursor slurry there are introduced into blender 31, 24.5 parts by weight of NaOH are introduced thereinto. This is approximately the stoichiometric amount of NaOH required to convert the sodium trimetaphosphate in the precursor slurry into sodium tripolyphosphate. Within less than a second, the NaOH is well blended with the precursor slurry in blender 31 due to the extremely violent agitation of the mixture achieved in the blender. The resulting final slurry is withdrawn from blender 31 through pipe 43 in which the final slurry remains for only a few seconds. From pipe 43, the final slurry 49 is poured onto one end of an endless stainless steel belt 45. At this point the slurry is still fluid, and at a temperature of about 95°C. Within the next several seconds the temperature of the final slurry is observed to decrease to about 105°C. The final slurry (trimetaphosphate with NaOH), at which point the slurry appears to expand internally, forming a light density foam 47. Steam is observed escaping from the surface of the foam as it moves along belt 45. At the same time, the foam becomes gradually solidified into a hot granulated detergent mass 51. The temperature of the formed material on belt 45 is maintained above about 100°C. For several minutes after the foam has been converted into the solidified detergent composition by means of a cover 53 over the belt as well as by steam-heating the underside of the belt. After about 8 minutes on belt 45, the granulated product 51 is gently wiped by a series of metal steel wires 55 in order to break up any soft agglomerated lumps, and then transferred via ramp 57 to transfer belt 59. From there it is dropped onto a vibrating screen 61 to break up any remaining agglomerates. At this point the detergent product contains about 12 weight percent of free water and 13 weight percent of combined (hydration) water in the form of sodium tripolyphosphate hexahydrate. This product is then passed through a conventional fluidized bed dryer 63 to remove almost all of the free water, and from there into product storage bin 65.

The bases that can be utilized in the practice of this invention are all of those which can cause the formation of sufficient hydroxyl ions, in the aqueous slurry, to react with the alkali metal trimetaphosphate, according to the foregoing suggested reaction. It has been found that of the group of materials known as "bases," only the relatively strong ones can cause the reaction of trimetaphosphate to tripolyphosphate to occur. Thus, throughout the present specification and the appended claims, the term "strong base" will be intended to encompass those bases that are sufficiently strong to cause the formation of "excess" hydroxyl ions in aqueous media that contain dissolved alkali metal tripolyphosphate. For purposes of this specification, it may be used to mean any base that be un-ionized, or that be ionized, or that be ionized, that yield a solution pH measured at 25°C of at least about 10.2 when they are dissolved in distilled water at the 1 weight percent level. It will be understood that the term "strong base" encompasses, for example, such basic compounds as for example, alkali metal carbonates, alkali metal silicates, tri-alkali metal orthophosphates, alkali metal and alkaline earth metal oxides, and the like (compounds do not actually contain hydroxyl anions, but which cause hydroxyl ions (high pH) to result when they are dissolved in water), as well as some of the organic quaternary ammonium hydroxides, the alkali metal hydroxides and the alkali metal carbonates, calcium hydroxide, and magnesium hydroxide, etc. Economic considerations will generally dictate that "strong bases" which are inorganic be used. Of these, it is preferred that alkali metal hydroxides, carbonates, and silicates (having SiO₂/M₃O₃ ratios lower than 2.0, where M is an alkali metal cation) are utilized. Still other bases that are used are the sodium and potassium forms of these materials.

The amounts of the various strong bases described above which can be utilized in this invention will vary considerably, depending upon such factors as the molecular weight of the base, its basic strength, rate of dissolution in water, etc. The amount, however, will always be sufficient to furnish enough hydroxyl ions so that at least
a substantial amount or proportion (i.e., at least about one-half and preferably at least about seven-tenths) of the alkali metal trimetaphosphate in the slurry can be converted into the corresponding alkali metal tripolyphosphate. Thus, the amount of the particular inorganic base that can be utilized (in the slurry) in the practice of this invention will generally be at least enough to furnish about one and preferably at least about 1.4 mole equivalents of hydroxyl ions per mole of trimetaphosphate which is present in the slurry. Because 2 moles of hydroxyl ions are necessary to convert one mole of trimetaphosphate to tripolyphosphate, it is still further preferred, when substantially complete conversion of the alkali metal trimetaphosphate is desired, that the slurry be formulated to contain at least about 2 moles of strong base per mole of trimetaphosphate therein. Since very high concentrations of base in the detergent slurries will sometimes cause degradation of tripolyphosphate (particularly hydrated tripolyphosphate), and also because when a very large excess of base is utilized some of the excess base (that in excess of the amount required to convert the trimetaphosphate) must ordinarily be neutralized with acid before the "drying" step of the process (i.e. in order to maintain a desirable alkalinity in the final detergent product), the amount of strong base present in the detergent slurries which are utilized in the practice of the invention will generally not be more than about 10 moles, and preferably at most about 6 moles of base per mole of trimetaphosphate in the slurries. Additional precautions that should ordinarily be observed when such extremely strong bases as the alkali metal hydroxides, and particularly sodium hydroxides, are utilized for the conversion of trimetaphosphate to tripolyphosphate will be discussed subsequently, along with the discussion of the various manipulative procedures that can be utilized in the processes of this invention.

Although it is appreciated that some inorganic bases are conventionally employed in detergent compositions and processes, the amounts of base with which this invention is concerned will practically invariably be over and above those amounts presently employed. For example, two percent solutions of conventional spray-dried detergent composition in distilled water often exhibit alkaline pHs ranging from about 8 to about 10.5 or perhaps even slightly higher than 10.5. These levels of alkalinity are desired to be maintained in the final product because the products often perform better under slightly alkaline wash conditions. In addition, a certain degree of alkalinity is required in the product in order to maintain the silicate corrosion inhibitors in a water-soluble state. The practice of the present invention, however, generally requires that significantly more base be incorporated into the detergent slurries than was heretofore employed.

It is another advantage of the present invention that when alkali metal trimetaphosphates are utilized as described heretofore, ready control of the rate of hydration of the resulting tripolyphosphate salt within the detergent slurry can be obtained. This is a distinct advantage over detergent slurry processes of the prior art wherein sodium tripolyphosphate, for example, is the most widely used polyphosphate raw material, because the hydration rate of sodium tripolyphosphate is ordinarily a very difficult but important process variable to control. This ready control of the rate of hydration lends an additional advantage of wide flexibility to the processes of the present invention. Some of the implications of this flexibility will be discussed in greater detail below. Generally the higher the temperature of the aqueous mixture of strong base and alkali metal trimetaphosphate, the faster the rate of formation of the alkali metal tripolyphosphate that results from the alkali metal trimetaphosphate described in Equation 1, above. However, so long as the strong base is withheld from slurries containing alkali metal trimetaphosphate, very little, if any, conversion of the trimetaphosphate to tripolyphosphate occurs, no matter how high the temperature of the slurry is maintained.

The rate of conversion of trimetaphosphate to tripolyphosphate can be increased by increasing the ionic strength (concentration) of a given detergent slurry. Therefore, those who prefer to utilize very high rates of conversion in the processes of this invention can advantageously do so by utilizing highly concentrated detergent slurries. It has also been discovered that the presence of more than about 0.5 weight percent of sodium sulfate in the slurry (while the trimetaphosphate conversion reaction is being carried out) in some ways acts as a catalyst for the conversion reaction, sometimes increasing the rate of conversion as much as 50% or more.

Since a given amount of alkali metal trimetaphosphate in any given detergent slurry contributes substantially less to the apparent viscosity of the slurry than would a corresponding amount of sodium tripolyphosphate (which is generally largely present in the slurry as the hexahydrate), for example, slurries having unexpectedly low viscosities during the crutching stage of the detergent processes can be made. This low slurry viscosity results in a considerable savings, as compared to otherwise equivalent slurries containing hydrated or hydrating tripolyphosphates, in the total amount of power consumed in the overall detergent processes, and particularly in the crutching step of such processes. That is, for example, when a detergent slurry is handled in a given crutching vessel, for example in a vessel of crutching or pumping equipment, if desired, as compared to equivalent tripolyphosphate hydrate-containing slurries. Data illustrated in Table 1, below, give some idea of how great this reduction in slurry viscosity can be when sodium trimetaphosphate (plus about 2 moles of NaOH per mole of trimetaphosphate) is utilized in the preparation of detergent slurries, as compared to a conventional procedure for preparing an equivalent detergent slurry utilizing sodium tripolyphosphate in the form of the low temperature modification. Ordinary one need not be concerned over how hot the detergent slurries containing the alkali metal trimetaphosphates are maintained while the strong base is essentially absent from the slurries. However, because of the extremely high rate of degradation of hydrated tripolyphosphates (such as the preferred sodium tripolyphosphate hexahydrate) in strongly basic systems when the temperatures are raised substantially above about 115° C, the temperatures of slurries formulated with alkali metal trimetaphosphate that are utilized in accordance with this invention should generally be maintained below about 135° C, and preferably below about 120° C, while the alkali metal trimetaphosphate is being converted to tripolyphosphate.

Similarly, the rate of conversion of trimetaphosphate to tripolyphosphate with a strong base increases with increased slurry temperature, slurry temperatures above about 50° C, and preferably above about 70° C, should generally be maintained during at least the latter half of the conversion step. However, even lower temperatures than about 50° C can be used if desired. (Temperatures higher than about 105° C cannot be obtained in the slurries and reaction mixtures by carrying out the processes under pressures higher than atmospheric.) Even when fairly low slurry temperatures below about
70–89° C. are utilized during a large fraction or even most of the time during which the trimetaphosphate is being converted to tripolyphosphate, it is distinctly advantageous to permit the temperature of the slurry to rise to the boiling point of the free water in the slurry during the latter stages of the conversion reaction so as to actually convert all of the water in the slurry to steam. The steam, in turn then, usually being generated initially in the form of discrete bubbles of gas (steam) in the slurry can cause the conversion of the slurry into a fairly light density foam. Then as the remainder of the trimetaphosphate is converted into tripolyphosphate (while the slurry is in the foamed state), and solid tripolyphosphate in turn hydrates, the apparent viscosity of the slurry becomes higher and higher until, after a substantial propor-
tion of the free water in the slurry has either been absorbed by the tripolyphosphate to form the hydrated salt, or has been evaporated out of the slurry, or both (generally both), the reaction mixture becomes a solid. Seemingly, "wet" mass generally still containing several weight percent of free water, which can be removed if desired by subsequently drying the wet mass, or by addi-
tional absorption of the free water via hydrate forma-
tion. Such "delayed" hydrate formation has been ob-
served to take place subsequent to the above-de-
scribed conversion reaction. It can take place readily, for example, in compositions which contain hydratable ma-
terials such as sodium sulfate, and certain of the phos-
phate salts that form their hydrates at temperatures be-
low those that are generally utilized in the foaming-
hydration step (described above) of the processes of the present invention.

When the foregoing foaming-hydration step is per-
formed under atmospheric pressure and detergent slurries having water alone as the continuous phase, it is usu-
ally necessary to heat the slurries to a temperature be-
tween about 100° C. and about 105° C. in order to generate foam via the conversion of water to steam as described above. Sometimes, when it is desirable to con-
duct the foaming-hydration step of these processes at lower temperatures than about 100–105° C., a quantity of a relatively low boiling, completely water-miscible organic solvent such as methanol, ethanol, isopropanol, acetone, dioxane, and the like, or combinations of these, can be utilized along with the water as the fluid continu-
ous phase in the preparation of the detergent slurries de-
scribed heretofore.

It will be noted that in either of these approaches the temperature of the reaction medium (the slurry which subsequently is converted into a solid detergent product during the foaming-hydration step) is maintained suf-

ciently high to generate steam—in the form of pure
water vapor or as the low boiling organic solvent/water azeotrope, for example, depending upon the composition of the slurry's fluid continuous phase—which steam is the

cause of the light density foam. It is not absolutely neces-

sary, however, that the gas which forms the foam be steam. Actually, particularly where lower slurry temperatures and trimetaphosphate conversion rates are desired in the processes of this invention it is sometimes advantageous to create a gap (place, or gap) during the foaming-hydration step described heretofore, by blowing, dispersion, or injecting a gas other than steam into the slurry. This can be done by any of a number of ways which will become evident to those reasonably skilled in the art from the present disclosure. The gas which is injected can be air, oxygen, carbon dioxide, sulfur dioxide, nitrogen, nitrous oxide, hydrogen, propylene, methane, ethane, argon, neon, super-

heated steam, hydrogen sulfide, and the like. It can also be any of a number of relatively lower boiling synthetic materials which are either gases at temperatures below about 100° C. and atmospheric pressure, or which can be converted readily into gases by making relatively minor adjustments in temperature and/or pressure, such as for example, the fluorinated hydrocarbons including CClF₂, CCl₂F₂, CCl₃F, CCl₄F, and the like. Generally, it is prefer-

red that these "gaseous" materials be non-reactive with the other materials in the detergent compositions at tempera-
tures used during the practice of these processes.

When conditions during the foaming-hydration step are such that the rate of hydration of the polyphosphate is relatively slow (such as when slurry temperatures be-
low about 70° C. are utilized during the conversion of one of the alkali metal trimetaphosphates) the reaction (hydrating) mixture must generally be maintained in the foamed state for a longer period of time than when con-
ditions are such as to encourage a higher rate of hydra-
tion, provided most of the benefits that can be attained by practicing the present invention are desired. This amount of time can be reduced (other conditions remain-
ing the same in any given process) by using a procedure involving the injection of a gas, the gas being heated prior to its introduction into the hydrating mixture to a temperature high enough to result in the removal of several of the free water from the slurry via evaporation. Heat can also be applied directly to the slurry by means of a conventional heat exchanger or through the walls of the crucible pipe, belt, or other container in which the foaming-hydration step is being carried out.

Although several specific methods for the production of the requisite foam in the detergent slurries have been outlined above, it will be evident from this disclosure that other procedures for generating the foam can be utilized without necessarily detracting substantially from the ben-

fits that can result from practicing this invention. All this is ordinarily necessary in this respect (in so far as the foaming-hydration step of these processes is concerned) for the practice of the present invention is that the slurry be foamed, and that at least a substantial part of the hydration of the polyphosphate is performed while the slurry is in the foamed state. It is extremely difficult, for example, to obtain final detergent products having very low bulk densities via the processes of the invention if the maintenance of the foam in the slurry and at least part (preferably the latter part of) the hydration of the "hydratable" polyphosphate described above are not performed simultaneously. Generally, acceptable low-

density detergent products can be obtained when at least about 5 weight percent (or even less) of the total "hydratable" tripolyphosphate in the composition of slurry is hydrated while the slurry is in the foamed condition, al-

though it is preferred that at least about 10 weight per-

cent of the hydration occurs during this foaming-hydra-

tion step of the processes of the instant invention.

It will be noted that the foam during the foaming-hydration step can be continually generated during the entire period, or during only a portion of the latter part of the period during which the polyphosphate is hydrated. Or sufficient foam can be generated initially, and the reaction conditions then adjusted and maintained so that at least a large proportion of the bubbles of gas are maintained (held) in the slurry until it solidifies.

Generally, the more (i.e., the greater the volume of) bubbles that can be generated and held in the slurry during the foaming-hydration step, the lighter or lower the bulk density of the final detergent product will be. Thus, for extremely low bulk density detergent products, generally the total volume of the foamed slurry (or the "light density foam") should be at least about 150 per-
cent, and preferably at least about 200 percent (by vol-
une) of the unerated volume of the slurry. The volume of the slurry volume, before it is transformed into the foamed state.

It should be noted that in the foregoing discussion of the foaming-hydration step of the processes of this invention, generally a better foam, and consequently gen-

erally a more uniform final detergent product can be manufactured (particularly when the invention is utilized as a continuous detergent process) when there is at
least an effective amount of a "foaming agent" in the slurry at the time the slurry is transformed into the foamed condition. The term "foaming agent" is intended to include synthetic organic anionic, nonionic, and even amphoteric active detergent materials that are generally compatible with the alkali metal polyphosphates in both solutions and slurries of the overall detergent compositions. Thus, the term foaming agent includes, for example, such individual organic detergent-active ingredients as the well-known water-soluble soaps (i.e., the sodium and/or potassium salts of coconut fatty acids, oleyl fatty acids, and other water-soluble alkyl sulfate sulfonates having from 6 to 20 carbon atoms, and preferably from 9 to 17 carbon atoms, in their alkyl chain, such as sodium dodecylbenzene sulfonate and potassium tetradecylbenzenesulfonate; water-soluble alkyl sulfates, such as those that are manufactured by sulfurizing aliphatic alcohols having from 9 to 20 carbon atoms in their either branched or unbranched alkyl chains, including, typically, sodium and potassium lauryl (C12) sulfate, sodium and potassium hexadecyl sulfate, sodium and potassium octadecyl sulfate, etc.; as well as alkali metal salts of sulfonated ethylen oxide oxide/propylene oxide condensation products manufactured by ethoxylation and/or propoxylation (and subsequently sulfating) various organic hydrophobic compounds containing active hydrogen such as alcohols, mercaptohans, phenols, and amines; sodium and potassium alkyl glyceryl ethers such as those derived from tallow and coconut oil, including for example, sodium coconut oil fatty acid monoglyceride sulfonate, etc.; fatty alcohols such as N-dodecylmonooethanolamine, N-octadeyl diethanolamide and the like; alcohol-alkylene oxide condensates (i.e., alcohols having from 8 to 20 carbon atoms, in either straight or branched chain configuration, having from about 6 to about 30 moles of ethylene oxide and/or propylene oxide per mole of alcohol in the molecules) alkylphenol-alkylene oxide condensates (i.e., those made by condensing alkylphenol, having an alkyl group that contains from about 6 to about 20 carbon atoms in the chain with from about 6 to about 30 or more moles of ethylene oxide and/or propylene oxide per mole of alkylphenol); and the like. Of these, those in the anionic class are preferred, while the fatty alkyl (or alcohol) sulfates having from 8 to 20 carbon atoms in their carbon chains are still further preferred for use in the processes of this invention. Sometimes when the nonionic detergent active materials are utilized in the absence of a significant amount of one of the anionic detergent active materials in the manufacture of detergent products in accordance with this invention, an unexpectedly high slurry viscosity develops at one stage of the crutching operation. It has been found that this problem can be alleviated by adding the "hydratable" triphosphate last or nearly last, and very slowly (i.e., over a period of 2 minutes or more) with agitation into the other detergent ingredients.

2. The term "foaming agent" also includes materials which, when added to the slurry, contribute to some extent to the tenacity or the toughness or stability of the bubbles in the foam slurry. Such materials (other than the well-recognized detergent-active ingredients such as those described above) include polymers that are water-soluble to an extent sufficient to contribute to the stability of the foam such as sodium croboxymethylcellulose; sodium hydroxyethyl cellulose, polyvinylpyrrolidone; hydrolyzed and partially hydrolyzed polymers made by reacting a lower alkylene such as ethylene, propylene, and methyl vinyl ether with maleic and/or fumaric anhydride, for example, ethylene-maleic anhydride, propylene fumaric anhydride, methyl vinyl ether-maleic anhydride, polyvinyl alcohol; and the like.

3. The amount of foaming agent in the slurries during the foaming-hydration step of this invention can be varied considerably. Generally, more than about 0.1 weight percent, based on the weight of the completely formulated slurry, should be utilized when final detergent products having fairly low bulk densities are desired. However, for very low bulk densities in the final detergent products made via these processes, usually at least about 0.25 and preferably at least about 0.3 weight percent of the foaming agent should be used. Since different foaming agents perform with different degrees of efficiency, depending upon many factors including slurry temperature, slurry "solids" concentration, the actual ingredients contained in the slurry, and many others, optimum concentration for each foaming agent cannot be set out herein with definiteness. However, it is believed within the ability of those reasonably skilled in the art, in view of this disclosure, to ascertain the optimum concentrations for the manufacture of their own particular detergent product.

Practically any manipulative procedure can be utilized in the practice of the present invention in order to accomplish the various steps or stages in the processes set out above. For example, the order of addition of the various ingredients in the preparation of any of the slurries, except those that contain more than a few weight percent of alkali metal triglycinate, is not at all critical. Normally the only precaution one needs to observe in order to obtain certain excellent results is that compositions which contain triglycinate should generally not be blended with the strongest bases such as sodium hydroxide unless the base is diluted to below about 50 weight percent, and preferably below about 35 weight percent, with water before the strong base is blended with the alkali metal triglycinate. Otherwise, the strong base should be effectively diluted by the water in the slurry itself as quickly as possible after the base is added to the slurry. However, if a manufacturer is not particularly concerned about completely minimizing the degradation of the triglycinate during his manufacturing operations, even this precaution need not be strictly observed. When this precaution is observed, one advantageous method for doing so which combines several of the unexpectedly desirable attributes from using alkali metal triglycinophosphate, and especially sodium triglycinophosphate, is to first prepare a practically completely formulated detergent slurry, which usually contains any foaming agent, antideposition agent, optical brighteners, bleaches, fabric softeners, alkali metal silicate or fluosilicate corrosion inhibitors, or whatever other materials that are desired in the final detergent composition or product, but which does not contain the strong base (called herein the "precursor slurry"). The precursor slurry, then should also contain the triglycinophosphate. Because of the unexpectedly low viscosity of slurries that contain the triglycinophosphate, precursor slurries have been found comparatively little water (as compared to conventional detergent slurries that practically invariably contain hydrating or hydrated tripolyphosphate), but which retain their pumpability and other fluid characteristics, can be made.

For example, precursor slurries containing as much as 90 weight percent of non-volatile material ("solids"—including the triglycinophosphate) can be manufactured and utilized in the processes of this invention. So long as the strong base is withheld from the precursor slurry, its low viscosity can generally be maintained almost indefinitely, with substantially no degradation of the triglycinophosphate occurring. Thus a detergent manufacturer can prepare his precursor slurries well in advance of the time he wants to produce his final detergent product if he desires. In addition, if part of his processing equipment breaks down, a detergent manufacturer can hold his precursor slurry for long periods of time if need be, practically without incurring any degradation, whereas, if he had prepared conventional slurry using sodium tripolyphosphate, hydrolytic degradation of the tripolyphosphate in the slurry upon prolonged storage could practically destroy the utility of the slurry for his processes.

Having prepared his precursor slurry, the detergent manufacturer can now utilize several approaches to the final essential step in the processes of this invention. Since
is desirable that the foaming-hydration step be performed relatively quickly, and because the rate of conversion of the trimetaphosphate to tripolyphosphate is very high at elevated temperatures, the precursor slurry can be heated to a temperature above about 50°C, and preferably above about 60°C, at the pretreatment step of the invention before the strong base is intermixed therewith. In that case, the conversion reaction proceeds quickly (usually within about 2 minutes when an alkali metal hydroxide such as sodium hydroxide or potassium hydroxide is utilized, for example, at the higher precursor slurry temperatures), after the strong base is blended into or with the precursor slurry. As a matter of fact, the heating of the conversion of the trimetaphosphate to tripolyphosphate, and thence to hydrated tripolyphosphate is generally sufficiently high that the conversion reaction can become essentially autocatalytic in nature if most of this heat is not deliberately removed from the slurry. For example, when a precursor slurry containing more than about 10 weight percent of sodium trimetaphosphate and having a temperature of about 80°C is quickly intermixed with about 2 moles of sodium hydroxide per mole of trimetaphosphate under practically adiabatic conditions, the conversion reaction commences immediately. The heat from the conversion exerts an increase in the temperature of the mass, which in turn causes an increase in the rate of conversion of the trimetaphosphate to tripolyphosphate. Increases of tenfold or more in this rate of conversion can be accomplished by raising the temperature of the reaction mass above 25°C.

Thus, by intermixing the strong base with the precursor slurry at a relatively high temperature, the manufacturer can be reasonably assured that his foaming-hydration step will not require an excessively long time. Actually, provided the heat is not removed from the system, steam and foam can usually be generated from slurry which are treated like that described immediately above (precursor slurry + strong base) within a few minutes of the time the strong base is intermixed with the hot precursor slurry. Practically equivalent results can also be obtained by intermixing the precursor slurry and strong base, or even by formulating the slurry in any particular manner desired, at a fairly low temperature (i.e., below about 50°C) and subsequently raising the temperature of the slurry to about 70°C, for example, by means of externally applied heat. This can be accomplished by passing the slurry through or over an electric or steam heated jacket.

Another method by which a manufacturer can accomplish this same result is by passing the fairly cool, completely formulated slurry (containing both trimetaphosphate and strong base) through a steam-traced pipe, using higher than atmospheric pressures and temperatures above about 105°C, if desired to obtain still higher conversion rates. Before the conversion has been completed it is generally preferred that the slurry be deposited into or onto some container in order for the above-described foaming-hydration step to be completed in the absence of an excessive amount of agitation. (Excessive agitation during the stage of these processes wherein the "setting up" of the detergent slurries occurs can result in a considerable increase in the bulk density of the final detergent product, as compared to that of one that has not been substantially agitated during the latter portion of the foaming-hydration step.) Thus, when the foaming-hydration step is performed in a vessel containing a paddle or stirring blade or other means for internally agitating the slurry, it is best that the agitating means be stopped while the foamed slurry solidifies. Or, if desired, the slurry can be dumped into a pan or other container, or onto a movable belt from the internally agitated vessel shortly before the foamed slurry solidifies in order to minimize the agitation during this "setting up" period. The strong base should be thoroughly and evenly distributed through the slurry before the solidification stage is reached, however.

Still another convenient method for manufacturing low bulk density detergents via the precursor slurry procedure described above is to do so continuously. For example, the hot precursor slurry can be metered into a conventional mixing device in which the precursor slurry can be thoroughly and quickly intermixed with the strong base, which is also metered into the device at a rate calculated to yield the desired final product. Then the completely formulated slurry can be poured or dropped or pumped from the mixing device onto or into a container and there permitted to either begin or continue to foam (a) and subsequently solidify into the final detergent product. This method is described hereinafter and is illustrated in FIGURES 1 and 2. Cold precursor slurry can be metered through an electric or steam-traced pipe or series of pipes prior to its being inserted into the mixing device. When such a procedure is utilized continuously, it is convenient and advantageous to pour the completely formulated slurry onto a movable belt that is designed to hold fluid substances. The slurry can then foam and steam on the belt, and subsequently solidify thereon. Then the lighter density product can be passed through a drying oven usually operated at a temperature which at least partially degrades the hydrated tripolyphosphate in it) when it is desired to remove some of the excess free water that may be present. This drying oven step is not essential for the successful practice of the invention, however. Or the hot, completely formulated slurry can be held in a pipe or conduit or other container under conditions of much lower than atmospheric pressure, if desired, until the temperature of the slurry reaches the boiling point of the water therein. Then it can be sprayed or dribbled into a high tower similar to a conventional spray-drying tower and dropped through the tower. The tower can contain warm, dry air to aid in the removal of some of the free water, but the temperature in the tower should generally be held considerably lower than those that are utilized in conventional spray-drying operations. Thus, foaming, hydration and solidification during the drop through the warm tower can result in the formation of a low bulk density detergent product via a completely different mechanism then is conventionally employed in similar equipment (i.e., a spray-drying tower).

Since the addition of heat into a chemical process is expensive, it is generally desirable to develop and utilize means for carrying out the chemical processes with as little consumption of added heat as possible. Consequently, one of the particularly preferred embodiments of the present invention involves the efficient utilization of heat resulting from (a) the reaction of the trimetaphosphate with the strong base, and (b) the hydration of the resulting tripolyphosphate. In this particularly preferred embodiment, the heat evolved during these chemical processes is utilized to both (a) raise the temperature of the slurry to that at which the steam is formed and (b) to cause the evaporation of some of the "free" water from the resulting particulated, light density product. Thus, it is preferred that the interreaction of the trimetaphosphate and the strong base be carried out in such a way that the reaction is essentially adiabatic, in which practically none of the heat resulting from the exothermic reaction is allowed to escape from the slurry, so that the temperature of the slurry is increased by the "internal" addition of such "heat of reaction" into it. In order to properly utilize this approach in the practice of the present invention, it is necessary, however, that the initial temperature of the "final" slurry (containing both trimetaphosphate and strong base, as well as any other desired detergent ingredients) be at least a certain minimum level, the actual value of which certain minimum temperature being determined by a few factors including, for example, the total amount of trimetaphosphate that is to be reacted with the strong base (generally the larger this amount the
lower the initial temperature needs to be), (b) the type of triopolyphosphate hydrate to be made (the "heats of hydration" differ), (c) the proportions and kinds of other ingredients in the slurries (this effect is relatively minor, however) and (d) the "final" reaction temperature expected (i.e., the temperature of the slurry during the "forming-hydration" step). In processes involving the manufacture of detergent compositions containing sodium triopolyphosphate hydrate, in which processes tri-sodium trimetaphosphate is reacted with a strong sodium cation-containing base such as sodium hydroxide, for example, it was pointed out hereinbefore that the use of at least about 5 weight percent of sodium trimetaphosphate is preferred. In the present processes, when 15 weight percent of sodium trimetaphosphate is reacted with a stoichiometric amount of NaOH in a typical detergent slurry containing at least about 50 weight percent of total "solids" (at most about 50 weight percent of water), the "initial" temperature of the slurry (immediately after the tri-metaphosphate and the sodium hydroxide are intermixed) must be at least about 80° C. (in order for the "heats of reaction" described above to carry the temperature of the slurry to about 105° C., which is about its boiling point under 1 atmosphere of pressure). But when as much as 50 weight percent of sodium trimetaphosphate (in the "living" slurry) is to be converted to sodium tripolyphosphate hydrate via reaction with NaOH, the initial temperature of the slurry normally need only be about 60° C. Tabulated below are ranges of the various essential elements that must be observed in order to practice successfully this particularly preferred embodiment of the present invention.

Element 1: Range
Percent water in slurry 2 20-30
Percent sodium trimetaphosphate 15-60
Percent NaOH 4-16
Temperature 2 45-90

1 In terms of percent by weight of the slurry immediately prior to the beginning of the reaction of NaOH with trimetaphosphate.
2 Just after the sodium trimetaphosphate and the NaOH have been intermixed (immediately prior to the beginning of their interaction).

This particularly preferred embodiment of the present invention is illustrated in Example I, below. It should be understood that when relatively lower amounts (within the above range) of sodium trimetaphosphate are to be converted in these processes, relatively higher initial slurry temperatures must be used, and when relatively larger amounts of trimetaphosphates are to be converted, relatively higher reaction temperatures can be used.

In the following examples, which are illustrative of some of the embodiments of the present invention, all parts are by weight unless otherwise specified.

Example I

Into a conventional stainless steel mixing vessel which is fitted with a conventional paddle-type stirrer and jacketed so that either hot or cold water or steam can be used in the jacket, are charged 2,000 parts of water, 900 parts of sodium dodecylbenzene sulfonate, 600 parts of sodium laurel sulfate, 1,000 parts of sodium sulfate, 2,840 parts of sodium trimetaphosphate, 1,140 parts of sodium silicate (470% solids) having an SiO2/Na2O ratio of 2.40 and 55 parts of detergent grade sodium carboxymethylcellulose. The resulting precursor slurry is stirred for about 10 minutes, during which time the temperature of the slurry is raised to 80° C. by circulating steam through the mixer jacket.

Into the hot precursor slurry which is being moderately agitated is then quickly poured 1,590 parts of a 50% aqueous sodium hydroxide solution. After about 45 seconds of moderate agitation, during which the sodium hydroxide is blended well with the precursor slurry, the temperature of the slurry beings to rise. The agitation is halted just before the temperature of the slurry reaches 100° C. When the slurry temperature reaches about 103° C, the slurry begins to expand in volume, rising in the mixing vessel, so that the volume of the foamed slurry is at least about 2-8 times that of the precursor slurry. Steam begins to escape from the bubbling mass, and it hardens quickly, to a particulated, seemingly wet, soft mass. Within about 15 minutes, no more steam is evolved from the solidified reaction mass, and its volume decreases slightly while it is cooled to room temperature. At this point it contains about 30 weight percent of water of which about 12.7% is considered free water and about 92% of the theoretical equivalent (based on the amount of sodium trimetaphosphate charged into the precursor slurry) of sodium tripolyphosphate, which is substantially all present in the form of the hexahydrate. After being air-dried overnight to remove most of the excess free water, the final detergent product is free flowing, non-caking, essentially non-hygroscopic, has a bulk density of about 0.955, and contains about 52 weight percent of sodium tripolyphosphate hexahydrate.

Note that in Example I, no difficulty whatever is experienced with respect to lumps in either the precursor or the completely formulated slurries. Had the same slurry preparation procedure been followed utilizing anhydrous sodium tripolyphosphate instead of sodium trimetaphosphate, many troublesome lumps of undissolved, partially hydrated tripolyphosphate would probably have formed, especially if the high temperature modification had been utilized, which lumps are generally not desired by detergent manufacturers in either their slurries or in their final detergent products.

Another surprising result which can be obtained by practicing the processes of this invention is that final detergent products that are manufactured via a procedure such as that shown in Example I, above, yield substantially clear aqueous solutions, even when they are dissolved in water to the extent of about 0.5 to 1.0 weight percent. By comparison, conventional heat-dried (generally spray-dried) detergent products practically invariably yield turbid aqueous solutions. Data in Table 2 aptly illustrate this advantage:

<table>
<thead>
<tr>
<th>TABLE 2.—CLARITY OF 0.5% AQUEOUS DETERGENT SOLUTIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detergent: 1</td>
</tr>
<tr>
<td>Invention product</td>
</tr>
<tr>
<td>Conventional-detergent A (spray-dried)</td>
</tr>
<tr>
<td>Conventional-detergent B (spray-dried)</td>
</tr>
</tbody>
</table>

1 Invention product, made in Example I, but formulated to substantially match conventional detergent B.
2 Percent transmitted light through a 1-inch cell containing 0.5 weight percent detergent solutions, as compared with distilled water.

Conventional-detergent B and the "Invention Product" used as a basis for the data in Table 2 contained about 20 weight percent of a mixture of sodium dodecylbenzene sulfonate and lauryl isopropanolamide, plus about 50 weight percent of sodium tripolyphosphate, about 5 weight percent of sodium silicate solids, about 23 weight percent of sodium sulfate, and a total of about 2.5 weight percent of minor adjuncts. Conventional-detergent A is a well-known "nonionic" detergent. While the data in Table 2 is illustrative of only a few specific detergents, practically all conventional spray-dried detergents yield relatively opaque "solutions" similar to those of detergents A and B in Table 2, while those made via the present processes are considerably more clear in every instance (when similar formulations are compared and no water-insoluble materials are utilized in the formulations).

Example II

A precursor slurry similar to that prepared in Example I is formulated, except that 3,100 parts of a physical blend containing about 50 weight percent of sodium trimetaphosphate and 50 weight percent of anhydrous...
high temperature crystalline modification sodium tripolyphosphate are utilized in place of the sodium trimetaphosphate.

After the temperature of the precursor is raised to about 90° C., 1,160 parts of a 35 weight percent aqueous solution of sodium hydroxide is quickly (within about 30 seconds) blended into the precursor slurry. Then the mixing is stopped, and the slurry permitted to form. As soon as the volume of the foamed slurry is about 5 times that of the precursor slurry, the foamed slurry is poured from the mixing vessel in a layer about 4 inches deep and about 2 feet wide on a moving belt. The reaction mixture on the belt quickly solidified into a soft, particulated mass which, after passing through a tumbling rotary dryer in which dry air at 100° C. is passed over counter-currently against the showering solids in about 10 minutes, is an excellent free flowing, non-caking, particulated detergent product which can readily be packaged and sold directly to the consuming public. Its bulk density is about 0.45.

EXAMPLE III

A precursor slurry is prepared which is similar to that made according to Example I, above. Its temperature is about 45° C. It is then poured into a stainless steel conduit having an inside diameter of about 1 inch. The conduit is traced for a distance of about 30 feet with a pressurized steam jacket to heat the precursor slurry to a temperature near boiling. The heated precursor slurry is joined by a 50 weight percent aqueous solution of sodium hydroxide metered through a mixing nozzle at a rate proportional to 2.01 moles of NaOH per mole of sodium trimetaphosphate in the precursor slurry. The mixing nozzle is equipped with an agitator and several baffles spaced and designed to achieve quick and intimate mixing of the precursor slurry with the strong base. The temperature of the resulting completely formulated slurry is raised to about 115° C. by the heat of reaction and the pressure is increased to above about 25 p.s.i.g. From the open end of the mixing nozzle the slurry is discharged onto a moving belt, where steam is quickly generated and the product foams, and solidified into a soft sponge material. After being air cooled the final detergent product has a bulk density of about 0.65. The cooled sponge material can be easily disintegrated into a free flowing granular product or properly sized for laundry detergents.

The processes of the present invention can be advantageous in detergent manufacture in many ways, some of which are present in the slurries and therefore. Additionally, however, it is a very valuable advantage that manufacturers can now utilize a "hydratable" polyphosphate (the trimetaphosphate) in only one physical form for the manufacture of a variety of forms and types of products. For example, the final relatively low bulk density detergent products can be passed through a compressing machine and then ground to produce a product having a higher bulk density if desired. Control of the density of the final detergent products can also be obtained by utilizing a small amount of a conventional anti-foam agent in the slurry during the foaming-hydration step. Generally, the more the foam agent (such as vegetable oil or silicons, for example) the higher will be the bulk density of the final detergent product. In addition, by simply changing the types and quantities of ingredients in the precursor and/or completely formulated slurries, described above, a detergent product having practically any desired final formula (provided it also contains sufficient alkali metal trimetaphosphate) can be manufactured via the processes of this invention. Manufacturers of tableted or formed detergents can also utilize this invention to advantage. For example, some conventional detergent tablets physically deteriorate when they are exposed to a highly humid atmosphere for more than a few hours, apparently because they initially contain anhydrous sodium tripolyphosphate which tends to swell in volume when it is hydrated to the hexahydrate upon contact with the humid atmosphere. Tablets prepared from a final detergent product such as that prepared in Example I, above, remain physically stable for weeks or more even though they are exposed to high humidity and relatively high temperatures.

EXAMPLE IV

A part of the soft, spongy, particulated product of Example III is taken from the moving belt (before it is cooled and air dried) and in addition introduced into a conventional soap milling machine (often called a "plodder"). In the milling machine, the temperature of the detergent is maintained at about 100° C. The detergent is milled very briefly (because it is already homogeneous) and then extruded on conventional equipment into bar form at a temperature of from about 50° C. to about 100° C. preferably from about 50° C. to about 50° C. After they are cooled to about 25° C., the resulting detergent bars are uniform, homogeneous and excellent detergent laundry bars. Detergent bars and tablets can also be produced by simply compressing in suitable conventional molding equipment any of the porous, particulated products resulting from processes such as are illustrated in FIGURE 2 and Example I, above, under pressure of from about 200 to about 4000 pounds per square inch.

It is still another advantage of the present invention that it can be utilized to manufacture relatively low bulk density formed solid detergent products that contain a network of air spaces or cells. This cellular structure, combined with the overall formed shape (such as in the form of a bar of soap or practically any other desired shape), can result from a closely controlled release of steam during the foaming-hydration step of the processes of this invention. Essentially, in order to manufacture such solid, cellular, formed products, the total amount of steam that is formed should be controlled so that very little, if any, of the steam bubbles out of the foamed slurry. Thus, ordinarily in the manufacture of one of these formed solid compositions, the reaction rate, and/or concentration of the alkali metal trimetaphosphate and other "hydratable" polyphosphate materials in the slurry should be controlled or regulated so that the total volume of steam and/or other gas that is generated in the slurry is not more than about four times the total un aerated volume of the completely formulated slurry (i.e., the foamed slurry volume is preferably less than about 5 times its un aerated volume). When one of the more efficient foaming agents is used, the volume of steam can be increased to about 5 or even 10 times the un aerated volume of the slurry without an excessive breaking of the steam or gas bubbles within the foam before it solidifies (which breaking and excessive evolution of steam or gas from the slurry at or near the time the slurry solidified can result in the participation of the final detergent product, which is generally not desired in the manufacture of formed solid products having cellular internal structures). Perhaps the best way to accomplish the above-described control of the total amount of gas formed in the slurry is to handle the slurry in such a way that the desired volume of gas is all that is formed therein, and such gas is formed only during the latter portion of the foaming-hydration step. For example, when slurries containing between about 10 and about 60 weight percent of sodium trimetaphosphate are utilized in these processes at least about half of the sodium trimetaphosphate should be converted to tripolyphosphate without the formation in the slurry of a substantial proportion of gas or steam. Then, during the foaming-hydration step, only enough gas should be injected into or generated in the slurry to increase the volume of the foamed slurry as indicated above. It can be understood from the above that since the evolution of large quantities of gas from the foamed slurry in this particular aspect of the invention is not desired, the greater
proportion of the free water initially in the slurries should be removed or tied up via hydration of the tripolyphosphate, and other hydratable materials in the composition such as sodium sulfite, sodium silicate and the like. Generally, it is preferred that at least about 50 weight percent of the free water be bound as the hydrate of the tripolyphosphate. This limitation on the amount of gas generated in the slurry can be accomplished, for example, by intermixing the strong base and tripolyphosphate at a fairly low temperature, so that a large part of the heat from the conversion of tripolyphosphate to tripolyphosphate can be consumed in raising the temperature of the slurry to the boiling point of the water contained therein, or to that point at which some other gas is generated therein. Some of the heat can also be removed from the slurry by means of appropriately placed heat exchangers.

Another procedure that can be effectively utilized for the manufacture of formed low bulk density solid detergent products is one that involves the passage of a completely formulated slurry through a hot conduit, under pressure if necessary in order to prevent the evolution of steam through most of the tripolyphosphate hydration period. Then, when there remains only a fraction of the hydration to be completed, which fraction is sufficient to cause the formation of about the desired amount of foam in the slurry, the slurry is poured into a mold or container. At this point, the temperature is generally above the temperature above which gas is formed in the slurry. The continued hydration (and conversion when the tripolyphosphate reaction is utilized) causes the generation of gas in the slurry, and also the final solidification of the slurry into the desired cellular product. When conditions are utilized in these processes such that no gas is generated in the slurry, the correct proportion of gas can be injected into the slurry shortly prior to the time it solidifies in any particular desired manner, as outlined above.

It can readily appreciated from the foregoing that practically any materials that can be used in conventional processes for manufacturing detergent compositions can be used in the processes of the present invention. It is also significant that the invention need not be limited to being practiced with slurries that contain all of the ingredients usually found in conventional heat-dried detergent compositions. When alkali metal carbonate is used as the strong base in some of the processes of this invention, the resulting final products contain several percent of alkali metal bicarbonate in addition to the hydrated polyphosphate salt. And when excess alkali metal carbonate is utilized, it can appear in the final detergent product either as the carbonate or as its hydrate, depending upon the particular process conditions that are utilized. In addition, the processes described herein can be utilized for the manufacture of practically pure low bulk density sodium tripolyphosphate hexahydrate, as well as many mixed hydrated polyphosphate compositions that in turn can be utilized as raw materials in conventional processes for manufacturing detergent products.

Detergent products that are manufactured via the preferred processes of the present invention (i.e., via reaction of a sodium tripolyphosphate with a strong base containing sodium cations, such as sodium hydroxide) can be specifically identified as such due to the surprising fact that the crystalline sodium tripolyphosphate hexahydrate contained therein yields peculiar (but specific and reproducible) results when tested via conventional differential thermal analysis (D.T.A.) techniques. Thus, while crystals of sodium tripolyphosphate hydrate (STP-6H₂O) in detergents made conventionally (via hydration of anhydrous sodium tripolyphosphate) yield D.T.A. curves like that of FIGURE 3 (of the drawings), crystals of STP-6H₂O in detergent compositions made via the processes of the present invention surprisingly yield D.T.A. curves like that of FIGURE 4 (of the drawings).

One can immediately differentiate between these two types of crystals by applying conventional D.T.A. techniques to STP-6H₂O crystals that have been separated (by conventional techniques) from the other materials in the original detergent formulation. Note that while the STP-6H₂O resulting from the present processes (FIGURE 4) remains initially stable up to a temperature of about 120° C., that resulting from conventional detergent processes (FIGURE 3) never approaches 120° C., and actually loses all of its water of hydration before a temperature significantly above about 110° C. is approached. The reason or reasons for this amazing stability (of the STP-6H₂O crystals in the detergents made via the processes of the present invention) to initial thermal degradation is not known. However, lack of an explanation of why this peculiar thermal stability exists does not prevent its proper use as a method for identifying detergent products made via the present processes. Thus, if the detergent does not contain particles that have been spray-dried, if it does not contain flakes (such as would be present in drum-dried products), and if the STP-6H₂O crystals contained therein exhibit initial D.T.A. thermal degradation at a temperature between about 115° C. and about 125° C., it is a detergent composition of the present invention. In the differential thermal analysis of STP-6H₂O during the preparation of the curves shown in FIGURES 3 and 4, 0.05 gram of the material to be tested were introduced into 4 mm. glass tubes and heated under nitrogen at a rate of 4° C. per minute, starting at 20° C.

What is claimed is:

1. A process which comprises forming an aqueous slurry containing (a) at least about 8% by weight of a water-soluble alkali metal tripolyphosphate salt, (b) an amount, sufficient to convert a major proportion of said tripolyphosphate salt to a tripolyphosphate, of a base of a strength such that a 1% by weight solution of the base in distilled water provides a pH of at least about 10.2 at 25° C., (c) an amount of water at least 5% in excess of that required to hydrate said tripolyphosphate and equal to at least about 10% by weight, but not more than 50% by weight of said slurry; interpersing a gas in said slurry to form a foam; said gas being selected from the group consisting of water vapor and gases which are not reactive with the other materials in said slurry at temperatures of from about 50° C. to 135° C. while maintaining the temperature of said foam within the range of from about 50° C. to about 135° C. while removing sufficient free water from said foam to form a porous solid product containing a substantial proportion of hydrated tripolyphosphate.

2. A process as in claim 1, wherein said foam is maintained at a temperature between about 50° C. and about 12° C. while removing sufficient free water from said foam to form a porous solid product.

3. A process as in claim 1, wherein said alkali metal tripolyphosphate is sodium tripolyphosphate and said alkali metal tripolyphosphate is sodium tripolyphosphate hexahydrate.

4. A process as in claim 1, wherein said slurry also contains at least about 0.1 weight percent of a foaming agent selected from the group consisting of water soluble organic detergent active materials and water-soluble organic polymer materials.

5. A process as in claim 4, wherein said foaming agent is a water soluble organic anionic surface active agent which is compatible with said alkali metal tripolyphosphate.

6. A process as in claim 5, wherein said surface active agent is a fatty alcohol sulfate containing from about 6 to about 22 carbon atoms.

7. A process as in claim 3, wherein the amount of water initially in said slurry is at least about 20 weight percent, based on the total weight of said slurry.

8. A process as in claim 1, wherein said strong base is
selected from the group consisting of alkali metal hydroxides, alkali metal carbonates, and alkali metal silicates having SiO₂/MgO ratios, wherein M is an alkali metal cation, below about 2.  

9. A process which comprises forming an aqueous slurry by intermixing with water at least about 10 weight percent, based on the weight of the total solids of said slurry, of trisodium trimetaphosphate; interpersing a gas into at least a portion of said slurry under conditions permitting formation of light density foam, said gas being selected from the group consisting of water vapor and gases which are non-reactive with the other materials in said slurry at temperatures of from about 50° C. to 135° C.; intermixing into said slurry an amount of said surfactant group consisting of sodium hydroxide, sodium carbonate, and sodium silicates having SiO₂/Na₂O ratios below about 2; reacting a substantial proportion of said trisodium trimetaphosphate with said strong base to thereby produce sodium triphosphate hexahydrate; and removing sufficient free water from said foam to result in the production of a solid, porous composition containing said sodium triphosphate hexahydrate; the amount of water in said slurry in excess of that amount required to produce said sodium triphosphate hexahydrate being such that the heat generated by the exothermic reaction of said trisodium trimetaphosphate with said strong base is sufficient to result in the formation of said surfactant group consisting of sufficient water to convert said foam into said solid, porous product.  

10. A process which comprises the steps of (a) rapidly mixing into a stream of a precursor slurry a metered quantity of an aqueous basic solution said precursor slurry being at a temperature of from 50° C. to 135° C. and containing at least about 8% by weight of a water-soluble alkali metal trimetaphosphate salt, an amount of water such that subsequent to the addition of said basic solution the slurry contains from about 10% by weight to about 50% by weight of water, and at least about 0.1% by weight of a foaming agent selected from the group consisting of water-soluble organic detergent active materials and water-soluble organic polymer materials, and said basic solution being of a concentration such that said metered quantity thereof contains an amount of base sufficient to convert a major portion of said trisodium trimetaphosphate to sodium triphosphate and such that said slurry subsequent to the addition of said basic solution contains an amount of water at least 5% in excess of that required to hydrate said triphosphate, said base being of such strength that a 1% by weight solution thereof in distilled water provides a pH of at least about 10.2 at 25° C. (b) foaming the stream containing said basic solution onto a moving surface such that it is in a substantially unconfined state free to expand in volume due to the formation of foam and such that it loses moisture by evaporation; and (c) maintaining said foam at a temperature above about 80° C. but below about 135° C. on said moving surface until it has lost sufficient free water to form a porous solid product.  

11. A process as in claim 10, wherein said slurry initially contains at least about 10 weight percent of said sodium trimetaphosphate and at least about 0.5 weight percent of a sodium surfactant.  

12. A process as in claim 10, wherein said base is selected from the group consisting of alkali metal hydroxides, alkali metal carbonates and alkali metal silicates having SiO₂/MgO ratios (where M is an alkali metal cation) below about 2.  

13. A process as in claim 12, wherein said alkali metal trimetaphosphate is sodium trimetaphosphate.  

14. A process as in claim 13, wherein said slurry initially contains from about 13% by weight to about 60% by weight of said sodium trimetaphosphate, said foaming agent is selected from the group consisting of anionic and non-ionic detergent active materials and is present in said slurry in an amount equal to at least about 0.5% by weight of said slurry, the stream of said slurry to which said basic solution is added is at a temperature of from about 50° C. to about 120° C., said slurry, subsequent to the addition of said basic solution, contains at least 20% by weight of water, and said metered quantity of said basic solution contains a quantity of base at least stoichiometrically equivalent to the sodium trimetaphosphate present in said slurry but not more than six times that required to react with said sodium trimetaphosphate.  

15. A process as in claim 14, wherein said strong base is sodium hydroxide.  

16. A process as in claim 14, wherein said strong base is potassium hydroxide.  

17. A process which comprises intermixing water and sodium trimetaphosphate to thereby form a fluid dispersion having a continuous aqueous phase and a dispersed phase containing sodium trimetaphosphate, the total amount of said sodium trimetaphosphate in said dispersion being between about 8 and about 60 weight percent; adjusting the temperature of at least a portion of said dispersion to between about 60° C. and about 120° C.; intermixing into said portion an aqueous solution containing at least about 1.4 moles of sodium hydroxide per mole of said trimetaphosphate in said portion to thereby form a blend; allowing the heat of conversion of said sodium trimetaphosphate to sodium triphosphate to vaporize a substantial portion of the water in said blend at a temperature above about 50° C. below about 135° C. whereby said portion is formed into a light density foam; and simultaneously evaporating some of said water and hydrating said sodium triphosphate, whereby sufficient free water is removed from said portion to result in the formation of a solid, particulated composition containing sodium triphosphate hexahydrate.  

18. A process as in claim 17, wherein the temperature of said portion is maintained below about 120° C. subsequent to the addition of said sodium hydroxide.  

19. A process as in claim 17, wherein said blend additionally contains an effective amount of a water-soluble foaming agent selected from the group consisting of water-soluble organic detergent active materials and water-soluble organic polymer materials.  

20. A process as in claim 19, wherein said foaming agent is present in said blend in an amount equal to at least about 0.1 weight percent, based on the total weight of said blend.  

21. A process as in claim 19, wherein said foaming agent is a water-soluble organic detergent which is compatible with sodium trimetaphosphate.  

22. A process as in claim 21, wherein said organic detergent is a water-soluble anionic organic detergent.  

23. A process as in claim 22, wherein said anionic organic detergent is a water-soluble alkylbenzene sulfonate.  

24. A process as in claim 22, wherein said anionic organic detergent is an alkylol sulfate containing from 8 to 20 carbon atoms in its alkyl chain.  

25. A process as in claim 24, wherein the concentration of said alkylol sulfate in said blend is at least about 0.5 weight percent, based on the total weight of said blend.  

26. A process as in claim 25, wherein said blend additionally contains between about 1 and about 30 weight percent of an alkylbenzene sulfonate having from 12 to 26 carbon atoms in its molecule.  

27. A process which comprises intermixing water, sodium trimetaphosphate, and a foaming agent to thereby form an aqueous slurry containing between about 10 and about 60 weight percent of said sodium trimetaphosphate and at least about 0.5 weight percent of said foaming agent, said foaming agent being selected from the group consisting of water-soluble organic detergent active materials and water-soluble organic polymer materials; adjusting the temperature of at least a portion of said slurry to between about 70° C. and about 120° C.; intermixing into said portion an aqueous solution containing at most...
about 50 weight percent, based on the weight of said solution, of sodium hydroxide, and containing therein from about 2 to about 10 moles of said sodium hydroxide per mole of said trimetaphosphate in said portion to thereby form a blend; and thereafter maintaining the temperature of said blend below about 120° C. and at the boiling point of the water in said blend until a substantial proportion of said water is converted into steam, whereby a light density foam is formed in said portion and sufficient water is removed from said foam to result in the formation of a solid, porous composition containing sodium tripolyphosphate hexahydrate.

28. A process which comprises forming a slurry initially containing from about 20 to about 50 weight percent of water, from about 15 to about 60 weight percent of trisodium trimetaphosphate, from about 4 to about 16 weight percent of sodium hydroxide, and at least about 0.5 weight percent of a water-soluble anionic organic detergent; adjusting the temperature of at least a portion of said slurry to from about 45 to about 90° C.; permitting the temperature of said portion to increase to the boiling point of the water in said portion as a result of the exothermic reaction of said sodium hydroxide with said sodium trimetaphosphate; maintaining the temperature of said portion at about said boiling point until a substantial proportion of the water in said portion is converted into steam, whereby said portion is initially converted into a light density foam and slurry; and sufficient water is removed from said foamed slurry to thereby convert said foamed slurry into a solid, porous composition containing from about 20 to about 93 weight percent of sodium tripolyphosphate hexahydrate.

29. A process as in claim 28, wherein said slurry also contains at least about 0.5 weight percent of sodium sulfate.

30. A process for manufacturing a formed solid composition containing hydrated alkali metal tripolyphosphate and a multitude of gas-filled cells, which process comprises the steps of:

(a) intermixing sodium trimetaphosphate, water, and a strong base selected from the group consisting of alkali metal hydroxides, alkali metal carbonates, and alkali metal silicates having SiO₂/M₂O ratios (where M is an alkali metal cation) below about 2, to thereby form a fluid slurry containing from about 10 to about 60 weight percent of said sodium trimetaphosphate, at least about 10 weight percent of water and an amount of said strong base, equal to at least about the stoichiometric amount required to convert said trimetaphosphate to tripolyphosphate; (b) reacting together at least about half of said trimetaphosphate and said base without the formation in said slurry of a substantial proportion of foam;

(c) thereafter generating gas in said slurry at a temperature above about 50° C. but below about 135° C. to thereby form a foamed slurry, said gas being selected from the group consisting of water vapor and gases which are non-reactive with the other materials in said slurry at temperatures of from about 50° C. to 135° C., and the total volume of said foamed slurry being at most about 10 times the unaerated volume of said slurry; and

(d) removing a quantity of free water from said foamed slurry, said quantity being sufficient to result in the formation of said solid composition and at least about 50 weight percent of said quantity being reacted with said tripolyphosphate to form said hydrated alkali metal tripolyphosphate.

31. A process as in claim 30, wherein said alkali metal is sodium.

32. A process as in claim 31, wherein said base is sodium hydroxide.

33. A process as in claim 32, wherein step (c) is performed at a temperature below about 120° C.

34. A process as in claim 32, wherein the total volume of said foamed slurry is between about 1.5 and about 5 times the unaerated volume.

35. A process for manufacturing a detergent bar composition, which process comprises the steps of:

(a) intermixing water, a water-soluble organic detergent active material, and a material which reacts with water at a temperature below about 135° C. to produce a water-soluble alkali metal polypolyphosphate hydrate to thereby form a fluid slurry;

(b) incorporating a gas into at least a portion of said dispersion to thereby form a light density foam, said gas being selected from the group consisting of water vapor and gases which are non-reactive with the other materials in said slurry at temperatures of from about 50° C. to 135° C., and allowing at least a substantial proportion of said material to react with at least a portion of said water to form said polypolyphosphate hydrate while said portion of said dispersion is in a foam condition and at a temperature of from about 50° C. to about 135° C.;

(c) removing sufficient free water from the continuous aqueous phase of said foam while said material is being reacted with said water to thereby form a solid, particulated porous product containing hydrated alkali metal polypolyphosphate and said water-soluble organic detergent active material; and

(d) compressing, extruding and cutting said product to thereby form said detergent bar composition.

36. A tabulated composition manufactured in accordance with the process of claim 35.

37. A solid, particulated detergent composition manufactured in accordance with the process of claim 28.

38. A detergent composition containing a water-soluble organic detergent active material from about 10 to about 75 weight percent of sodium trimetaphosphate hexahydrate crystals, said crystals exhibiting an initial de-hydration point, by differential thermal analyses, between about 115° C. and about 125° C.

39. A detergent bar composition manufactured in accordance with the process of claim 35.

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