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2,897,155

PROCESS FOR PREPARING A DETERGENT COMPOSITION CONTAINING ANHYDROUS FORM II TRIPOLYPHOSPHATE

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No Drawing. Application July 27, 1955
Serial No. 524,820

5 Claims. (Cl. 252-109)

The present invention relates to a process for preparing non-caking, free flowing detergent compositions containing sodium tripolyphosphate, and more particularly to a process for preparing a heat dried detergent composition containing sodium tripolyphosphate in anhydrous Form II.

Sodium tripolyphosphate is either anhydrous or hydrated and the anhydrous crystalline form may be either Form I or Form II, the anhydrous tripolyphosphate produced in the high temperature regions being known as Form I, while the anhydrous tripolyphosphate produced in the low temperature regions is known as Form II. The process of this invention utilizes the Form II anhydrous sodium tripolyphosphate.

Detergent compositions containing tripolyphosphates have advantages over detergent compositions containing other phosphates, such as pyrophosphates or orthophosphates. Repeat washing tests in hard water indicate that clothes washed with detergent compositions containing tripolyphosphates have a lower ash content than clothes washed with detergent compositions containing a pyrophosphate. A given weight of a tripolyphosphate sequesters more calcium from the wash water than does a pyrophosphate, and hence clearer solutions are obtainable in hard waters with detergent compositions containing tripolyphosphates than with detergent compositions containing pyrophosphates.

Under the conditions of preparation of detergent compositions containing sodium tripolyphosphate in granulated, powdered, or flake form, difficulty has been encountered heretofore due to decomposition of the sodium tripolyphosphate into less desirable and sometimes objectionable pyrophosphates and orthophosphates. One objectionable result of such decomposition is a drop in the pH of solutions of the resulting product. The art has compensated for this result by adding additional alkaline material to the composition rather than by devising ways of avoiding the decomposition. Another objectionable result of the decomposition is the release of free silica by the reaction of the acid phosphate formed with the silicate usually present in such compositions. This free silica causes solutions of the product to have a turbid, cloudy appearance which the consumer finds objectionable. It is, therefore, the object of the present invention to provide a process of preparing a detergent composition in heat dried form containing primarily anhydrous Form II sodium tripolyphosphate and a minimum of the decomposition products thereof.

In addition to overcoming the disadvantages enumerated above and at the same time providing a detergent composition containing and having the advantages of so-

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dium tripolyphosphate, the process avoids troublesome viscosity changes in a spray mix of the detergent composition both in the crutcher and during the time between the completion of the mixing operation and the arrival of the mix at a spray nozzle. Such viscosity changes normally occur when the sodium tripolyphosphate is allowed to hydrate slowly to the hexahydrate. The process further prevents the formation of hard lumps in a spray mix which are troublesome in pumping and spraying. Moreover, the process employs small amounts of water and thereby results in high production rates of the dried detergent composition and minimum consumption of heat energy for the evaporation of free and combined water during the heat drying of the detergent composition. The process further provides a heat dried detergent composition which is free flowing and which does not cake in packaged form.

Form II sodium tripolyphosphates from different suppliers or from different lots from the same supplier or which have been exposed to different conditions in transit or in storage exhibit markedly different rates of hydration upon addition to an aqueous mixture. These differing hydration rates make it impossible to obtain a uniform detergent product without frequent adjustment of processing conditions. The process of the invention can make use of any Form II sodium tripolyphosphate without regard to its hydration rate, to yield a substantially uniform product.

In general, the process of the invention comprises adding any anhydrous Form II sodium tripolyphosphate to an aqueous slurry of an organic detergent and inorganic salt builders, the slurry having a low water content and a high temperature, and then agitating and heat drying the slurry. More specifically the process is one of preparing a free flowing heat dried detergent composition containing primarily anhydrous Form II sodium tripolyphosphate and a minimum of decomposition products thereof comprising adding any anhydrous Form II sodium tripolyphosphate to an aqueous slurry containing at least one organic detergent and inorganic salt builders to form a slurry having only sufficient moisture to maintain a pumpable and sprayable slurry, the slurry having a temperature in the range from about 160° F. to about 200° F.; agitating the slurry within this temperature range; and heat drying the slurry.

Primarily anhydrous Form II sodium tripolyphosphate means that no more than about 10% of the sodium tripolyphosphate present in the heat dried detergent composition is in the hexahydrate form. A minimum of decomposition products of anhydrous Form II sodium tripolyphosphate denotes (that the detergent composition contains) at least 90% of the sodium tripolyphosphate originally charged to the crutcher.

The water content of the aqueous slurry, the temperature thereof during agitation in a crutcher and during any interval between the agitation and heat drying, and the order of addition of the tripolyphosphate to the slurry are critical features of the process.

The moisture content of the aqueous slurry should be kept at a minimum to prevent the hydrolytic decomposition of the tripolyphosphates into the undesirable ortho- and pyrophosphates and to minimize hexahydrate formation. The moisture content, however, must still be maintained at a sufficient level to enable the slurry to be

pumped from a crutcher wherein the detergent composition may be compounded to a heat dryer, such as a spray dryer. The exact amount of water necessary to maintain a pumpable and sprayable slurry will vary with the physical state of the components of the composition, and the ruggedness of the processing equipment. If, for example, the organic detergent component is in a liquid state rather than in a solid state, then less water is necessary in the aqueous slurry. Also, if the processing equipment is capable of handling a viscous slurry, then too the water content might be quite low. The exact moisture content necessary may be readily determined by those skilled in the art. Thus, in some instances, the water content may be about 15% if one or more of the components of the composition is a fluid, whereas if the components are primarily solids when added to the aqueous slurry, then the water content of the slurry may be about 40%, or even 50% provided a slow hydrating anhydrous Form II sodium tripolyphosphate is being processed.

The high temperature of from about 160° F. to about 200° F. and preferably from about 185° F. to about 195° F. (particularly for the fast hydrating sodium tripolyphosphates) greatly lessens the extent of the hydration of the anhydrous Form II sodium tripolyphosphate. Since the hexahydrate formed by hydration is known to decompose into objectionable ortho- and pyrophosphates upon heat drying, it is essential to eliminate the formation of the hexahydrate to the greatest extent possible. While any hexahydrate formed during processing may be reconstituted into anhydrous tripolyphosphate by heat drying at very high temperatures, such an expedient is undesirable from the standpoint of cost.

The sodium tripolyphosphate preferably is added to the aqueous slurry as the last-added component of the detergent composition, or is added to the slurry at least as late in point of time prior to heat drying as possible. Earlier addition results in the formation of excessive amounts of the hexahydrate. The presence of the inorganic salt builders in the aqueous slurry at the time of addition of the sodium tripolyphosphate thereto, delays the formation of the hexahydrate and decomposition products.

The time of agitating the aqueous slurry containing the added sodium tripolyphosphate and any subsequent interval between the agitating and heat drying thereof should be kept at a minimum. In general, this time should not exceed about one hour and a half and it is preferred that this time not exceed about one hour. A longer period permits hydration and hydrolysis of the of the anhydrous Form II sodium tripolyphosphate into undesirable decomposition products.

Any organic detergent may be employed in this process. The organic detergent may include ordinary soaps, such as the alkali metal salts, e.g., sodium, of the higher saturated and unsaturated fatty acids containing from eight to twenty-four carbon atoms and synthetic organic non-soap detergents including the well known anionic, nonionic, and cationic detergents. Typical anionic detergents include water-soluble salts of sulfuric and phosphoric acid reaction products of alkyl and substituted alkyl compounds containing from eight to eighteen carbon atoms in the alkyl group. Nonionic detergents include, for example, the reaction products of higher alcohols and higher fatty acids with considerable amounts of alkylene oxides, while cationic detergents include certain quaternary ammonium groups and certain amine groups neutralized with acids each of which is preferably employed in its water-soluble salt form. Such synthetic organic non-soap detergents are well known to those skilled in the art and suitable detergents are well described in the literature, for example, in U.S. Patents Nos. 2,396,278, 2,477,383, 2,674,619 and 2,677,700.

The amount of the organic detergent present in the detergent composition may vary with the product desired

and is in no way critical to this process, conventional proportions being used, for example 18%.

The amount of the anhydrous Form II sodium tripolyphosphate is generally in the range from about 25% to about 40%, but here too the amount is not critical to the process of the invention.

The aqueous slurry containing an organic detergent and the detergent compositions formed by this process contain in addition to the organic detergent inorganic salt builders such as alkaline, e.g., sodium, phosphates, carbonates, sulfates, borates and silicates, and may contain organic builders, dyes, perfumes, preservatives and other substances commonly employed in preparing detergent compositions.

In the process any heat drying step may be used, such as spray drying or drum drying to form a dried detergent composition in powdered, threaded or flaked form. Spray drying may be done, for example, in a conventional spray drier at an air inlet temperature of from 400° F. to 435° F., and an air outlet temperature of from 230° F. to 240° F.

The process will be further illustrated in detail in connection with the following examples.

EXAMPLE I

1050 pounds of anhydrous Form II sodium tripolyphosphate was added as the last component of the composition to an aqueous slurry of an organic detergent having a temperature of 185–190 F. in a conventional crutcher and the slurry agitated, the slurry then having the following composition:

	Weight in pounds
Water -----	200.00
Dried soap chips from a kettle charge of 80% tallow, 20% coconut oil saponified with caustic soda -----	30.00
Sodium silicate (46.8% solids of a ratio of Na ₂ O to SiO ₂ of 1 to 2.4) -----	640.00
Sodium carboxymethyl hydroxyethyl cellulose -	15.00
Pluronic L-64 (a compound having the empirical formula	
$\text{HO}-(\text{C}_2\text{H}_4\text{O})_a(\text{C}_3\text{H}_6\text{O})_b(\text{C}_2\text{H}_4\text{O})_c\text{H}$	
prepared by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol where <i>b</i> is an integer selected from the group consisting of 26 to 30, and <i>a</i> plus <i>c</i> is an integer such that the molecule contains from 40% to 50% of ethylene oxide) -----	262.50
Oronite dispersant NIW (a polypropylene alkyl phenol averaging tetradecyl in the alkyl radical condensed with ethylene oxide to an average of nine ethylene oxide groups) ----	39.50
Monastral Green (copper halophthalocyanine) -	.81
Monastral Blue (copper phthalocyanine) -----	.27
Sodium carbonate -----	450.00
Sodium sulfate -----	552.70
Fluorescent whitening agent (sodium diethanol-amino anilino amino stilbene disulfonate) --	2.10
Sodium tripolyphosphate -----	1,050.00
Total -----	3,243.88

The crutcher charge contained 15.2% water.

The crutcher charge, or slurry, was maintained at a temperature of 185–195° F. while being pumped from the crutcher to a booster tank and then into a conventional spray drying tower in one hour's time. The air inlet temperature of the spray drying tower was 435° F. and the air outlet temperature was 240° F.

The resulting free flowing spray dried detergent composition contained 1.06% sodium orthophosphate, 4.70% tetrasodium pyrophosphate, and 31.81% sodium tripolyphosphate. All of the sodium tripolyphosphate was an-

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hydrous Form II with no hexahydrate being detectable by X-ray diffraction analysis.

It will be noted that in the above example the anhydrous Form II sodium tripolyphosphate was added as the last component to the aqueous slurry, that the temperature of the slurry was maintained within the preferred range of 185–195° F., and that the slurry contained only sufficient moisture to maintain it pumpable and sprayable. In this example, the moisture content was quite low, 15.2%, since the organic detergent components of the composition were liquids rather than solids.

The following two examples set forth in Table I further illustrate the process of the invention. In these examples the slurries were spray dried in a tower having an air temperature of 550° F.

Table I

Compositions (percent by weight)	Ex. 2	Ex. 3	Ex. 4
Sodium polypropylene benzene sulfonate (C ₁₂ alkyl) (sodium oronite).....	18	18	18
Lauric isopropanolamide.....	3.5	3.5	3.5
Sodium toluene sulfonate.....	2	2	2
Sodium tripolyphosphate.....	40	40	40
Sodium silicate.....	6	6	6
Sodium carboxymethyl cellulose.....	0.5	0.5	0.5
Water.....	7	7	7
Sodium sulfate.....	20.1	20.1	20.1
Miscellaneous.....	2.9	2.9	2.9
Operating data:			
Percent water in slurry.....	40	40	50
Temperature of slurry (°F.).....	160	190	190
Mixing time (after addition of tripolyphosphate) (minutes).....	30	45	45
Order of addition of anhydrous Form II tripolyphosphate.....	Last	Last	Last
Analytical data of final product:			
Percent moisture.....	4.6	3.9	6.4
Percent of tripolyphosphate which is in anhydrous Form II.....	90	100	100
Percent of tripolyphosphate which is in form of the hexahydrate.....	10	0	0

In Examples 2 and 3 a slow hydrating anhydrous Form II sodium tripolyphosphate was added last to the aqueous slurries, the temperature of the slurries was maintained at from 160° F. to 200° F., and the slurries contained only sufficient moisture to maintain them pumpable and sprayable. In these examples, however, the moisture content of the aqueous slurries was higher than in Example 1, i.e., 40%, since the components of the detergent compositions were in a solid state rather than some of them being in a liquid state. Example 4 shows that the moisture content of the slurry may be raised slightly at a temperature in the preferred range provided a slow hydrating anhydrous Form II sodium tripolyphosphate is being processed.

In Table II below, there are set forth Examples 5–7 which show the criticality of adding the anhydrous Form II sodium tripolyphosphate last to the aqueous slurry of the detergent composition, of maintaining the tempera-

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ture of the slurry at from 160° F. to 200° F., and of providing in the aqueous slurry only sufficient moisture to make the slurry pumpable and sprayable. In these examples the spray drying conditions were the same as in Examples 2–4 illustrating the process of the invention.

Table II

Compositions (percent by weight)	Ex. 5	Ex. 6	Ex. 7
Sodium polypropylene benzene sulfonate (C ₁₂ alkyl) (sodium oronite).....	18	18	18
Lauric isopropanolamide.....	3.5	3.5	3.5
Sodium toluene sulfonate.....	2	2	2
Sodium tripolyphosphate.....	40	40	40
Sodium silicate.....	12	6	6
Sodium carboxymethyl cellulose.....	0.5	0.5	0.5
Water.....	7	7	7
Sodium sulfate.....	14.1	20.1	20.1
Miscellaneous.....	2.9	2.9	2.9
Operating data:			
Percent water in slurry.....	40	40	50
Temperature of slurry (°F.).....	160	190	160
Mixing time (after addition of tripolyphosphate) (minutes).....	5	45	45
Order of addition of anhydrous Form II tripolyphosphate.....	¹ Third	² Second	Last
Analytical data of final product:			
Percent moisture.....	6.4	2.2	11.4
Percent of tripolyphosphate which is in anhydrous Form II.....	70	80	20
Percent of tripolyphosphate which is in form of hexahydrate.....	30	20	80

¹ After water and oronite.

² After water.

Examples 5 and 6 show that when the anhydrous Form II sodium tripolyphosphate is not added last or at least as late as possible, that even at the preferred temperature of 190° F., as well as the lower operable temperature of 160° F. for agitation of the slurry, undesirably high amounts of the hexahydrate form of the tripolyphosphate are obtained, i.e., the sodium tripolyphosphate content of the detergent composition is not primarily anhydrous Form II. Example 7 shows that even if the anhydrous Form II sodium tripolyphosphate is added last to the slurry, a moisture content of the aqueous slurry in excess of that which is only sufficient to maintain the slurry pumpable and sprayable will produce undesirably high amounts of the hexahydrate at a temperature of 160° F.

The following Examples 8–13 in Table III below further explain the process of the invention and the necessity for the conditions used therein. In these examples the tower temperature and the compositions were identical to those shown in Examples 2–4 except that a fast hydrating anhydrous Form II sodium tripolyphosphate was used rather than a slow hydrating one. The fast hydrating anhydrous Form II sodium tripolyphosphate added to the slurry analyzed 0.92% orthophosphate, 11.39% pyrophosphate, and 87.70% tripolyphosphate, expressed as percentages of P₂O₅ due to ortho, pyro, and tripoly phosphates respectively of the total P₂O₅ content.

Table III

	Example 8	Example 9	Example 10	Example 11	Example 12	Example 13
Operating data:						
Percent water in slurry.....	40	40	50	50	50	50
Temperature of slurry (°F.).....	190	190	160	160	190	190
Mixing time (after addition of tripolyphosphate) (minutes).....	45	240	45	240	45	240
Order of addition of anhydrous Form II tripolyphosphate.....	Last	Last	Last	Last	Last	Last
Analysis of phosphate content of slurry after mixing time.....	90% anhydrous, 10% hexahydrate.	100% hexahydrate.	100% hexahydrate.	100% hexahydrate.	40% anhydrous, 60% hexahydrate.	100% hexahydrate.
Analytical data of final product:						
Percent moisture.....	3.2	4.6	4.2	4.2	5.2	4.2
Percent of tripolyphosphate which is in anhydrous Form II.....	90				Some	
Percent of tripolyphosphate which is in form of hexahydrate.....	10	20	50	40	30	40
Percent sodium tripolyphosphate (expressed as percent P ₂ O ₅ due to polyphosphates/total P ₂ O ₅).....	86.93	35.20	45.41	54.35	41.04	30.44
Percent sodium pyrophosphate (expressed as percent P ₂ O ₅ due to pyrophosphates/total P ₂ O ₅).....	10.26	56.11	47.90	40.34	51.48	60.15
Percent orthophosphate (expressed as percent P ₂ O ₅ due to orthophosphates/total P ₂ O ₅).....	2.81	8.60	6.69	5.31	7.48	9.40

Example 8 was run in accordance with the process of the invention while the remaining Examples 9-13 departed from the process of the invention in the moisture content of the slurry, and/or the time of mixing prior to heat drying. In Examples 9-13 very high percentages of the hexahydrate were formed in the slurry by the end of the mixing time and large amounts of decomposition products, i.e., ortho- and pyrophosphates were present in the final product. This clearly demonstrates the importance of preventing the formation of the hexahydrate by following the conditions of the process of the invention, since it is the hexahydrate which has decomposed into these objectionable ortho- and pyrophosphates.

It will be understood that various modifications may be made in the process of this invention without departing from the spirit thereof and hence the invention is to be limited only within the scope of the appended claims.

I claim:

1. The process of preparing a free flowing heat dried detergent composition containing from about 25% to about 40% of primarily anhydrous Form II sodium tripolyphosphate and a minimum of decomposition products thereof comprising adding last any anhydrous Form II sodium tripolyphosphate to an aqueous slurry of the detergent composition containing an organic detergent of the group consisting of water-soluble alkali metal soaps and water-soluble non-soap synthetic detergents plus water-soluble inorganic builder salts to form a slurry having only sufficient moisture to maintain a pumpable and sprayable slurry, the slurry having a temperature in the range from about 160° F. to about 200° F.; agitating the slurry within said temperature range for a period not more than about one hour; and then heat drying the slurry.

2. The process as set forth in claim 1 wherein the slurry contains from about 15% to about 50% water and has a temperature in the range from about 180° F. to about 195° F.

3. The process of preparing a free flowing spray dried detergent composition containing from about 25% to about 40% of primarily anhydrous Form II sodium tripolyphosphate and a minimum of decomposition products thereof comprising adding last any anhydrous Form II

sodium tripolyphosphate to an aqueous slurry containing at least one liquid water-soluble non-soap synthetic organic detergent and water-soluble inorganic builder salts, said slurry containing about 10% water, and having a temperature in the range from about 180° F. to about 195° F.; agitating the slurry within said temperature range for a period not more than about one hour; and then spray drying the slurry.

4. The process as set forth in claim 3 wherein the slurry contains a compound having the empirical formula $\text{HO}-(\text{C}_2\text{H}_4\text{O})_a(\text{C}_3\text{H}_6\text{O})_b(\text{C}_2\text{H}_4\text{O})_c$ prepared by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol where b is an integer selected from the group consisting of 26 to 30 and a plus c is an integer such that the molecule contains from 40% to 50% ethylene oxide, a polypropylene alkyl phenol averaging tetradecyl in the alkyl radical condensed with ethylene oxide to an average of 9 ethylene oxide groups, a water-soluble alkali metal soap, and water-soluble inorganic builder salts.

5. The process of preparing a free flowing spray dried detergent composition containing from about 25% to about 40% of primarily anhydrous Form II sodium tripolyphosphate and a minimum of decomposition products thereof comprising adding last any anhydrous Form II sodium tripolyphosphate to an aqueous slurry of the detergent composition whose components were primarily solids when added to the slurry and include an organic detergent of the group consisting of water-soluble alkali metal soaps and water-soluble non-soap synthetic detergents plus water-soluble inorganic builder salts, said slurry containing about 40% water and having a temperature in the range from about 180° F. to about 195° F.; agitating the slurry within said temperature range for a period not more than about one hour; and then spray drying the slurry.

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