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METHOD FOR PREPARING DETERGENT COMPOSITIONS

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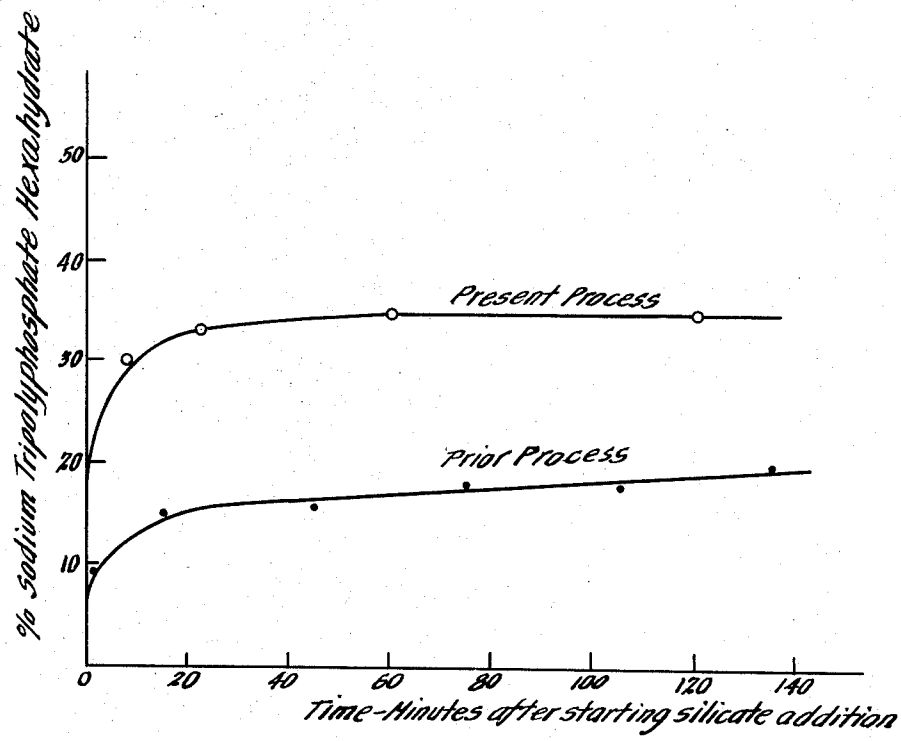

o Chlorinated trisodium phosphate added after silicate addition

• Chlorinated trisodium phosphate added before silicate addition.

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METHOD FOR PREPARING DETERGENT COMPOSITIONS

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This invention relates to a method for preparing detergent compositions.

More expressly, this invention relates to a method for preparing detergent compositions which are particularly useful in automatic dishwashing machines.

Detergent compositions comprising in combination an alkaline detergent salt (e.g. sodium metasilicate), an alkaline condensed phosphate (e.g. sodium tripolyphosphate), and chlorinated trisodium phosphate have been suggested as having particular utility for dishwashing applications (U.S. Letters Patent 2,689,225). The formulation of such compositions, which are made up of agglomerates of the various ingredients, has heretofore been accomplished through the addition of aqueous silicate to a mechanical mixture of alkaline condensed phosphate and chlorinated trisodium phosphate.

It has now been observed that a composition prepared in this manner and packed in cardboard cartons is characterized by a tendency to cake during normal storage and to form a gum or gel in use. This latter characteristic is particularly evident when such a composition is used in a dishwashing machine which has two wash cycles, i.e., two distinct intervals of operating time with a detergent present in the water. Machines of this type normally contain two cups for holding a detergent composition, each of which automatically releases the detergent into the machine near the beginning of the successive wash cycles. With detergent compositions prepared as pointed out above, the detergent present in the cup adjusted to release near the beginning of the second wash cycle usually becomes gummy and does not completely discharge from the detergent cup—a condition which is objectionable for several apparent reasons.

It is an object of this invention to provide a means for preparing detergent compositions suitable for dishwashing applications which are essentially free of the aforementioned undesirable characteristics.

Other objects and advantages will be apparent from the following detailed description and accompanying drawing, which is a comparison of the rate of hydration of sodium tripolyphosphate in a particular detergent composition when that composition is prepared in accordance with the process of the present invention and when the composition is prepared by prior methods.

Although we do not wish to be bound by any theoretical considerations, it is our belief that the undesirable characteristics of the aforementioned compositions prepared by previously known methods is due to the slow rate at which the condensed phosphate in the mixture hydrates. Thus, with these prior processes, extremely long curing times for the mixture (during which time, hydration of the phosphate apparently proceeds to substantial completeness) prior to grinding, screening to size, and packing are necessary if caking and gumming of the product is to be avoided. We further believe that the chlorinated trisodium phosphate in the mixture apparently inhibits rapid hydration of the condensed phosphate and

thus gives rise to the above mentioned defects in the product.

We have now found a method whereby detergent compositions may be prepared which exhibit none of the aforementioned undesirable characteristics although such compositions comprise the constituents set forth hereinbefore.

Generally speaking, this process comprises adding water and a water-soluble alkali-metal silicate to a condensed anhydrous water-soluble alkali-metal phosphate whereby substantial hydration of the phosphate is obtained before any chlorinated trisodium phosphate is introduced into the mixture.

Wherever it appears herein, the term "alkaline condensed phosphate" is used to designated those polyphosphates of the calcium and magnesium ion sequestering type whose Na_2O/P_2O_5 ratios range from 1:1 to 1.67:1. The term "alkali metal silicate" indicates those silicates having an average SiO_2/alkali metal oxide ratio of about 2.0 to 3.4 and includes mixtures of silicates having dissimilar SiO_2/alkali metal oxide ratios. The term "chlorinated trisodium phosphate" is used to designate a composition consisting of trisodium phosphate and sodium hypochlorite in intimate association in a crystalline form. The chlorinated trisodium phosphate may contain from 1% to 5% available chlorine and may be prepared by the methods of U.S. Letters Patent 1,555,474 or 1,965,304, or modifications thereof.

The essence of our invention lies in the particular sequence in which the various constituents of the detergent compositions are admixed. We have found that in order to obtain a composition comprising the aforementioned constituents which is characterized by resistance to caking on storage and formation of difficultly soluble gels in use, the particular sequence of steps herein described must be closely adhered to.

By way of illustration, a dishwashing composition comprising, by weight, 45 parts sodium tripolyphosphate, 32 parts of a 41% aqueous solution of sodium silicate having an average SiO_2/Na_2O ratio of about 2.9, and 20 parts chlorinated trisodium phosphate was prepared in accordance with the process of our invention in the following manner:

The sodium tripolyphosphate, in a substantially anhydrous condition, and at room temperature, was placed in a ribbon mixer wherein the sodium silicate in the form of a 41% aqueous solution, heated to a temperature of about 100–120° F. to control viscosity, was sprayed onto the phosphate while it was being agitated. The addition of the aqueous silicate caused hydration of the tripolyphosphate to take place with the evolution of heat. Consequently, in order to maintain the phosphate-silicate mixture in a non-liquid condition, precautions were taken to prevent the temperature of the mix from rising above about 130° F. (Above this temperature, this mixture losses its discrete particle characteristic and becomes pasty.) Following the addition of the entire amount of silicate solution, the chlorinated trisodium phosphate was added and the entire mixture was then cooled to room temperature with continuous agitation. The resultant mixture was then allowed to age for about four hours. During this aging period, while hydration of the tripolyphosphate was proceeding to substantial completion, the mixture was intermittently stirred to prevent solidification into a hard mass. After completion of the aging period, the agglomerates resulting from the foregoing process were reduced to the desired size for subsequent packaging.

In connection with the theoretical considerations hereinbefore expressed, a comparison was made of the rate of hydration of the alkaline condensed phosphate in deter-

gent composition comprising the aforementioned ingredients when such composition was prepared (1) according to the method of our invention and (2) according to prior art methods. This comparison is graphically shown in the accompanying drawing.

Of the two detergent compositions represented in the drawing and comprising the constituents of the foregoing illustration, one was prepared in accordance with the process of the said illustration—the process of our invention—and the second was prepared by first mechanically mixing the sodium tripolyphosphate and the chlorinated trisodium phosphate and then spraying the aqueous silicate solution onto this mixture. The rate of hydration of the sodium tripolyphosphate in each of these mixtures, as depicted by the curves of the drawing, was based upon the amount of the hexahydrate of this phosphate present in the composition after certain periods of time as determined by X-ray diffraction measurements.

It is apparent from the drawing that the sodium tripolyphosphate in the detergent composition prepared in accordance with the present process hydrates at a much more rapid rate than it does in the detergent composition prepared according to prior methods.

Although our process has been described herein as a batch operation, it is to be appreciated that it can also be readily carried out as a semi-continuous or continuous operation. Moreover, phosphates other than tripolyphosphate, for example, tretrasodium pyrophosphate and the higher phosphates, can be used to advantage. It is also to be appreciated that other silicates can be used, the average SiO_2/alkali metal oxide ratio of such silicates as we have found suitable being in the range from about 2.0 to about 3.4 and more preferably in the range from about 2.7 to about 2.9.

These silicates can be added in our process in a number of different ways. They can be in dry powder form—this would call for the independent addition of water to hydrate the alkaline condensed phosphate—or they can be in aqueous solution—serving as the carrier for at least a portion of the water required for the desired hydration of the phosphate. Alternatively, a portion of the silicate, normally in the form of an aqueous solution, can be added to the alkaline condensed phosphate prior to addition of the chlorinated phosphate with the remaining amount of silicate being added after the chlorinated phosphate addition. We have found that when observing the precautions relative to moisture addition, as pointed out hereinafter, at least about 50% of the water which is to be added, whether such water is added independently or in combination in an aqueous silicate solution, should be added prior to addition of the chlorinated trisodium phosphate if the benefits of our invention are to be realized. In any event, the addition of the alkali-metal silicate prior to the chlorinated trisodium phosphate addition appears to promote the desired agglomeration of the product constituents.

Regardless of whether the water is added independently, as when the silicate is in the form of a dry powder, or in combinaiton in an aqueous silicate solution, the addition of amounts of water from about 12% to about 25% by weight of the finished product (exclusive of that water introduced with the chlorinated trisodium phosphate) find ready application in our process. However, the amount of water must be at least adequate in all cases to wet the condensed phosphate sufficiently to induce agglomeration of the constituents. Normally, the total amount of water which we prefer to add, either independently or in combinaton in an aqueous silicate solution, is sufficient to theoretically completely hydrate the condensed phosphate. The total amount of water added, however, should not be in excess of that amount which will allow the condensed phosphate-silicate mixture to maintain its discrete particle characteristic.

If desired, a non-ionic detergent, such as the Pluronics (condensates of ethylene oxide with a hydrophobic base formed by condensing propylene oxide with propylene glycol—marketed by Wyandotte Chemicals Corp.) or the Hyonics (e.g. fatty alkylolamides—marketed by Nopco Chemical Co.) can be used in conjunction with the aforementioned constituents in a detergent composition. Although in our process the point of addition of such nonionic detergent, normally in the form of an aqueous solution, is not critical, we have found indications that it aids in promoting agglomeration of the constituents and promotes, in general, further improvements in the caking and gumming or gelling characteristics of the product.

Detergent compositions which can be advantageously prepared by our process comprise in combination from about 35% to about 60% alkaline condensed phosphate, from about 8% to about 20% alkali metal silicate as silicate solids, and from about 15% to about 30% of chlorinated trisodium phosphate with or without the addition of a non-ionic detergent agent.

Also, we have found that some additional benefits in product caking and gumming or gelling characteristics can be obtained by adding other ingredients to the detergent composition prepared in accordance with our process. Additives which we have found to be particularly advantageous for these purposes include such endothermic, rapidly dissolving salts as urea and potassium nitrate, hydrated salts such as hydrated ortho-, pyro-, and tripolyphosphate, and inert diluents such as silica and talc.

In the following examples, which are merely illustrative, our invention being limited only by the scope of the appended claims, all parts are by weight.

Example I

3.6 parts of substantially anhydrous granular sodium tripolyphosphate and 1.6 parts of chlorinated trisodium phosphate crystals were placed in a paddle-type mixer. 2.6 parts of a 41% aqueous solution of sodium silicate having an average SiO_2/Na_2O ratio of 2.8 was slowly poured, at room temperature, over the phosphates, while they were being agitated, during a period of about 3 minutes. During this silicate addition, agglomerates ranging from the size of grains of sand to marbles formed, while the temperature of the mixture rose from 82° to 95° F. These agglomerates were then aged in the mixer for about 15 minutes with periodic agitation every two to three minutes. The temperature of the agglomerates rose to 113° F. during this aging period.

The agglomerates were granulated in a low-speed hammer mill to pass a 10-mesh Tyler screen, and this product was immediately packed into cardboard cartons. After two hours, the pouring characteristics of the product were noted. The product was then repacked in cardboard cartons, allowed to stand at room temperature for 24 hours, and the pouring characteristics were again noted.

A second detergent composition was prepared in accordance with the above procedure except that the silicate solution was added prior to the addition of the chlorinated trisodium phosphate. During the silicate addition, the temperature in the mixer rose from 84° to 114° F. and then dropped to 108° F. after a 15-minute aging period. The pouring characteristics of the product were observed in the same manner as above described.

It was observed from these pouring tests that the addition of the silicate solution prior to the addition of chlorinated trisodium phosphate resulted in a product having markedly superior characteristics, especially with regard to resistance to caking.

It has been pointed out hereinbefore that detergent compositions comprising an alkaline condensed phosphate, an alkali-metal silicate, and chlorinated trisodium phosphate, when prepared by adding aqueous silicate to a mechanical mixture of the the phosphates, tend to form a gum or gel in use and that this characteristic is particularly evident when such composition is used in a dishwashing machine having two wash cycles. In the

following examples, a comparison is made of the gumming and/or gelling tendencies of detergent compositions prepared by the above method and by the method of our invention. Since this characteristic can be appropriately evaluated through practical use in an automatic dishwasher utilizing two wash cycles, the data appearing in the subsequent examples were obtained through this medium.

The particular dishwashing machine used for the evaluations had two separate detergent cups, each having a capacity of about 20 cc., which were filled with the product to be tested. The machine cycle was as follows: First wash, second wash; first rinse; second rinse. During the first wash cycle, the detergent in one of the cups was washed out by the water action in the machine and was utilized in this wash cycle. During this time, the detergent in the second cup was protected against washing out but did come into contact with steam and spray during the first wash cycle. At the beginning of the second wash cycle, the detergent in the second cup was made available to the water action in the machine and was washed out of the cup and utilized in this second wash. The degree of gumming and/or gelling was determined by observing the proportionate amount of detergent retained by the second cup after each of the second wash, first rinse, and second rinse cycles.

Example 2

The detergent compositions prepared in accordance with the processes outlined in Example 1 after aging for two hours were used in a dishwasher of the type described above. The figures appearing in the table below represent the proportionate amount of detergent retained in the second detergent cup after completion of the cycle indicated.

Chlorinated Trisodium Phosphate Added	Amount of Product Retained in Second Cup	
	Before Silicate	After Silicate
Second Wash Cycle	1/3	1/8
First Rinse Cycle	1/4	0
Second Rinse Cycle	1/8	0

It may be readily seen from the above data that the process of our invention results in a detergent product which has remarkably superior resistance to gumming or gelling.

Example 3

A number of detergent compositions, each comprising 45 parts by weight sodium tripolyphosphate, 32 parts by weight of a 41% aqueous solution of sodium silicate having an average SiO_2/Na_2O ratio of 2.9, and 20 parts by weight of chlorinated trisodium phosphate, were prepared according to the following general processes. In all cases, subsequent to the addition of the last product constituent, the products were aged for about 15 minutes during which time they were intermittently agitated, and the resultant agglomerates were reduced in size to pass a 10-mesh Tyler screen.

Sample A.—The sodium silicate, in the form of a 41% aqueous solution, was added to a mechanical mixture of the sodium tripolyphosphate and chlorinated trisodium phosphate.

Sample B.—The sodium silicate, in the form of a 41% aqueous solution, was added to the sodium tripolyphosphate prior to the addition thereto of the chlorinated trisodium phosphate.

Sample C.—90% of the total aqueous sodium silicate solution to be used was added to the tripolyphosphate prior to the addition thereto of the chlorinated trisodium phosphate. The remaining 10% of the silicate solution was added subsequent to the chlorinated trisodium phosphate addition.

Sample D.—70% of the total aqueous sodium silicate solution was added prior to the chlorinated trisodium phosphate addition and the remaining 30% was added subsequent to the chlorinated trisodium phosphate addition.

Each of the samples was evaluated for gumming and gelling characteristics by means of the double cup dishwasher test described above, with the results indicated in the table below. All figures shown represent the proportionate amount of detergent retained in the second detergent cup.

	Product Retained in Second Cup			
	Sample A	Sample B	Sample C	Sample D
Second Wash Cycle	1/3	1/8	0	0
First Rinse Cycle	1/4	0	0	0
Second Rinse Cycle	1/8	0	0	0

Example 4

300 parts of substantially anhydrous sodium tripolyphosphate and 114 parts of sodium silicate having an average SiO_2/Na_2O ratio of about 2.6 were placed in a paddle-type mixer and thoroughly mixed. 88 parts of water were then added to the phosphate-silicate mixture. To the resultant mixture, 133 parts of chlorinated trisodium phosphate and 20 parts of Pluronic L62 (a condensate of ethylene oxide with a hydrophobic base formed by condensing propylene oxide with propylene glycol, the composition having a molecular weight of 2500) were added and thoroughly mixed. The resultant mixture was allowed to age with intermittent agitation. The agglomerates formed during the foregoing process were reduced to the desired size.

The product was evaluated for gumming and gelling characteristics by means of the double cup dishwasher test described hereinbefore with the results indicated below:

Second wash cycle	0
First rinse cycle	0
Second rinse cycle	0

These values, representing the proportionate amount of detergent contained in the second detergent cup, may be compared with the values obtained in the previous examples wherein the chlorinated trisodium phosphate was added before the silicate addition.

Having thus described our invention, we claim:

1. A process for preparing detergent compositions comprising a water-soluble alkaline condensed phosphate, a water-soluble alkali metal silicate, and chlorinated trisodium phosphate which comprises adding to a substantially anhydrous alkaline condensed phosphate an alkali-metal silicate having a SiO_2/alkali metal oxide ratio in the range from about 2.0 to about 3.4, and water in an amount at least adequate to wet the said condensed phosphate sufficiently to induce agglomeration and insufficient to destroy the discrete particle characteristic of the condensed phosphate-silicate mixture, agitating the mixture while keeping the temperature from using above about 130° F., then adding chlorinated trisodium phosphate to the said mixture, agitating the resultant mixture, aging the said resultant mixture to substantially complete hydration while intermittently agitating it and reducing the agglomerates formed to the desired size, the total amount of water added, exclusive of water introduced with the chlorinated trisodium phosphate, being from about 12% to about 25% by weight of the final detergent composition, whereby a composition characterized by resistance to caking on storage and formation of difficultly soluble gels during use is produced.

2. The process of claim 1, wherein the water and silicate are added in the form of an aqueous silicate solution.

3. The process of claim 2, wherein the water-soluble

alkali metal silicate is sodium silicate having an average SiO_2/Na_2O ratio of from about 2.7 to about 2.9.

4. The process of claim 2, wherein a non-ionic synthetic detergent is added to the anhydrous alkaline condensed phosphate simultaneously with the aqueous silicate solution.

5. The process of claim 1, wherein the alkaline condensed phosphate is sodium tripolyphosphate.

6. The process of claim 1 wherein the total amount of water to be added is applied directly to the substantially anhydrous alkaline condensed phosphate.

7. A process for preparing detergent compositions comprising a water-soluble alkaline condensed phosphate, a water-soluble alkali metal silicate, and chlorinated trisodium phosphate which comprises adding to a substantially anhydrous alkaline condensed phosphate an aqueous solution of an alkali metal silicate having an average SiO_2/alkali metal oxide ratio in the range from about 2.0 to about 3.4, the amount of said silicate solution comprising at least 50% of the total amount of silicate solution to be added, the total amount of moisture in said aqueous silicate solution being at least adequate to wet the said condensed phosphate sufficiently to induce agglomeration and insufficient to destroy the discrete particle characteristic of the resultant condensed phosphate-silicate mixture, agitating the mixture while keeping the temperature thereof from rising above about 130° F., then adding thereto chlorinated trisodium phosphate, agitating the mixture, then adding the balance of the said aqueous silicate solution while agitating the mixture, the total amount of water incorporated in the said mixture by the addition of aqueous silicate solution being from about 12% to about 25% by weight of the final detergent composition, aging the resultant mixture to substantially complete hydration while intermittently agitating it, and thereafter reducing the agglomerates formed to the desired size, whereby a composition characterized by resistance to caking on storage and to formation of difficultly soluble gels during use is produced.

8. A process for preparing detergent compositions comprising a water-soluble alkaline condensed phosphate, a water-soluble alkali-metal silicate, and chlorinated trisodium phosphate which comprises adding to a substantially anhydrous alkaline condensed phosphate an aqueous solution of an alkali-metal silicate having an average SiO_2/alkali-metal oxide ratio of from about 2.0 to about 3.4, the total amount of moisture in said aqueous silicate solution being at least adequate to wet the said condensed phosphate sufficiently to induce agglomeration and insufficient to destroy the discrete particle characteristic of the resultant condensed phosphate-silicate mixture, agitating the mixture while keeping the temperature thereof below about 120° F., the total amount of water added being from about 12% to about 25% by weight of the final detergent composition, thereafter adding chlorinated trisodium phosphate, agitating the mixture while cooling to room temperature, aging the resultant mixture to substantially complete hydration while intermittently agitating it, and thereafter reducing the agglomerates formed to the desired size, whereby a composition characterized by resistance to caking on storage and to formation of difficultly soluble gels during use is produced.

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