Properties of Detergent Phosphates and Their Effects on Detergent Processing

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Abstract

Phosphates are usually key ingredients in detergent formulations ranging from liquids to free-flowing powdery material to hard cakes. Their functional properties, which contribute to the over-all detergency by controlling the alkalinity, lowering the critical micelle concentration, sequestering metal ions, and decreasing soil redeposition, are generally considered to be the reason for their wide use. Another important but less recognized reason is their versatile role in improving the handling properties and lowering the cost of the finished products.

The sophistication of the phosphate manufacturing processes makes it possible to turn out a large number of phosphates with different properties and physical forms. Trisodium orthophosphate, tetrapotassium pyrophosphate, and sodium phosphate glass are for the specialties. Sodium tripolyphosphate, the work-horse of the detergent phosphates, has many grades. Some are designed to give the desired hydration properties for different detergent-processing conditions. Size and density are varied for granular grades to reduce segregation and degradation in dry-blended detergents. Sodium trimetaphosphate, which converts rapidly into tripolyphosphate, offers a new detergent-processing technology. Effervescent phosphate is an intriguing new detergent phosphate with many possible new applications.

The properties of these phosphates and their effect on the detergent products and processes are discussed in detail.

Introduction

PHOSPHATES ARE CONSIDERED an essential and major ingredient in most detergents. The phosphate is prepared in powder, granular, glassy, or liquid form so that it can be readily formulated with other ingredients. Before getting into the details of detergent phosphates, it is desirable to review the reasons why phosphate is preferred for detergent formulations.

Usefulness of Phosphates

Cost Performance. It is believed that no other chemical can perform the various cleaning functions at a lower cost than the phosphates. Despite increased labor and distribution costs, the price that the consumer pays for detergents has remained fairly constant over the past decade. A major reason for this has been the reduction in the bulk price of sodium tripolyphosphate (STP), which constitutes about 30–50% of a heavy-duty detergent. The price of STP has dropped from 7.95¢/lb in 1954 to 6.75¢/lb in 1966.

Toxicity. Most of the phosphate consumed in the United States is derived from pure phosphorus. To meet competition, the few producers using wet-process phosphoric acid as the raw material have also purified their product to contain low levels of fluorine and heavy metals. Thus most phosphates for detergent use are almost completely free of toxic materials and, in fact, meet the reagent grade standards. Phosphates themselves, being essential biological building blocks, pose no potential danger of accumulative poison effects. The amount of phosphates from detergents which finds its way into sewage however has been of increased concern to water-pollution-control authorities in recent years (1). A method for removing phosphorus in the waste-treatment plant may be a solution of this problem (2).

Improving Handling Properties. It has been generally recognized that the stable hydrate salts of phosphates, especially sodium tripolyphosphate hexahydrate which does not lose its water easily even at 100C, contribute to the crisp and free-flowing character of detergents. It is less known however that one probable mechanism is that phosphates promote the dehydration of silicates, as shown by differential thermal analysis. The dried phosphate and silicate mixture is a nonsticky, relatively hard, and water-soluble substance. Although infrared analyses indicate the presence of silicate-phosphate complexes, the chemistry and properties of the complexes are largely undefined.

Sequestration Power. Sequestration is a phenomenon in which the precipitation of metal cations by an anion is prevented by the formation of soluble complexes with the sequestration agent. In hard water the precipitation cations are calcium and magnesium, usually in the ratio of about two to one. Unless sequestered, the calcium and magnesium ions will form insoluble salts, called "soap curds," with anionic surfactants. Calcium and magnesium ions also show a high tendency to be bound on cotton fibers, and this fact has been considered to be the major cause of soil retention (5).

The polyphosphates are good sequestration agents. Their ability to sequester calcium and magnesium in a typical hard water is given in Fig. 1, determined by a technique developed by Irani and Callis (6).

Alkalinity. Washing is preferably done under highly alkaline conditions to enhance the emulsification of oily and greasy substances. Polyphosphates, especially tripoly- and pyrophosphates, are at peak performance at their normal pH of about 10 and have a great capacity for buffering the detergent solution at a high pH value. This is an important property because it eliminates the need for other alkaline agents, such as washing soda. The latter precipitates calcium as calcium carbonate on cotton fiber and gives a hard, unpleasant texture. The ash content of cloth after repeated washing is used as a measure of such precipitation.

Antiredeposition. Polyphosphates are good deflocculation agents. This is attributable to the adsorption of polyphosphate anions on suspended particles to produce negatively charged particles which repel each other. Perhaps these charges also cause a repulsion between dirt particles and a fabric so that dirt worked loose by mechanical washing-action cannot redeposit on the fabric. This antiredeposition property is enhanced by a small amount of sodium carboxylmethyl cellulose, which forms some type of protective colloid.

Threshold Effect. Polyphosphates are effective inhibitors in stopping the formation of nuclei (7) which initiate precipitation. This property is a key factor in the rinsing of the cloth. The detergent concentration at this stage is very low, and the precipitation of calcium soap is prevented only by the remaining trace amount of phosphate. For this reason it is believed that organic sequestration agents cannot completely replace the phosphate in a detergent (8).

Other Builder Properties. Phosphate builder-properties have been reviewed by a number of publications (7,9–13). Besides those properties mentioned earlier, phosphates reduce the adsorption of surface-active ingredients, increase the nonionic surfactants' detergency probably through a synergistic action, and lower the critical micelle concentration of the ionic surfactants. No other single builder has yet been found that can do so many things so well.

Detergent Phosphates

The most important detergent phosphates are listed in Table I. Sodium trimetaphosphate (TMP) and effervescent phosphate are new, but their unusual properties, as described in the following section, justify their potential as large-volume detergent phosphates. The normal solubilities of these salts are given in Fig. 2.

Anhydrous Trisodium Orthophosphate. TSP, Na_3PO_4, is generally selected for its high alkalinity and its ability to precipitate calcium and magnesium salts. The major use of this phosphate is for industrial cleaning agents and for metal cleaners. Although seldom used in built detergents where the sequestration ability of STP is preferred, the recent consumption of TSP in the United States has remained relatively constant at about 110 million pounds per year (14).

Anhydrous TSP absorbs water readily to form hydrates. Two commercial forms are available for the convenience of users, a powdered grade for rapid dissolution with good agitation and a granular form which has less tendency to form lumps when agitation is poor.

Crystalline Trisodium Orthophosphate. Crystal TSP is a physically attractive material. It is used in many of the household cleansers and hard-surface scouring powder formulations. As a hydrate, crystalline TSP has much less lumping tendency during the dissolution stage. This advantage, plus its better appearance, apparently justify paying a premium for the water present in the crystalline TSP. The particle-size distribution of each grade of crystalline TSP is carefully controlled to reduce segregation in the final formulation. In a dry-blended mixture it is more important to keep particles of various ingredients close to a uniform size rather than to a uniform density (15).

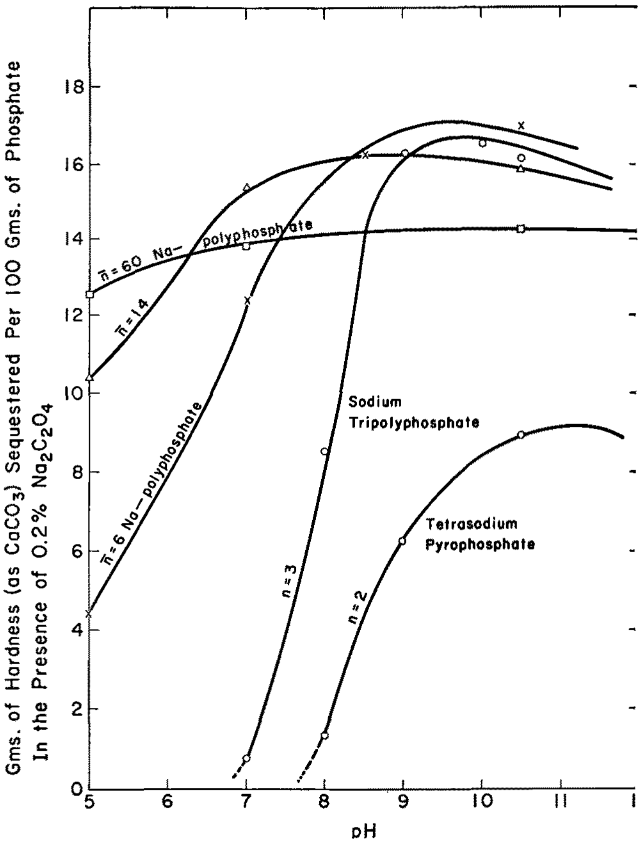

FIG. 1. Sequestration of water hardness ions by linear phosphates at 25C. Hard water contained 2:1 weight ratio of $Ca^{++}:Mg^{++}$.

Tripotassium Orthophosphate. TKP is really a specialty. It is very hygroscopic, and the product is generally made in a large granular size to reduce the exposed surface area. The major use of TKP is in built liquid soap.

Tetrasodium Pyrophosphate. TSPP is still an important detergent builder although its share of the market continues to be eroded away by STP. This is not surprising since STP has a much higher sequestration value (Fig. 1). The TSPP which may be found in STP-based, spray-dried detergents results from the degradation of the STP. This represents a net loss in the phosphate efficiency but is difficult to avoid completely. TSPP does not hydrate easily, especially

TABLE I

Properties and Major Uses of Detergent Phosphates

Name	Grades	Major uses
Na_3PO_4 Anhydrous	Powder and granular forms	Industrial cleaning compounds, metal cleaners, water softeners
$Na_3PO_4 \cdot 1/4NaOH \cdot 12H_2O$	Narrow cuts of crystal size	Hard-surface cleaners, water softeners
K_3PO_4	Coarse granular, —4 mesh	Liquid soap-builder
$Na_4P_2O_7$	Powder and granular	Heavy-duty detergents, built-soap water-softeners, cleaning compounds
$K_4P_2O_7$	Granular and liquid	Liquid detergents
$Na_5P_3O_{10}$	Powder, light, medium, and dense granulars. Varying Form-I and Form II proportions. Special grades	Detergent builder, water softener, cleaning compounds, deflocculation agents. Dishwashing compounds
Sodium polyphosphate glass	Powder, granular, and flake	Water softeners, built detergents, dish washing compounds
$(NaPO_3)_3$	Powder	Built detergent. Converts to $Na_5P_3O_{10}$ with sodium hydroxide
Effervescent phosphate	Granular	Water softener, light-duty detergent

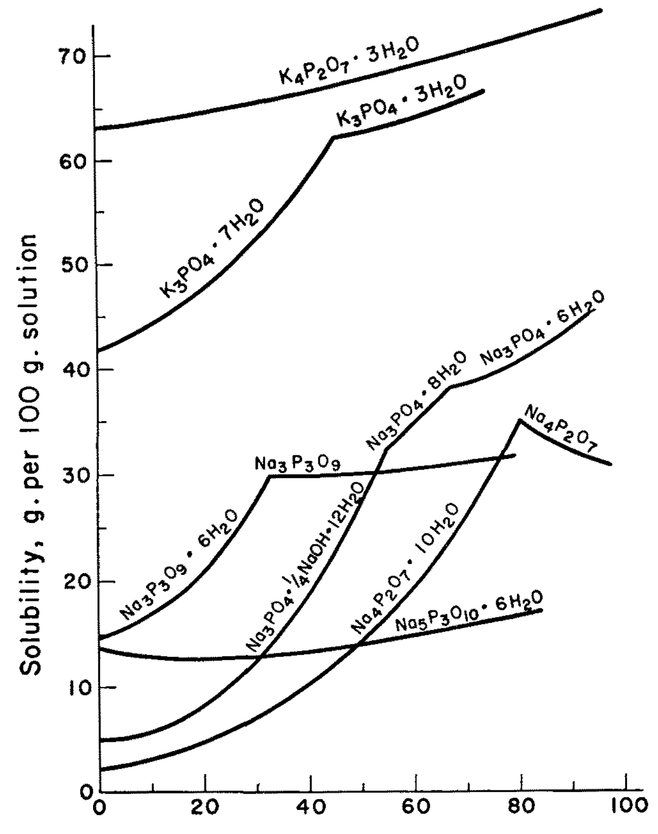

FIG. 2. Solubilities of various detergent phosphates and the equilibrium crystalline phases.

at higher temperatures and in high solids detergent slurries (16); its presence also inhibits the hydration of STP. For this reason a thinner detergent slurry may be derived from TSPP or a mixture of TSPP and STP than from STP alone at the same phosphate content. The spray-dried detergent with higher TSPP content however must be dried to a lower moisture content and aged longer before packaging to avoid caking in the box since the hydrate water of TSPP exhibits a high water-vapor pressure (17).

For preparing spray-dried detergents, powdered TSPP is used. The granular grade has been used for dry-blended formulations, dish-washing compounds, and water conditioners. A relatively small amount of TSPP is converted to the hydrate, $Na_4P_2O_7 \cdot 10H_2O$, for water conditioners.

Tetrapotassium Pyrophosphate. TKPP is the most popular liquid detergent builder (18,19), based on solubility, stability, and functional performance. The ability of TKPP to form a highly soluble double salt with TSPP (up to about 20% TSPP) permits the use of some sodium salts in the liquid formation (20). For short-distance delivery TKPP is supplied in the form of 60–65% sparkling clear solution. At this high solids concentration, trace amounts of calcium and iron are not soluble. High clarity must be accomplished by stringent process-quality control since the undesired impurities would supersaturate and precipitate sluggishly, a common behavior for a phosphate system. For long-distances TKPP is transported in the anhydrous granular form. TKPP dissolves with little agitation, and hopper cars are unloaded by filling a car with water and pumping it out as a 50–60% solution.

Polyphosphates with a chain length greater than the pyrophosphate degrade too rapidly in aqueous media and are not considered suitable for liquid detergents. If stable slurries and emulsions are considered to be liquid detergents, it is possible to prepare a slurry type of liquid detergent by using submicron-size polyphosphates in an organic substrate (19). This approach however is hampered by the lack of a good supply of submicron material.

Sodium Tripolyphosphate. The prolific use of STP iin various types of detergents has resulted in more than 30 different grades with different combinations of values of particle size, bulk density, amount of Form-I content, and other variables. Most STP used in the United States is tailor-made to suit different detergent-process conditions. Although scattered information, mostly given in patents, indicates the possible effect of a particular grade of STP on a single detergent process step, there is a lack of information about the effect of the grade of STP on the over-all detergent process.

The Work-Horse STP

The major portion of STP is used in a powder form for preparing spray-dried detergents. The major concerns are the rate of hydration and the degradation of STP in the spray-drying step. These properties are discussed in the following sections.

Crystalline Forms of STP. Anhydrous STP exists in two crystalline forms, commonly referred to as STP-II and I. STP-II is formed at calcining temperatures below about 410C whereas STP-I is formed at higher temperatures (4). The phase transition is unusual in that it is, for practical purposes, not reversible in the absence of an amorphous phase. A mixture of STP-II and -I formed by calcination at temperatures around 450C can be cooled to room temperature (or even tempered at temperatures up to 400C), milled, stored, and shipped without detectable loss of STP-I through conversion to the thermodynamically stable, low-temperature form, STP-II.

STP-I, being metastable at crutching temperatures, shows a higher tendency to form the stable hydrate, $Na_5P_3O_{10} \cdot 6H_2O$, and a pronounced tendency to form gritty, partially hydrated lumps. This is one of the reasons why STP-II is generally used for preparing detergent slurries. Another reason is the erroneous belief that little hydration actually occurs when STP-II is used and that as a result liquid water is not lost to the tripolyphosphate but remains free to make possible a slurry of high solids content and tolerable viscosity. In fact, however, unless stringent means are used to prevent hydration by using long-chain phosphates as inhibitors or operating at higher slurry temperatures or higher solids levels (16), at least 60–70% of the added STP will hydrate during normal crutching cycles. Also, satisfactory noncaking, high-moisture-content detergent powders cannot be made unless the STP is largely hydrated before it reaches the spray tower.

Hypothetically, for each detergent process, STP of a specific hydration rate should be used for optimum results. The hydration rate is influenced by the STP-I content, which is measured by a temperature-rise method (21). The test itself is simple and involves measurement of the temperature rise of a glycerine-water STP mixture, which occurs when the phosphate hydrates. Because the hydration of STP-II is inhibited by glycerin, the temperature rise measured is caused almost entirely by the hydration of STP-I. By correlating TR values of tripolyphosphate samples

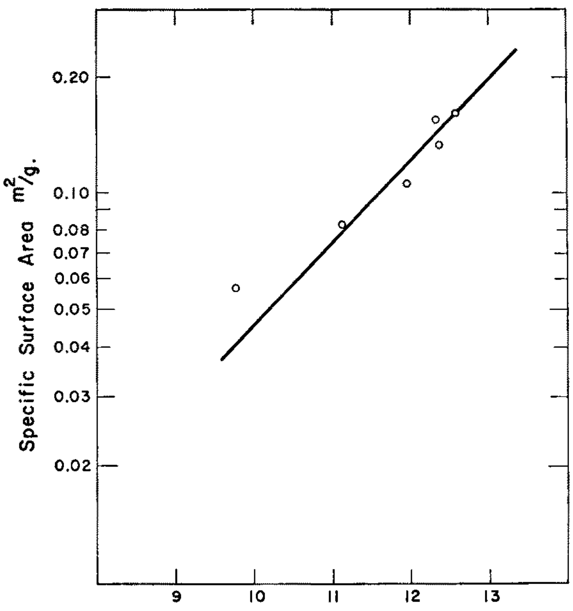

FIG. 3. Temperature rise versus apparent specific surface of sodium tripolyphosphate (containing 28% $Na_5P_3O_{10}$-I).

with STP-I content as determined by x-ray diffraction (23), the following empirical relationship between the TR and the Form-I content was derived: % $Na_5P_3O_{10}$-I = 4 (TR–6), where TR is the temperature rise in °C. It was noticed by McGilvery (21) that samples of STP-II, prepared by the dehydration of $Na_5P_3O_{10} \cdot 6H_2O$, gave abnormally high TR values, and this deviation was attributed to a high specific surface area. This finding was not surprising since one would expect the rate of hydration to be directly related to exposed surface area. Since the rate of hydration of STP in glycerin-water mixtures is not necessarily the same as the rate in detergent slurries, the possibility of significant errors exists in using the TR test to predict behavior of the salt in detergent operations (16).

A quantitative study of the effect of particle size on TR was made. The TR value of the test sample was increased by repeatedly milling though concurrent determination of the Form-I content by x-ray measurement revealed no change in this component. Fig. 3 illustrates the effect. The apparent specific surface area given in the figure was estimated from the geometric main diameter by using the assumption that the particles were solid spheres. Roughly the data show the TR increases about 1.45C each time that the specific area is doubled.

Particle-size variation of powdered STP manufactured in the United States is generally kept small by using efficient milling and size-control machines. However, in some areas, the term STP powder is loosely used for a product coming directly from a calciner without further reduction in size. The hydration rate of this type of product, as expected, is considerably slower than that of the finely milled material.

Other Factors Affecting the STP Hydration Rate. Bivalent cations, especially calcium, will reduce the hydration rate of STP. This property was first noticed when STP derived from wet-process phosphoric acid, containing as much as 0.2% calcium, showed a considerably slower hydration rate than similar STP derived from furnace acid. Sodium sulfate, which is present in STP from wet-process acid, also tends to inhibit the hydration of STP. Long-chain glassy phosphates are good inhibitors for hydration of STP-II.

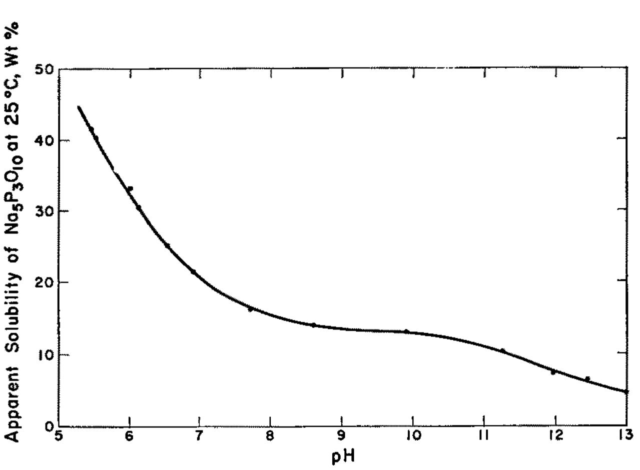

FIG. 4. Apparent solubility of $Na_5P_3O_{10}$ (in the presence of NaOH or H_2SO_4) at various pH values.

The presence of dissolved solids, whether inorganic or organic, usually retards the rate of STP hydration. Maximum hydration in minimum time is ordinarily achieved for any type of STP by admixing with water containing as little foreign matter as possible. In many cases, better hydration of STP can be achieved by withholding sodium sulfate, sodium silicate, and actives until after the STP has been added.

The solubility of STP changes drastically with pH as shown in Fig. 4. If one assumes that the STP hydration involves a dissolved intermediate, then a higher pH should result in a lower hydration rate. Actual tests however showed that for some anionic detergent slurries hydration was faster at a higher pH (23). The deflocculation effect of the hydroxyl ion, which causes the release of water from the active phase, more than compensates for the effect of decreased solubility.

The rate of hydration of STP in the crutcher may be increased by the presence of the hexahydrate seed crystals. An amount of less than 5% $Na_5P_3O_{10} \cdot 6H_2O$, or 1% as water, is required (16). The effect is more pronounced for thin slurries containing nonionics or low (50–55%) solids than for thick slurries containing anionics and/or high (above 60%) solids.

Generally the hydration rate of STP decreases with an increase in temperature and/or solids concentration. Unfortunately the expense of the greater water evaporation load usually rules out slurry dilution. The optimum conditions have to be determined by actual tests.

Degradation of Sodium Tripolyphosphate Hexahydrate During Dehydration. The dehydration of sodium tripolyphosphate hexahydrate has been studied by a number of investigators (3,24–33) because of its importance in commercial applications and because of its unusual aspects. The results reported so far indicate that the mechanism of dehydration is quite complicated. It appears that the amount of the hexahydrate degraded to ortho- and pyrophosphates depends on temperature, water-vapor pressure over the converting material, bed depth, rate of heating, trace impurities, and crystal size. Groves et al. (31) showed that the degradation of $Na_5P_3O_{10} \cdot 6H_2O$ could be controlled by controlling the water-vapor pressure and temperature of the gas stream. Their data, with some additional points from Quimby (29), were analyzed, and the response surface plot which was de-

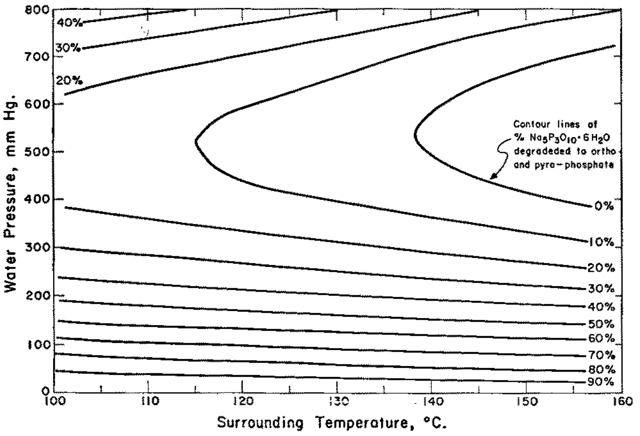

FIG. 5. Dehydration of $Na_5P_3O_{10} \cdot 6H_2O$.

veloped is shown in Fig. 5. It can be seen that, over the 100–160C range, the water-vapor pressure has a much greater effect than does temperature. An extrapolation of these data indicates that, at temperatures above 200C, the degradation of $Na_5P_3O_{10} \cdot 6H_2O$ will be nearly negligible at any water-vapor pressure below atmospheric pressure.

Generally speaking, water-vapor pressures of 400–600 mm are more desirable. The increase in amounts of degradation at high water-vapor pressures could be owing to reaction of STP with water from the vapor phase. It should be noted that this study is based upon analyses of the initial and final product only and upon measurements of the temperature and partial pressure of water vapor in the surrounding medium. Neither the rate of dehydration nor the actual temperature of the dehydrating phosphate was considered. It does however give a reasonable picture of the degradation of $Na_5P_3O_{10} \cdot 6H_2O$ upon drying of detergent slurries since the test conditions, in general, are close to those used in commercial spray-drying operations. For example, all investigators show that some degradation will occur when the temperature of the surroundings is below 140C and that very little will occur at temperatures above 230C.

Both Shen (3) and Groves (31) revealed that large crystals dehydrate at a much slower rate than do smaller ones, indicating that some control of degradation during spray drying of detergents is possible by control of crystal size. Finally Budenheim (32) indicated a decrease in degradation with an increase in heating rate, which fits in well with Fig. 5. With high-temperature surroundings, the rate of dehydration (or heating rate) will be fast, and less decomposition would be expected to occur.

Granular STP. A significant portion of the total STP used for manufacturing detergents is in granular form. This form is mainly used in dry mixed formulations, in detergent tablets, and in small crutching operations. The recent trend has been toward more varieties with different sizing and density for different detergent formulations. Relatively little work has been reported on the properties of granular STP although certain properties, such as resistance to breakage in mixing operations, are important in detergent processing. A good method for evaluating these properties must be developed before the desired information can be obtained.

Since an increase in the void fraction of low density granular STP results in a decrease in structural strength, there is a definite correlation between the frangibility of granular STP and density as shown in Table II. Frangibility of a granular STP is defined as the percentage of minus 100 mesh fines generated during a given period of time on a Ro-Tap sieve shaker from 100 g of plus 100 mesh granular material in an 8-in. 100 mesh screen containing three 1⅜ in. pure gum rubber balls obtained from Southwestern Engineering Company, Los Angeles. These values will vary with the type of process used for producing STP.

TABLE II

Effect of Form II Granular STP Density on Frangibility

Bulk density g/cc	Frangibility No.	
	15 min	30 min
0.45	3.7	7.0
0.53	2.5	4.6
0.79	1.7	2.9
1.01	1.4	2.0

The frangibility numbers of STP samples containing an appreciable amount of Form I are about 50–100% higher than the values given in Table II. The increase in frangibility is considered attributable to the conversion of STP-II crystals to STP-I after the gross structure is set. This is accompanied by a slight change in volume, which tends to weaken the bridge between STP crystals in a granular particle.

If all other factors are equal, an increase in bulk density will cause a decrease in solution rate (Table III). Exact amounts of granular STP were added 100 ml of distilled water at a specific temperature. After a given period of time the undissolved residue was filtered out, oven-dried at 110C, and weighed. The solution rate will increase with better agitation. For tests given in Table III, the glass stirrer was located 18 mm from the side of a 50-mm D×70 mm H 150-ml beaker and about 4 mm from the bottom. The stirrer had two 18-mm diameter blades with a 45° pitch, and the stirrer speed was calibrated before each series of runs.

The rate of dissolution of granular STP generally increases with temperature, as expected. In a few cases it has been noticed that the increased hydration rate at temperatures around 50C causes the granular to cake if agitation is not adequate. Caked material dissolves slowly, and an erroneous result could be obtained.

Active Absorption. The physical properties of dry mixed detergents, such as flowability, caking tendency, and appearance are usually related to the active absorption characteristics of the granular used in the mix. It is important that the oily active does not exude from the finished detergent and soak into the paper container. Light-density granular STP is preferred for dry mixed detergents because of the high level of internal voids. However light-density granular STP with a hollow-bead structure, made by a spray-drying and calcining process, does not work as well as a similar-density material of porous structure prepared by an agglomeration process (34) as shown by results in Table IV.

TABLE III

Dissolution of Granular STP-II in 20C Water

Bulk density of −20 +100 mesh granular STP-II g/cc	%Residue, 15 seconds after addition of 3-g sample in 100 ml of water at 20C	
	540 rpm	1080 rpm
0.44	1.49	0.54
0.52	5.85	0.90
0.76	22.64	16.30
1.03	57.50	34.75

TABLE IV

Effect of STP Particle Structure on Physical Properties of Dry Mixed Detergents

Type of granular STP	% Active level	g Active soaking out	Cake strength g
Porous structure	7.5	0.12	60
	15.0	0.22	60
Hollow-Bead structure	7.5	0.34	60
	15.0	0.45	280

The test was conducted by mixing 1,000 g of granular STP with 7.5 or 15.0% Sterox® AJ-100 in a one-gallon size Hobart mixer for 10 min. At the end of this period a 200-g sample was placed in a 4-ft D × 4-ft H wooden mold which contained seven sheets of Whatman's No. 1 filter paper at its base, and the mixture was loaded by a 10-pound weight for 24 hours. The breaking strength of the cake was determined with a penetrometer, and the amount of active that was absorbed by the paper was determined from the weight increase.

Other Developments

Sodium Polyphosphate Glass. As the name implies, sodium polyphosphate glass is obtained by quenching a melt on a cold surface. The glass is a mixture of phosphates of varying chain-length; the average length depends on the Na_2O to P_2O_5 ratio (4). Commercial sodium phosphate glass usually has an average chain-length between 6 and 20. Extremely long chains are difficult to obtain because a trace of moisture serves as a chain breaker. It should be noted that the term sodium hexametaphosphate commonly used for the glass is a misnomer. The true sodium hexametaphosphate, a 12-membered ring, has been recently isolated and characterized (35).

Sodium polyphosphate glass is completely miscible with water, forming essentially neutral solutions. The hygroscopicity of sodium phosphate glass and its tendency to cake in contact with water greatly limit its use in built detergents. Most of the glass is sold as flakes and is used directly for water conditioning. Granular and powdered glasses are available for special formulations, such as bath salts, dishwashing compounds, and food processing. Cartons with a vapor barrier are generally used for packaging products containing phosphate glass.

Sodium Trimetaphosphate. One of the most significant developments in detergent processing in recent years is the use of sodium trimetaphosphate to produce a light-density granular detergent directly from a high-solids detergent slurry (36,37). The process is based upon the reaction of sodium trimetaphosphate and sodium hydroxide to form sodium tripolyphosphate hexahydrate and the utilization of the heat of reaction to vaporize a part of the water. The steam bubbling through the reaction mass and the crystallization of the hydrate change the slurry into porous granules. In distinguishing this from the spray-drying process, the new approach is called the fluff process. The principal steps involved in a continuous fluff detergent plant are shown in Fig. 6. Commercial fluff plants are being built by Ballestra S.P.A., Milan, Italy, a licensee. The major advantages over spray drying appear to be lower building and construction costs, reduced auxiliary service equipment, less dust and lumps production, simple start-up and shut-down procedures, lower phosphate-degradation, and higher product-moisture.

The feasibility of quantitative conversion of sodium trimetaphosphate to STP hexahydrate in a few minutes in a detergent slurry also offers many potential advantages for preparing spray-dried detergents. The use of sodium trimetaphosphate will overcome the difficulty of hydrating STP in highly concentrated detergent slurries, thus giving the desired moisture content of the spray-dried products. If some anhydrous STP is desired in the finished product, a mixture of STP and trimetaphosphate may be used. The potentiality of sodium trimetaphosphate in spray-dried detergents has not yet been fully evaluated, but the results obtained so far (36) are quite encouraging.

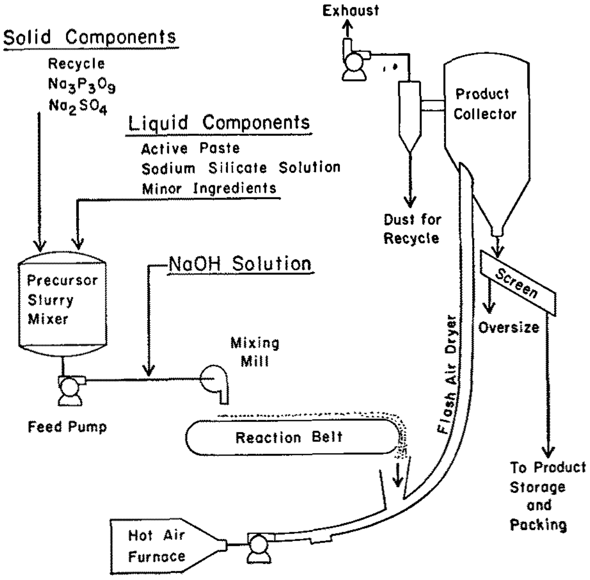

FIG. 6. Fluff detergent process.

Essentially minus 100 mesh trimetaphosphate powder is used because the conversion rate to tripolyphosphate will be slower for larger particles. Products of different size and density can be obtained from the fluff process. Since the fluff process can produce a product with a density greater than 0.5 g/cc, which cannot be accomplished in a spray dryer, the fluff process in some respects is a more versatile unit.

Effervescent Phosphate. Effervescent phosphates are prepared by a unique process developed by Monsanto (38). These products consist of finely divided acidic phosphates or polyphosphates, which are encapsulated or intimately mixed with a carbonate-containing material. The dry, free-flowing solids are so produced that the potential reaction to produce CO_2 does not occur to any large extent. When the mixture comes in contact with water, the reaction between the acidic material and the carbonate results in the evolution of CO_2 to give an effervescent effect. The solution rate, as a result of the chemical reaction, is so fast that an effervescent phosphate dissolves nearly instantly even in cold water.

Effervescent phosphates appear to be stable in dry storage. There was a negligible change of composition after three months of storage in a 7-mil polyethylene bag under a temperature of 100F and 90% relative humidity. Under direct contact with high humidities there was a gradual loss of CO_2 though the product did not cake. The CO_2 gas, during dissolution, tends to buffer the solution to near neutral pH. These properties would suggest that effervescent phosphate is a desired ingredient to increase the solution rate for such products as detergent cakes, tablets, or pills.

TABLE V

Properties of Effervescent Phosphate

Loose bulk density, g/cc	0.67
Composition, wt. %	
P_2O_5	46.1
Na_2O	34.6
H_2O	7.1
CO_2	12.2
pH, 1% solution	7.1
Gas evolved in contact with room-temp. water, cc/g	53.5
Calcium sequestration value g $CaCO_3$ per 100-g sample	9.0

A typical analysis of an effervescent phosphate is given in Table V. It is of interest to note that this material has a calcium sequestration value comparable with tetrasodium pyrophosphate despite the high content of CO_2 and H_2O.

There are several limitations in using effervescent phosphate in heavy-duty, built-detergent formulations. The most serious one is that the CO_2 from the dissolution of an effervescent phosphate can cause the precipitation of silicates as water-insoluble flocs unless there is enough alkaline material with a slower dissolution rate to redissolve the silicate. Furthermore, the free moisture content in the detergent would have to be low so that the effervescent phosphate would not react and lose its effervescence. Effervescent phosphates are compatible with chlorinated cyanuric acid derivatives and are useful in dry bleach formulations.

Summary

The detergent industry today can select from a number of established phosphates the one or ones best suited for each manufacturing process and/or for the performance of the finished product. To meet the challenge of supplying the desired chemical and physical properties for detergent processing, phosphate production processes have continually undergone sophisticated changes. The hydration properties of STP are better controlled, and the frangibility of granular STP has been improved, for example, to meet detergent process needs. The introduction of the fluff process, which can supply a light foam-intermediate for subsequent conversion to various forms of products may meet the quest of detergent manufacturers for new methods of making new types of detergents in the future. Effervescent phosphate is an intriquing addition to the detergent phosphate family which has not yet been exploited.

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