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TREATMENT OF WATER WITH SOLUBLE DEHYDRATED SODIUM PHOSPHATES

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Fig 1

Fig 2

Fig 3

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Fig 4

% Total Solids in Solution

Fig 5

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TREATMENT OF WATER WITH SOLUBLE DEHYDRATED SODIUM PHOSPHATES

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We have furthermore found that readily soluble mixtures of molecularly dehydrated sodium phosphates of a predetermined hydrogen ion concentration may be obtained by heating to the fusion point appropriately proportioned mixtures of sodium ortho-phosphates, or mixtures of orthophosphoric acid and the sodium salt of a replaceable acid and then rapidly cooling. Suitable sodium salts for this purpose are the chloride and carbonate of sodium, although others may be used. The latter compound is preferable since it is difficult, when producing mixtures having a high alkali content to expel all of the chlorine from the melt.

In the accompanying drawings, Figure 1 shows certain solubility relationships of the sodium and potassium series of dehydrated phosphates. Figure 2 shows the hydrogen ion concentration of the sodium phosphates prepared by our process. Figure 3 shows the hydrogen ion concentration of the dehydrated potassium phosphates. Figure 4 illustrates the solubility of the sodium and potassium series of phosphates in concentrated solutions. In Figure 5 is given the melting points of the sodium phosphates.

Our invention will be illustrated by the following examples:

Example 1

Mix together 76.5 lbs. of mono-sodium orthophosphate (NaH₂PO₄.2H₂O) and 134.7 lbs. of di-sodium ortho-phosphate (Na₂HPO₄.12H₂O). Dehydrate and heat in a gas fired reverberatory furnace to the melting point of the mixture which is at a temperature of approximately 620° C. When a uniform melt has been obtained, cool quickly by pouring the molten mass on a cold metal surface in thin layers. The layers of molten salt should not be over ¼ inch thick and preferably less than ½ inch thick. The metal surface on which the molten salt is poured, if in substantially continuous use as in the case of continuously operated chill rolls, may be water cooled in order that accumulated heat may be carried away rapidly. We have found that water at ordinary temperatures is preferable. However, it is possible to operate satisfactorily when cooling with water at or near its boiling point.

We have found that it is particularly desirable, in order to develop the amorphous condition, to cool rapidly during the first portion of the cooling period. For example, the maximum benefit from quick cooling is obtained by cooling from the melting point to say in the neighborhood of 100 to 300° C. If this is done rapidly, then it is
not necessary that the remainder of the cooling be at so rapid a rate. For the purpose of this specification, we shall designate as "quickly cooling," both the process of cooling at a rapid unbroken rate from the original to the final temperature, and the process of cooling at a rapid unbroken rate from the original to an intermediate temperature, followed by cooling at a different rate (either faster or slower) than the original rate.

The product from the melt as above designated, Example 1 is approximately 100 lbs. of a solid consisting theoretically of 50% tetrasodium pyro-phosphate and 50% sodium meta-phosphate.

A sample of this material as produced in commercial operation and dissolved in water to make a 1% solution will show a pH of approximately 8.6. See curve C' of Figure 2.

The reactions for stoichiometrically determining the theoretical proportions in this example are:

\[
\text{NaH}_{2}\text{PO}_{4} \cdot \text{H}_{2}\text{O} = \text{NaPO}_{3} + \text{H}_{2}\text{O} \\
2(\text{Na}_{2}\text{HPO}_{4} \cdot 12\text{H}_{2}\text{O}) = \text{NaPO}_{3} + 25\text{H}_{2}\text{O}
\]

Example 2

Mix together 74.14 lbs. of sodium carbonate (soda ash) and 78.26 pounds of phosphoric acid, \(\text{H}_{3}\text{PO}_{4}\) (or 104.2 lbs. of 75% \(\text{H}_{3}\text{PO}_{4}\)). Heat slowly in a gas fired reverberatory furnace as long as carbon dioxide and water vapor are evolved, then raise the temperature gradually to the melting point, which is approximately at a temperature of 940° C. Heating may be carried out in a carbon crucible or on a firebrick hearth heated by radiation. When a uniform melt has been obtained, cool the melt quickly by pouring it on a cooled metal surface as described in the previous example. Approximately 100 lbs. of a mixture having a theoretical composition consisting of 80% tetra sodium pyro-phosphate and 20% of sodium meta-phosphate will be obtained. A sample of this material as produced in commercial operation and dissolved in water so as to make a 1% solution will show a pH in the neighborhood of 9.5. See curve C' of Figure 2.

The reactions for stoichiometrically determining the theoretical proportions in this example are:

\[
\text{NaCO}_{3} \cdot 2\text{H}_{2}\text{PO}_{4} = 2\text{NaPO}_{3} + \text{CO}_{2} + 3\text{H}_{2}\text{O} \\
2\text{Na}_{2}\text{CO}_{3} \cdot 2\text{H}_{2}\text{PO}_{4} = \text{NaPO}_{3} + 2\text{CO}_{2} + 3\text{H}_{2}\text{O}
\]

The examples above illustrate two ways by which two of our improved dehydrated phosphates may be made. Obviously any one method might be used for both mixtures, as well as other mixtures not specifically mentioned. In general, it may be said that the results of both methods applied to any one mixture yield a very similar product, hence it becomes an economic question of choice of raw materials as to which method is employed.

The proportioning of the raw materials is done on a simple stoichiometric basis as indicated which is familiar to persons skilled in the art.

Fusion may be carried out in each instance in an ordinary carbon or graphite crucible or it can be done on a brick hearth with reverberatory heating.

Mixtures of these two salts containing stoichiometrically between 50% and 100% of sodium meta-phosphate and 50% to 0% tetra-sodium pyro-phosphate, on being quickly cooled from the melting point as above described, are clear amorphous glass-like solids as distinguished from crystalline bodies and do not exhibit a sharp freezing point, being presumably super-cooled liquids.

Mixtures containing stoichiometrically from 50% to 100% of tetra-sodium pyro-phosphate and 50% to 0% sodium meta-phosphate, exhibit a gradually increasing crystalline fracture and a sharper freezing point, becoming less and less transparent as the theoretical tetra-sodium pyro-phosphate content approaches 100%.

When carrying out our process on an industrial scale, heating of the phosphate salts or mixtures of suitable salts and phosphoric acid, is preferably carried out in a reverberatory furnace with gas heating. In such cases we have found that the product formed by our process contains a relatively small proportion of, if any, less than 5% ortho and acid pyro-phosphate. The presence of this impurity in our fused mixtures is probably due to the presence of water vapor in the combustion gases and also, in part, due to the rapidity of the heating and melting operation as carried out on such a scale. The presence of this small amount of impurity is immaterial in the various uses in which the product is employed, its effect being merely to change somewhat the hydrogen ion concentration of the solutions which are prepared therefrom.

For this reason we have shown on Figure 2 of the accompanying drawings two curves labelled C and C'. Curve C has been prepared from the sodium phosphates by first carefully dehydrating the material in an electric furnace at temperatures at which the meta phosphate is known to form and then raising the temperature to the fusion point of the mixture. Curve C' is representative of material which has been industrially prepared by fusion in the presence of water vapor in an industrial furnace. By varying the conditions of dehydration of the ortho-phosphates some variation can be made in the acidity relations of the products formed therefrom. It may be said that in general the range of hydrogen ion concentrations obtained by products produced according to our process will lie between the values given by curves C and C' on Figure 2.

In the above description we have referred to the composition as containing "theoretically" or "stoichiometrically" a certain amount of sodium meta-phosphate and tetra-sodium pyro-phosphate. We have used this terminology because although the stoichiometric proportions are based upon the presence of these two compounds, a chemical examination of our new product indicates that these compounds, along with some water, have in some cases lost their chemical identity, while in other cases such chemical identity has been extensively altered.

This may be illustrated by the following test.

If a solution be prepared by dissolving in water a fused mixture containing the 60% sodium meta-phosphate and 40% tetra-sodium pyro-phosphate equivalent and the solution then tested for pyrophosphate content according to the method of Birske and Dragunov, J. Chem. Ind. Moscow, 4, 49-51 (1927) Chem. Abstr. 22, 2900 (1928), a surprising result is obtained.

On the addition of zinc sulphate to the neutralized solution no precipitate is formed. On the other hand if a mechanical mixture as distinct from a fused mixture and having the same theoretical proportions as that given above is similarly tested, a heavy precipitate of zinc pyrophosphate is obtained. This test shows that tetra-sodium pyrophosphate can be precipitated from a solution of the mechanical mixture while no such
precipitate is formed in a solution of the fused mixture. This indicates that the pyro-phosphate content has lost its chemical identity in the fused mixture, and while such mixture contains the stoichiometric alkali and acid equivalent of the pyro-phosphate it no longer behaves chemically as if any pyro-phosphate were present.

In the same manner it can be demonstrated that in certain of the compositions the meta phosphate has also lost its identity. This may be determined by testing solutions of mechanical mixtures of the sodium meta phosphate and tetrasodium pyrophosphate in comparison with fused mixtures of the same equivalent composition.

The solutions of the mechanical mixtures of these salts will give characteristic heavy precipitates of meta phosphate with silver nitrate and barium chloride. The solutions of the fused mixtures show either no precipitate or only a small amount, depending on the composition.

These chemical tests indicate that fused mixtures of the two salts no longer contain meta-phosphate or pyro-phosphate as such and hence differ from known compositions of the prior art.

An important distinction between our compositions and known compositions or compositions which might ordinarily be considered as equivalents thereof resides in the ready solubility of our product as compared with such other compositions. Such a property is important since one of the important applications of our product has to do with the treatment of water for various purposes.

The types of solubility effect will be illustrated, i.e. the preparation of dilute solutions and the preparation of concentrated solution.

Dilute solutions

Such solutions of our dehydrated and fused sodium phosphates may be prepared by dissolving a proportion of the phosphate directly in water. For example a 1% solution is prepared by adding 1% of the solid dehydrated sodium phosphate to 99% of water. Any and all of the phosphates prepared according to our process and ranging in equivalent composition between say 99% sodium metaphosphate and 1% tetro-sodium pyro-phosphate to 1% sodium pyrophosphate and 99% tetrasodium pyrophosphate can be utilized in this manner to form a 1% solution, as shown in line A of Figure 1. As contrasted with this property of the sodium salts, we have found that the dehydrated and fused potassium salts do not form 1% solutions in all proportions throughout the series. If 1% of the corresponding solid dehydrated potassium salts are placed in contact with 99% of water, the solid phase will not dissolve completely. The extent of solubility of the dehydrated potassium phosphate series is shown as line B in Figure 1. The hydrogen ion concentration of the 1% solution of the sodium salts is shown in Figure 2 while the same data are given in Figure 3 for such solutions of the potassium salts as were formed under similar conditions. It is, however, that the latter data are not given for 1% solutions because of the impossibility of forming such solutions.

Concentrated solutions

Saturated solutions of these dehydrated sodium phosphates were prepared by mixing together water and any of the sodium phosphate compositions herein described in such proportions that some solid phase is present in the solution after equilibrium has been attained. We have found that the composition of the solution differed from that of the solid phase in equilibrium with said solution. This indicates a differential or selective solubility effect in which one or more constituents of the solid tend to dissolve while others tend to remain undissolved.

The nature of this solubility effect is shown on Figure 4 by curve E. From these data, it will be seen that high solubility i.e., over 50% total solids is obtained in the dehydrated sodium phosphate series in the range between about 99% and slightly less than 50% equivalent sodium meta phosphate content, while if less than 50% sodium meta phosphate is present the solubility of the salt rapidly declines, reaching a minimum of approximately 6% for the compound NaP2O7.

In the case of the potassium series the solubility effect as measured by the total solid dissolved in concentrated solutions is exactly reversed. In this case salt mixtures having a high content of potassium meta phosphate are relatively insoluble, the solubility of the series increases as the content of tetro-potassium pyrophosphate increases and reaches the highest value of the series for the pure compound K4P2O7. The solubility of the series of dehydrated potassium phosphates is given on curve F of Figure 4.

In connection with our experiments on the differential or selective solubility of the dehydrated sodium and potassium phosphates we have made the following additional observations:

Selective solubility in the dehydrated phosphate series

Our experiments show that when mixtures of water and members of the sodium series of phosphates are made under conditions so that some solid phase remains in contact with the solution after equilibrium that practically all of the constituent stoichiometrically equivalent to meta phosphate is dissolved and the solid phase is almost entirely composed of the constituent stoichiometrically equivalent to tetro-sodium pyrophosphate. In other words in the sodium series as herein prepared the sodium meta phosphate equivalent is the soluble constituent. The tetra-sodium pyrophosphate equivalent is in no case completely dissolved.

In the potassium series the conditions are exactly reversed. In this series the pyrophosphate constituent of the fused mixtures is completely dissolved throughout most of the range of compositions. The potassium meta phosphate constituent is in no case completely dissolved. Such properties are of importance as indicating a definite absence of equivalency in the sodium and potassium series of fused dehydrated phosphates. It has previously been proposed to utilize mixtures of the pyro-phosphate and meta phosphate for the treatment of water for boiler use. Such mixtures, however, present the following objections.

The mechanical or loose mixtures are difficult to maintain in uniform condition throughout the mass of the mixture. This is so because the meta phosphate is obtained as fairly large pieces resembling broken glass while the pyro-phosphate is either in crystalline form or in a finely ground condition. It is undesirable to grind the materials because the former is hygroscopic and readily becomes sticky and gummy if exposed to air of ordinary humidity. Even though a uniform powder could be prepared at the factory, shipment and the attendant handling of the mixture before...
4. use would tend to segregate one material from the mass and make the preparation of a definite solution of the material a difficult one.

We have furthermore determined that our fused homogeneous mixtures have a lower pH than mechanical or loose mixtures having the same original stoichiometric composition. For example a fused mixture containing the equivalent of 80% meta and 20% tetra pyro-phosphate in 1% solution has a pH of 7.5, a 60% meta 40% tetra-pyrophosphate has a pH of 8.0 while a 40% meta and 60% tetraphosphate has a pH of 8.7.

The pH of corresponding mechanical mixtures have values of 8.6; 9.1 and 9.4 respectively. From the above values we see that the fused mixtures have a greater acidity than the mechanical mixtures of from 0.7 to 1.1 pH units, all of which points to a greater alkali neutralizing capacity inherent in our improved product.

Further study of our improved product shows that we obtain a greater buffering action, in other words a greater reserve acidity than is obtained by simple mixtures of the meta phosphate and tetra-pyro-phosphate. This is confirmatory of the findings mentioned above which indicate a greater alkali neutralizing capacity. The buffering property is of value in other ways than those mentioned and this property will be found of value by those skilled in the art.

A further valuable property possessed by our fused dehydrated sodium phosphates is the enhanced water softening properties. Since it has already been proposed to soften water utilizing the meta phosphate, the properties of such phosphate in preventing the precipitation of the alkaline earth metal compounds are more or less well known. We have now found that solutions formed from fused mixtures, the equivalent of meta and pyro-phosphate in stoichiometric proportions, have the property of producing zero hardness using a considerably lesser proportion of our phosphate product than of an equivalent mechanical mixture.

Since it has been proposed to prepare solutions of mixtures of the two constituents namely the meta and tetra-pyro-phosphate, the relative rates of solution of corresponding mixtures of our fused product are of importance. In comparative tests with our fused homogeneous product and mechanical mixtures of equivalent stoichiometric composition we have found that our improved phosphates dissolve completely and in a relatively short time while the mechanical mixtures of equivalent composition require an inordinately long time for complete solution.

We have also noted, in this connection, that our product causes a lesser degree of corrosion on the dissolving equipment. This is believed to be due to the fact that the constituents of our product dissolve completely at a uniform rate provided sufficient water is present to form a complete solution, we have also noted that the acidity of the solution is at no time excessively high due to the acid constituent dissolving at a faster rate. This is a factor of considerable importance because of the universal use of iron dissolving equipment in water treating operations.

**Optical properties of the dehydrated sodium phosphates**

Sodium meta phosphate is an isotropic material having a refractive index of 1.490 plus or minus 0.002, for ordinary light. Tetra-sodium pyro-phosphate crystals are bidimensional and positive and have a small axial angle. The indices are:

\[
\begin{align*}
\alpha &= 1.473 \pm 0.002 \\
\beta &= 1.474 \pm 0.003 \\
\gamma &= 1.480 \pm 0.002
\end{align*}
\]

The crystals are orthorhombic, platy in shape, and have a negative elongation.

Composition stoichiometrically equivalent to a content of approximately 50 percent of sodium meta phosphate and 50 percent of tetra-sodium pyro-phosphate are mostly isotropic amorphous solids having an index of refraction of 1.480 plus or minus 0.002. There are a few anisotropic, biaxial crystals visible in the isotropic amorphous solid. Compositions ranging in content between the 50–50 composition mentioned above and a composition containing the stoichiometric equivalent of 90 percent sodium meta phosphate and 10 percent of tetra-sodium pyro-phosphate, have the same refractive index as that mentioned for the 50–50 composition and show fewer crystalline inclusions.

Compositions of our products ranging between the stoichiometric equivalent of 50 percent sodium meta phosphate and 50 percent of tetra-sodium pyro-phosphate to the 90 percent meta-sodium pyro-phosphate and 10 percent sodium meta phosphate compositions show a gradually increasing anisotropic biaxial crystalline content in the amorphous solid. The crystalline phase appears as plate-like or feathery crystals with the amorphous isotropic material between the crystals. The isotropic material has an index of 1.480. The crystalline phase has the optical properties of the tetra-sodium pyro-phosphate given above—that is the crystals are anisotropic and biaxial.

The optical examination of our improved product indicates therefore that those compositions having a major proportion of equivalent sodium meta phosphate consist of a homogeneous amorphous isotropic solid having a refractive index between the limits of 1.478 and 1.482 in which isotropic solid is suspended a relatively small proportion of anisotropic crystalline material.

The proportion of crystalline material in our product is present in smaller proportion than that indicated by the stoichiometric composition of the mass. This clearly indicates that a chemical combination of the constituents present has occurred which combination results in the formation of a new compound characterized by the properties given above. Such a conclusion agrees with the chemical properties which have already been mentioned.

Because of the complexity of the dehydrated sodium phosphates obtained by our process we are unable to more accurately define them. Since they are definitely reproducible by following the methods outlined in our disclosure above they are properly defined and characterized by the methods stated.

The products herein described embody the so-called polyphosphates as described in Gmelin's Handbuch 8th ed. volume "Natrium" pages 924–925. For example using proportions of sodium salts such that one obtains the stoichiometric equivalent, in the fused product of 1 mol of Na₅P₃O₁₀ and 1 mol of NaPO₃, the cooled fused product will contain the sodium salt of triphosphoric acid, namely the compound Na₅P₃O₁₀. In similar manner one may obtain the compound sodium tetraphosphate, Na₅P₄O₁₄, by using proportions being such that the fused product contains the equivalent of 1 mol of Na₅P₃O₁₀ and 2 mols of NaPO₃.

This compound is a salt of tetrathosphoric acid,
The compound sodium pentaphosphate Na\textsubscript{2}H\textsubscript{2}P\textsubscript{2}O\textsubscript{7} may likewise be made by combining by fusion 1 mol of Na\textsubscript{2}P\textsubscript{2}O\textsubscript{7} and 8 mols of NaF, this compound being the salt of pentaphosphoric acid, H\textsubscript{5}P\textsubscript{5}O\textsubscript{15}.

Intermediate products between the compounds specifically enumerated may be made by suitably choosing the proportions of the starting materials. For example, instead of producing the pure compound, Na\textsubscript{2}P\textsubscript{2}O\textsubscript{7}, one may by increasing the proportions of meta phosphate equivalent employed obtain a product containing the compound Na\textsubscript{2}P\textsubscript{2}O\textsubscript{7} plus some meta phosphate. The same applies to products containing the constituent sodium tetraphosphophosphate and sodium pentaphosphate.

These compounds may be used for water softening and as washing aids or ingredients because they tend to sequester the alkaline earth ions, as is described by Hall in U. S. Patent 1,856,515 in the case of sodium hexa metaphosphate alone. The result of such sequestration or combination is to eliminate or reduce the relatively large concentration of free calcium or other alkaline earth ions present in the hard water.

In view of the fact that water may be effectively softened by the use of alkaline earths of the polyphosphonic acids, the compounds herein described may be used in a variety of industries. The compounds may for example be employed as water softeners in boiler plants, in deliming leather, in dyeing textiles, scouring wool, kier boiling, silk degumming, general washing purposes with or without soap especially for hard water ordinarily precipitates an insoluble compound. They may also be incorporated into soap to produce a soap composition having water softening properties.

Having now particularly described our invention and the manner in which it may be worked, it will be apparent that our invention is susceptible of various changes and modifications without departing from the spirit thereof, and we desire therefore that our invention be not limited except as indicated by the prior art or as particularly pointed out in the claims.

What we claim is:

1. A process which comprises adding to hard water, so as to combine with an alkaline earth metal compound thereof, to prevent deposition of said compound, the fused reaction product of monosodium and disodium orthophosphate, to produce when dissolved in water an aqueous solution having a pH between 8 and 10, the weight proportions of NaF, derived from said monosodium orthophosphate, and Na\textsubscript{2}P\textsubscript{2}O\textsubscript{7}, derived from disodium orthophosphate in said reaction product, falling within the range of 50:50 and 20:80 respectively, said reaction product being further characterized in that its power to prevent deposition of said alkaline earth metal compound is greater than that of an unreacted mixture of sodium metaphosphate and tetrasodium pyrophosphate.

2. A process which comprises adding to hard water, so as to combine with an alkaline earth metal compound thereof, to prevent deposition of said compound, the fused reaction product of monosodium and disodium orthophosphate, to produce when dissolved in water an aqueous solution having a pH between 8 and 10, the weight proportions of NaF, derived from said monosodium orthophosphate, and Na\textsubscript{2}P\textsubscript{2}O\textsubscript{7}, derived from disodium orthophosphate in said reaction product, falling within the range of 50:50 and 20:80 respectively, said reaction product being further characterized in that its power to prevent deposition of said alkaline earth metal compound is greater than that of an unreacted mixture of sodium metaphosphate and tetrasodium pyrophosphate.