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SODIUM POTASSIUM PYROPHOSPHATES
AND METHOD FOR PRODUCING SAMECharles B. Durgin and Robert N. Foster, Annis-
ton, Ala., assignors to Monsanto Chemical Com-
pany, St. Louis, Mo., a corporation of DelawareNo Drawing. Application May 17, 1944,
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8 Claims. (Cl. 23-106)

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This invention relates to alkali metal pyrophosphates and more particularly to sodium potassium pyrophosphates and to a process for producing same.

The principal object of the invention is to produce sodium potassium pyrophosphates which are relatively non-hygroscopic and, therefore, resistant to atmospheric moisture.

Another object of the invention is to produce sodium potassium pyrophosphates which are free flowing and do not have the tendency to agglomerate or cake when stored alone or in combination with other materials such as, for example, soap powders.

A further object of the invention is to provide a novel soap builder which inhibits caking and dusting of soap powders.

An additional object of the invention is to provide a series of new products which are much less hygroscopic and much more economical to make than tetrapotassium pyrophosphate and which have a more rapid rate of solution and a higher total solubility than tetrasodium pyrophosphate.

A still further object of the invention is to provide novel soap builders which may be combined with soap much more readily than tetrapotassium or tetrasodium pyrophosphate and which are superior to both of these salts in that after they are incorporated with soap they do not crystallize out and produce therein the undesirable property known as graininess or sandiness.

Another object of the invention is to provide a new series of compounds which are suitable for softening water.

Other objects of the invention will be apparent as the description proceeds.

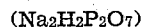
The tetra-alkali metal pyrophosphates and mixtures of these salts have been used quite extensively in recent years. For example, they have been used for water softening, washing, cleansing and rinsing of textiles, clothes, linen and the like. They have also been employed as detergents per se and as soap builders to replace such materials as soda ash, caustic soda, sodium silicate and trisodium phosphate and while they have enjoyed considerable success they have not been entirely satisfactory.

For example, tetrapotassium pyrophosphate is quite expensive to prepare, and it has the fur-

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ther disadvantage that it is very hygroscopic and tends to cake and become lumpy with the result that it loses its free flowing character in a relatively short time. Tetrasodium pyrophosphate can be manufactured at a lower cost than the corresponding potassium salt, but it lacks the desired rate of solution and the desired total solubility.

Mechanical mixtures of these salts or mixtures thereof with acid sodium pyrophosphate



and/or acid potassium pyrophosphate



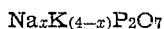
do not provide a solution to the problem as such mixtures do not possess the desired total solubility or the desired solution rate. Moreover, they are excessively hygroscopic and require considerable care in packing, transporting and storing to prevent them from caking into a solid mass.

The individual tetra-alkali metal salts and the above-mentioned mechanical mixtures are also objectionable because, when employed as soap builders, they tend to form soaps which are characterized by a lack of homogeneity due to the formation and the heterogeneous distribution of fine crystals throughout the body of the soap. Also, when such salts or mixtures of salts are incorporated with soap powders, the latter have the undesirable property of dusting, notwithstanding the fact that the added salts are hygroscopic. Dusting is objectionable because it causes the user to sneeze and also because it results in an excessive loss of soap powder.

There is, therefore, a rather urgent demand by the art for a highly soluble, substantially non-hygroscopic product having a high solution rate, which is readily compatible with soaps without producing graininess and which stabilizes soap powders against dusting without, at the same time, causing the powder to cake.

Now we have made the surprising discovery that if a mixed solution of dipotassium and disodium orthophosphate is dehydrated on an atmospheric drum dryer or other suitable surface and then heated to the pyrophosphate form-

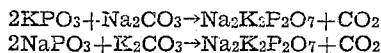
ing temperature, a new series of compounds is formed which possess the desirable properties set forth above. Moreover, they do not have any of the objectionable properties described in connection with the tetra-alkali metal pyrophosphates or mechanical mixtures thereof. These new compounds are designated herein as sodium potassium pyrophosphates and have a stoichiometric composition represented by the following general formula:



wherein x has a value varying from a positive fractional value up to a value of less than 4.

Another method of making our new products is to prepare the mixed orthophosphate solution by reacting liquid caustic potash and monosodium phosphate or by reacting caustic soda and monopotassium phosphate, drying these products and then heating the dried products to the pyrophosphate forming temperature.

A third and very economical method is to prepare KPO_3 or NaPO_3 by the method described in the patents to Kerschbaum (2,142,943 and 2,142,944) and then react these salts at the pyrophosphate forming temperature with sodium and potassium carbonate respectively in accordance with the following equations:



An example of the method of preparing our new products is as follows:

A 50 per cent solution of anhydrous Na_2HPO_4 is prepared by dissolving $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ in water in the proportion of 167 lbs. of $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ per 100 lbs. of water, care being taken to keep the solution close to the boiling point (about $105^\circ \text{C}.$) to prevent crystallization.

In another tank an approximately 46% solution of K_2HPO_4 is prepared by adding 75% H_3PO_4 to 45% KOH in the proportion of 63.2 lbs. of P_2O_5 per 100 lbs. of 100% KOH .

These two solutions are mixed in the proper proportions to give a ratio of 50.3 parts by weight of Na_2HPO_4 to 49.7 parts by weight of K_2HPO_4 . The adjustment of these solutions is preferably carried out in such a manner that the mix is slightly on the alkaline side as any excess acid present tends to form KH_2PO_4 which upon calcining gives an insoluble potassium metaphosphate, thus causing turbidity in the product. The mixed solution, if clear and free from suspended matter, is fed directly to drying rolls; if not, it is clarified by filtration and then fed thereto.

The drum dried product is then converted to pyrophosphate by calcining the same in a rotary converter at a temperature substantially in the range of from about $350^\circ \text{C}.$ to the fusion temperature of the product. In the interest of rapid conversion, however, we prefer to carry out the calcination at a temperature of $400^\circ \text{C}.$ or at higher temperatures.

The finished product is an anhydrous, readily soluble, substantially non-hygroscopic, white crystalline material which has a high solution rate. It is soluble in water to the extent of about 37 grams per 100 c. c. of water at $30^\circ \text{C}.$ and when prepared in the form of a 1% solution it gives a pH of about 10.3. X-ray analysis shows that it is either a double salt of tetrasodium and tetrapotassium pyrophosphate or the new compound $\text{Na}_2\text{K}_2\text{P}_2\text{O}_7$ and that it is distinct from both of these tetra-alkali metal pyrophosphates and not merely a mechanical mixture of the two.

If desired, the disodium and dipotassium orthophosphates may be intimately mixed with each other while in a finely divided solid state or they may be intimately mixed and prepared in the form of briquettes in any suitable manner and then subjected to the pyrophosphate conversion temperature.

By changing the proportions of the reactants in the conversion step it is possible to obtain products which vary in composition in accordance with the general formula indicated above. For example, if it is desired to obtain $\text{Na}_2\text{K}_2\text{P}_2\text{O}_7$, the disodium and dipotassium orthophosphate salts are heated together in equal molecular proportions to the pyrophosphate conversion temperature. On the other hand, if the compounds $\text{Na}_3\text{KP}_2\text{O}_7$ and $\text{Na}_4\text{K}_3\text{P}_2\text{O}_7$ are desired, then Na_2HPO_4 and K_2HPO_4 are reacted together in a molecular ratio of 3 to 1 and 1 to 3 respectively. It should be understood, however, that by properly adjusting the amounts of the two reactants, it is possible to obtain such compounds as $\text{Na}_{1.5}\text{K}_{2.5}\text{P}_2\text{O}_7$, $\text{Na}_{2.5}\text{K}_{1.5}\text{P}_2\text{O}_7$, $\text{Na}_{0.5}\text{K}_{3.5}\text{P}_2\text{O}_7$, $\text{Na}_{3.5}\text{K}_{0.5}\text{P}_2\text{O}_7$, etc.

The products prepared by the methods described above are stable in the presence of atmospheric moisture, have a high total solubility, a high solution rate and are relatively non-hygroscopic as compared with mechanical mixtures of tetrasodium and tetrapotassium pyrophosphate.

That these new products are markedly superior to mechanical mixtures of tetrasodium and tetrapotassium phosphates is evident from the following experimental data showing the results of hygroscopicity tests made on these materials:

Table I.—Exposure tests at 32% relative humidity at 25 to $30^\circ \text{C}.$

Samples	Per Cent Gain in Weight										Condition of Sample on 42nd Day
	1 Day	2 Days	3 Days	4 Days	7 Days	14 Days	21 Days	28 Days	35 Days	42 Days	
1. New Product Prepared from Equal Molecular Proportions of Na_2HPO_4 and K_2HPO_4	0.1	0.2	-----	0.25	0.33	0.37	0.37	0.41	0.47	10.46	Free flowing—dry.
2. Mechanical Mixture Prepared from Equal Molecular Proportions of $\text{Na}_2\text{P}_2\text{O}_7$ and $\text{K}_4\text{P}_2\text{O}_7$	5.35	6.23	6.40	6.62	6.74	7.18	7.20	7.47	7.65	7.63	Caked considerably.
3. New Product Prepared from Equal Proportions by Weight of Na_2HPO_4 and K_2HPO_4	0.12	0.17	0.19	0.23	0.27	0.33	0.33	0.39	0.43	0.41	Free flowing—dry.
4. Mechanical Mixtures Prepared from Equal Proportions by Weight of $\text{Na}_2\text{P}_2\text{O}_7$ and $\text{K}_4\text{P}_2\text{O}_7$	5.17	6.00	5.32	5.58	6.47	6.90	6.90	7.17	7.23	7.27	Caked considerably—moist.

¹ 40 days.

Table II.—Exposure tests at 57.5% relative humidity at 25 to 30° C.

Samples	Per Cent Gain in Weight										Condition of Sample on 42nd Day
	1 Day	2 Days	3 Days	4 Days	7 Days	14 Days	21 Days	28 Days	35 Days	42 Days	
1. New Product Prepared from Equal Molecular Proportions of Na_2HPO_4 and K_2HPO_4	0.68	-----	0.78	0.82	0.97	¹ 1.59	1.71	2.91	3.21	² 3.03	Caked slightly—dry.
2. Mechanical Mixture Prepared from Equal Molecular Proportions of $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{K}_4\text{P}_2\text{O}_7$	14.6	18.9	23.4	26.8	31.25	33.7	31.70	33.7	32.9	31.89	Caked considerably—moist.
3. New Product Prepared from Equal Proportions by Weight of Na_2HPO_4 and K_2HPO_4	0.33	0.39	0.39	0.48	0.45	1.03	1.03	2.07	2.09	1.84	Free flowing—dry.
4. Mechanical Mixtures Prepared from Equal Proportions by Weight of $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{K}_4\text{P}_2\text{O}_7$	13.9	19.0	25.1	28.95	35.25	39.0	36.0	38.9	38.3	36.53	Caked considerably—moist.

¹ 15 days.² 39 days.

In carrying out the foregoing tests equal molecular proportions of disodium and dipotassium orthophosphates were reacted to form the new compound and the stability of this compound in the presence of moisture was compared with the product formed by mechanically mixing equal molecular proportions of tetrasodium and tetrapotassium pyrophosphate. The tests were also carried out using the new product formed by reacting equal parts by weight of the above orthophosphates, and also a mechanical mixture of equal parts by weight of tetrasodium and tetrapotassium pyrophosphate.

Table I demonstrates the relative stability of the new products and the mechanical mixtures in the presence of air having a moisture content corresponding to a relative humidity of 32% at 25° C. to 30° C. For example, it shows that samples 1 and 3 (applicants' new products) absorbed up to 0.46% by weight of moisture within a period of from 40 to 42 days, whereas samples 2 and 4 (mechanical mixtures of tetrasodium and tetrapotassium pyrophosphates) absorbed in excess of 7.2% of moisture within the same period of time. The new products were free flowing and dry at the end of the tests and the mechanical mixtures had caked considerably and were moist. Moreover, it is significant that the gain in weight of the mechanical mixtures was due almost entirely to moisture absorbed on the first day, which clearly shows that mechanical mixtures of this type are very hygroscopic.

Table II illustrates the results of tests made to show the effect on the two products of air having a moisture content corresponding to a relative humidity of 57.5% at 25° C. to 30° C. These tests clearly demonstrate the stability of the new products and also the instability of mechanical mixtures of tetrasodium and tetrapotassium pyrophosphates. For example, sample 1, applicants' new product, absorbed in 39 days only 3.03% by weight of moisture and caked only slightly, notwithstanding the fact that the conditions were unusually severe. Sample 3, also applicants' new product, displayed remarkable stability under the above conditions since it absorbed only 1.84% by weight of moisture in a period of 42 days and remained in a dry free flowing condition. On the other hand, samples 2 and 4 (mechanical mixtures of tetrasodium and tetrapotassium pyrophosphate) absorbed 31.89% and 36.53% by weight of moisture respectively in a period of 42 days, and both samples caked considerably and were moist at the end of the tests. It is worthy of note also that the mechanical mixtures absorbed a substantial amount of moisture on the first day, and that practically

all the moisture taken up by samples 2 and 4 was absorbed within a period of seven days.

Tables I and II demonstrate in a very striking manner the marked difference in the hygroscopicity of the new products and mechanical mixtures of tetrasodium and tetrapotassium pyrophosphate of the same stoichiometric composition. This marked difference in hygroscopicity tends to confirm X-ray analyses made on the new products, which analyses showed that they are not merely mechanical mixtures of tetrasodium and tetrapotassium pyrophosphates but are either double salts or definite chemical compounds of the type represented by the above general formula.

The following table illustrates and makes a comparison of the solution rates of the new products and mechanical mixtures of the tetra-alkali metal pyrophosphates.

Table III

Material	Time (in seconds required to dissolve 5 grams of material in 95 grams of water at 30° C.
1. New Product Prepared from Equal Molecular Proportions of Na_2HPO_4 and K_2HPO_4	35
2. Mechanical Mixture Prepared From Equal Molecular Proportions of $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{K}_4\text{P}_2\text{O}_7$	60
3. New Product Prepared from Equal Proportions by Weight of Na_2HPO_4 and K_2HPO_4	45
4. Mechanical Mixtures Prepared from Equal Proportions by Weight of $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{K}_4\text{P}_2\text{O}_7$	80

It will be noted from an examination of Table III that the new products possess a solution rate which is substantially double that of a mechanical mixture of tetrasodium and tetrapotassium pyrophosphate of the same stoichiometric composition. This is a difference in kind and not merely one of degree, and it tends to further indicate that the products are definite chemical compounds and not mechanical mixtures of the tetra-alkali metal pyrophosphates.

The new compounds which are prepared in accordance with this invention may be employed in the household and in many branches of industry. They may be prepared in many different forms, such as cakes, beads, powder, solutions, flakes, shreds, paste, etc. and when in the form of a powder, they are readily soluble and substantially non-hygroscopic. Consequently, when placed in cardboard cartons, they will not cake on the shelves of the retailer or cake after

the packages have been opened by the housewife. Moreover, they do not have the tendency to dust when used alone or when combined with soap powders; in fact, they actually stabilize the latter against dusting, notwithstanding the fact that the new compounds are relatively non-hygroscopic.

The new compounds are efficient soap builders and can readily be incorporated with all types of soap without imparting graininess thereto. They may be combined with soap in any of its forms such as milled or unmilled bars, powders, flakes, gels or solutions. They may be mechanically mixed in; they may be crutched into the molten soap or they may be dissolved in a soap gel or solution or they may be incorporated with soap in any other suitable manner.

They may be employed as detergents per se and in combination with various types of synthetic detergents or soap substitutes such as water soluble mineral oil sulfonates, sulfonated and sulfated higher fatty alcohols, sulfonated long chain hydrocarbons and water soluble salts of alkylated aromatic sulfonic acids in which the alkyl group contains more than eight carbon atoms. If desired, they may be incorporated with mixtures of soaps and/or synthetic detergents.

The new compounds are excellent water softening agents. Their action, however, is different from the usual water softening compounds such as sodium carbonate, sodium silicate and trisodium phosphate which form precipitates with the calcium, magnesium, etc. in the water. They soften water by sequestering the calcium and magnesium ions in the form of a water soluble complex and if any insoluble salts are present they dissolve these salts by the formation of such a complex. Thus, when the compounds of this invention are employed alone or in combination with soap or other detergents, very little precipitation or the formation of insoluble soaps is encountered even in very hard waters. This is a very desirable result as if soap is allowed to precipitate on fabric, it tends to become rancid and to impart an unpleasant odor thereto. Moreover, when these compounds are added to water having a high iron content, clothes may be washed therein without producing iron stains as the iron content of the water is also apparently converted into a water soluble complex.

The new compounds may be used in detergent operations generally and to prevent alkaline earth salts from depositing in hot water systems, in steam boilers and their feed lines, and in automobile cooling systems. In fact, they find use in all operations known to the art where it is desirable to soften water by preventing the precipitation of calcium, magnesium and iron salts.

When the new compounds are dissolved in water, the solution has a pH of about 10 or a higher value. However, the pH of these products may be varied if desired by the addition of various alkaline salts. Such salts serve as adjusting agents to change the alkalinity of the solutions obtained, which accordingly may be adjusted to a higher or lower level. For this purpose caustic soda, sodium sulfate, sodium bisulfate, soda ash, sodium bicarbonate, sodium metasilicate, trisodium phosphate, sodium acid pyrophosphate or mixtures of these compounds are suitable. If desired, the corresponding potassium salts may be employed. Thus it is possible to vary the alkalinity of the solutions to meet the requirements of various detergent processes and waters of vary-

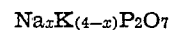
ing degrees of hardness such as occur in different sections of the country.

While we have described our invention in detail, it should be understood that many changes may be made without departing from the spirit of the same.

We claim:

1. The method of preparing sodium potassium pyrophosphate, which comprises mixing a 50% solution of Na_2HPO_4 with an approximately 46% solution of K_2HPO_4 in the proportions adapted to supply 50.3 parts by weight of Na_2HPO_4 to 49.7 parts by weight of K_2HPO_4 , drum drying the resulting mixture and then heating the dried material to the pyrophosphate forming temperature to produce a product consisting essentially of $\text{Na}_2\text{K}_2\text{P}_2\text{O}_7$, said product being characterized by having a substantially improved solution rate and resistance to moisture vapor absorption over the corresponding mechanical mixture of $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{K}_4\text{P}_2\text{O}_7$.

2. The method of producing sodium potassium pyrophosphates having a stoichiometric composition expressed by the following formula:



wherein x is selected from the group of values consisting of 1, 2 and 3, which comprises preparing an aqueous solution of disodium orthophosphate and an aqueous solution of dipotassium orthophosphate, mixing the solutions in the proportions calculated to yield the above compounds, drying the mixed solutions upon an evaporative surface and then heating the dried material to the pyrophosphate forming temperature to form a product having a substantially improved solution rate and resistance to water vapor absorption over the corresponding mechanical mixture of $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{K}_4\text{P}_2\text{O}_7$.

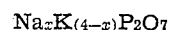
3. The method defined in claim 2, where x has a value of 1.

4. The method defined in claim 2, where x has a value of 2.

5. The method defined in claim 2, wherein x has a value of 3.

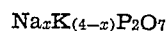
6. The method defined in claim 2, wherein the mixed solutions are drum dried and heated to a temperature substantially within the range of from about 350°C . to the fusion temperature of the reaction mixture.

7. The method of producing sodium potassium pyrophosphate, which comprises drum drying an aqueous solution of a mixture of disodium orthophosphate and dipotassium orthophosphate in the proportions calculated to yield a compound having the following general formula:



wherein x is selected from the group of values consisting of 1, 2 and 3 and then heating the dried material to the pyrophosphate forming temperature to form a product having a substantially improved solution rate and resistance to water vapor absorption over the corresponding mechanical mixture of $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{K}_4\text{P}_2\text{O}_7$.

8. The method of producing sodium potassium pyrophosphate, which comprises drying upon an evaporative surface an aqueous solution of a material providing Na_2O , K_2O and ortho P_2O_5 in the molecular proportions calculated to yield upon molecular dehydration a compound having the following general formula:



wherein x is selected from the group of values consisting of 1, 2 and 3, and then heating the

dried material to the pyrophosphate forming temperature to form a product characterized by having a substantially improved solution rate and resistance to water vapor absorption over the corresponding mechanical mixture of $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{K}_4\text{P}_2\text{O}_7$.

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