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PROCESS FOR THE CONVERSION OF WATER-INSOLUBLE POTASSIUM SALTS OF HIGH-POLYMERIC METAPHOSPHORIC ACIDS INTO A WATER-SOLUBLE STATE

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This invention relates to a process for the conversion of water-insoluble potassium salts of high-polymeric metaphosphoric acids into a water-soluble state.

The water-soluble alkali metal salts of polymeric metaphosphoric acids have been extensively applied in industry, for example in water-softening and washing, as cheese melting salts etc. The phosphoric salts of potassium, however, could, owing to their insolubility in water, up to now not be used for these purposes, in spite of the specific qualities of potassium. Therefore, it was a special necessity to treat water-insoluble potassium salts of high-polymeric metaphosphoric acids in a suitable manner, so as to make them water-soluble.

Potassium metaphosphate is known to become water-soluble by addition of sodium hexametaphosphate or sodium pyrophosphate. These anhydrous phosphates used as a solvent possess, however, an identical or homogeneous anion and have the further disadvantage of considerably reducing the effectiveness of the high-polymeric phosphate, as observed for example with the so-called phosphate-threshold-treatment.

Now the surprising discovery has been made that water-insolubility of potassium salts of high-polymeric metaphosphoric acids can be removed not only with the aid of anhydrous phosphates, viz. pyro- or hexametaphosphate, but also by addition of other sodium compounds, such as sodium hydroxide or sodium salts of anions different from that of anhydrous phosphoric acid. Moreover, other alkali metal salts, such as those of lithium and ammonium, have also proved suitable for this purpose. The effect obtained is quit surprising, since according to a general rule in chemistry the solubility of a chemical substance is greatest in an agent of homogeneous structure, so that the solubility of potassium metaphosphate in anhydrous phosphates could not simply be generalized and above all, since for example a saturated solution of sodium chloride is known to precipitate high-polymeric, water-soluble metaphosphates.

Among the alkali metal compounds suitable for the process of the present invention be enumerated the following ones: sodium hydroxide and the sodium, ammonium, and lithium salts of hydrochloric acid, carbonic acid, boric acid, silicic acid; further the salts of organic acids, such as fatty acids, benzoic acid, acetic acid, citric acid, as well as the alkali metal salts of a sulphonated product of fats, oils, fatty alcohols, and other organic compounds of high molecular weight which can be sulphonated. Sodium sulphate has proved to be especially opportune, because it delivers very viscous solutions and besides, owing to its low price, offers considerable economical advantages. The superiority of the sulphate iron over other anions, for example chloride, concerning their ability of dissolving potassium metaphosphate, is the more surprising as the former is generally a stronger precipitant for colloids than chlorides. The present process is favourably carried out by mixing solid potassium metaphosphate with a dilute aqueous solution of any sodium compound, whereat a certain concentration of the solvent should not be exceeded. This critical concentration varies for the different sodium compounds: it is for example for sodium hydroxide between 1 and 3 volume percent, for sodium chloride and sodium nitrate between 2,5 and 5 volume percent, for soda between 1 and 5 volume percent, for sodium acetate between 4 and 6 volume percent, and for sodium sulphate between 13 and 15 volume percent. The critical concentration is determined by adding to a high-polymeric, water-soluble phosphate varying concentrations of the sodium compound to be tested.

The potassium metaphosphate can be dissolved at ordinary temperature. Heating, however, accelerates and intensifies the dissolving process. Of course, the solid salts can also be mixed with each other before dissolution, and water then be added. The so obtained solutions can now be directly applied for the different purposes, for example as water softening agents, washing and cleaning agents, since they can be mixed in known manner with usual washing-active substances, thereby not only offering the particular advantake of linking the metal ions of the alkaline earths contained in the water into complex state, but—owing to their colloidal character—also increasing the capillary-activity of the washing agents. The special advantage of the claimed process consists among others in the fact that, in consequence of the multiplicity of possible combinations, mixtures of varying character, complying with all requirements, can be produced.

Example 1.—To 0,5 g of potassium metaphosphate are added 100 ccm of a 1% solution of sodium chloride. A clear solution with a specific viscosity of $\eta_{sp.}=0{,}800$ is obtained.

Example 2.—0,5 g of potassium metaphosphate are dissolved in 100 ccm of a 1% solution of sodium sulphate. The viscosity of this solution is $\eta_{sp.}=1.975$.

Example 3.—1 g of potassium metaphosphate is dissolved in 100 ccm of a 2% solution of sodium sulphate. The resulting solution has a specific viscosity of $\eta_{sp.}=3,04$.

Example 4.—1 g of potassium metaphosphate, dissolved in 100 ccm of a 10% solution of sodium sulphate, yields an aqueous solution with a specific viscosity of $\eta_{sp.}=0,545$.

Example 5.—With 2,5 g of potassium metaphosphate in 100 ccm of a 5% solution of sodium sulphate a solution with a specific viscosity of $\eta_{sp.}=0,379$ is obtained.

Example 6.—1 g of potassium metaphosphate is dissolved in 100 ccm of a 2% solution of sodium carbonate. The specific viscosity of this solution is $\eta_{sp.}=0,819$.

Example 7.—1 g of potassium metaphosphate is dissolved under heating in 100 ccm of a 5% solution of ammonium chloride and then cooled. The solution has a specific viscosity of $\eta_{sp.}=0,57$.

Example 8.—1 g of potassium metaphosphate is dissolved in 100 ccm of a 5% solution of lithium chloride with subsequent cooling. The specific viscosity of the resulting solution is $\eta_{sp.}=0,758$.

For certain applications, especially for the cleaning of the hands, it is desirable that the products be of well mouldable constitution. Now, after a series of experiments, we succeeded in obtaining potassium metaphosphate-containing, water-soluble, pilier (in German: pillerbar) products, by mixing potassium metaphosphate with the sodium or ammonium salt of a sulphuric acid reaction product with oils and fats, such as: "Monopol" soap, the sodium salt of the acid sulphuric acid ester of: castor-oil, oleic acid, fatty alcohols, fatty sulphonic acids etc., in presence of sufficient water, so that the mass becomes kneadable and mouldable.

Example 9.—22,5 g of the sodium salt of an acid ester from sulphuric acid with fatty alcohol with about 35% of sodium sulphate and 22,5 g of water-insoluble potassium metaphosphate are thoroughly mixed in a kneader under addition of as much water as is required for obtaining a doughy mass. Thereto are necessary about 7,5 g of water. In order to accelerate homogenization, it is recommendable to treat the kneaded mass on a rolling machine (in German: Walzenstuhl) as used in the manufacture of soap shavings and then to work the shavings in usual manner.

Example 10.—16 g of technical cetyl sulphuric acid sodium and 6,5 g of potassium metaphosphate as well as 2,5 g of a 10% aqueous solution of the sodium salt of cellulose glycolic acid ester are thoroughly kneaded. 1 g of water is slowly added for reasons of a suitable constitution. As soon as the mass has reached the desired homogeneousness, it is worked as per example 9.

The moulded pieces according to the present process can be used in the same way as normal soaps of fatty acid alkali. Just as these, they may have added any filling materials, such as water glass, cellulose derivatives, starch, nonionogen washing agents, kaolin, etc. Moreover, the products can be adjusted either acid or neutral or alkalins according to requirement. They can also be combined with soap or soap-like materials, or additions of usual organic or anorganic colouring matter, perfumes, glycerine etc. can be made.

It is a particular advantage of the described products that, even at an extremely low fat content, i. e. 30%, they have the appearance and lathering power of normal soap and can be employed in any water, such as hard or salty waters, without any loss of fat or reduction of washing power.

It has further been found that well soluble, dry alkali metal double salts of high-polymeric metaphosphoric acids can be easily produced by dissolving, as described above, potassium metaphosphate in a dilute solution of alkali metal or ammonium salts, such as sodium chloride, sodium sulphate, NH_4Cl etc. with following precipitation by means of a suitable precipitant under mechanical mixing, for example stirring. In this way a fine-flocculent, non-caking alkali metal double salt, such as potassium-sodium hexametaphosphate or potassium-ammonium hexametaphosphate, easy to dry, is obtained.

As a precipitant are suitable: solutions of alkali metal salts, the salt content of which is higher than the point of critical concentration, for example 25% solutions of sodium sulphate, 10% solutions of sodium chloride, 10% solutions of NH_4SCN etc. Still better precipitants are the organic solvents which can be mixed with water, such as alcohols, ketones etc. The organic precipitants for the alkali metal double salts according to the present process can be applied in their anhydrous or hydrated form, or can be mixed with each other or diluted with aqueous salt solutions. Methylalcohol has proved particularly suitable, since yielding a very fine-flocculent, non-adhesive, and non-caking precipitate.

Example 11.—50 g. of water-insoluble potassium metaphosphate are brought into 175 ccm of a solution of sodium sulphate, containing 61,3 g of $(NH_4)_2SO_4\cdot 10H_2O$, which mixture is left to itself until complete dissolution. Subsequently, the viscous liquid is diluted with water to a volume of 2 litres. Precipitation is accomplished by slowly stirring into 2 litres of 75% methyl alcohol. After some time the clear liquid is decanted, the deposit digested with 2 litres of 50% methanol and then filtrated. The potassium-sodium metaphosphate thus obtained is free from sodium sulphate and can be dried. In order to accelerate drying, the last traces of water are removed by treatment with pure methanol. Thereby, rapid drying is possible without heating. This product is easily soluble in water and its specific viscosity in a 0,5% solution is $\eta_{20^\circ}=11,5$.

Example 12.—10 g of potassium metaphosphate are dissolved in 1 litre of a 1% solution of ammonium chloride under heating with subsequent rapid cooling. For precipitation the solution is stirred into 1 litre of methanol, the turbidity formed at the beginning changing into an easily dispersing precipitate of high-polymeric potassium-ammonium metaphosphate. Further working as per example 11.

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