# Manufacturing of Neutral Sodium−Potassium Pyro- and Tripolyphosphates as Complexing Agents of Nutrient Microelements

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A low-temperature condensation process of a mixture of $KH_2PO_4$ and $NH_4H_2PO_4$—as a product of the conversion of potassium chloride with ammonium dihydrogen orthophosphate—was investigated. At the same time, $NH_4^+$ and $H^+$ ions have been replaced with sodium ion (as $Na_2CO_3$) to obtain neutral sodium and potassium pyro- or tripolyphosphates. The influences of the process temperature (350−500 °C) and the type of initial mixture on the phase composition of the obtained polyphosphates, on their water solubilities and on the quantitative constitution of the $P_2O_5$ forms (orthophosphates, pyrophosphates, tripolyphosphates, and higher condensed phosphates) in the product, were determined. It was proved that under the assumed conditions of the polycondensation reaction of the orthophosphates mixture, soluble condensed phosphates were obtained as products, mainly consisting of pyro- and tripoly- or tripolyphosphates, and the created crystalline phases were the suitable solid solutions of potassium−sodium pyro- and tripolyphosphates: $(K,Na)_4P_2O_7$, $(K,Na)_5P_3O_{10}$. The approximate chemical compositions these solid solutions using X-ray diffraction analysis were determinated.

**Keywords:** *Hydrophosphates; condensation; pyrophosphates; tripolyphosphates*

## INTRODUCTION

Such micronutrients as Cu, Zn, Mn, Mo, and Co belong to the heavy-metals group, so their application as additives to solid mineral fertilizers creates a problem from an environmental point of view (Czuba, 1996). However, these elements play important physiological parts in plant organisms, although their deficit, as well as their excess, is usually harmful (Kabata-Pendias and Pendias, 1993). Their assimilability by the plants depends mainly on such factors as the: sorption ability of the soil, the activity of microorganisms, the pH value and oxidation−reduction potential of the soil, and also total level of rainfall in the given area. Additionally, an application of mineral phosphate fertilizers into the soil decreases the assimilation of micronutrients and their translocation from the plants' roots to overground portions of the plants because of the formation of phosphates, which are poorly water soluble (Gembarzewski, 1982; Patorczyk-Pytlik et al., 1992).

The problem of fertilization with micronutrients has been considerably solved by supplying farmers with liquid, multicomponent fertilizers for onto-leaf fertilization, which consist mainly of trace elements. These elements show 10−30 times higher efficiency, when used for onto-leaf fertilization, than if they are used in the soil (Czuba, 1996). Additionally, this method of application protects the soil against contamination by heavy metals, because the quantity of delivered trace elements is insignificant and they are effectively utilized. In onto-leaf fertilization, micronutrients are introduced in the form of water-soluble complexes; however chelating agents, which are applied, should avoid salting out of components from the solution and should also penetrate through the leaf surface but not injure the plants. Lignosulfonic acids, citric acid, ethylenediaminetetraacetic acid (EDTA) and its deriva-

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**Chart 1**

| system | mole ratio | system no. |
|---|---|---|
| $K_2HPO_4$ | | 1 |
| $K_2HPO_4$−$KH_2PO_4$ | 2:1 | 2 |
| $Na_2HPO_4$ | | 3 |
| $Na_2HPO_4$−$NaH_2PO_4$ | 2:1 | 4 |
| $K_2HPO_4$−$Na_2HPO_4$ | 1:1 | 5 |
| | 1:0.5 | |
| $K_2HPO_4$−$KH_2PO_4$−$Na_2HPO_4$−$NaH_2PO_4$ | 2:1:2:1 | 6 |
| | 2:1:1:0.5 | |
| $KH_2PO_4$−$Na_2CO_3$ | 1:0.5 | 7 |
| | 1:0.33 | |
| $NH_4H_2PO_4$−$Na_2CO_3$ | 1:1 | 8 |
| $KH_2PO_4$−$NH_4H_2PO_4$−$Na_2CO_3$ | 1:1:1.5;1:0.5:1 | 9 |
| | 1:1:1.17;1:0.5:0.75 | |

tives, and also polyphosphates are used as complexing agents (Dankiewicz, 1986; Fleming, 1969; Grzmil and Trojanowski, 1992; Kotuła and Czuba, 1989; Klimova and Tarasevicz, 1992; Mortvedt, 1985).

The subject of the present investigations was condensated potassium, sodium, and calcium phosphates. As a substrate in the low-temperature polycondensation of phosphates, the solid product from the process of low-chloride NPK fertilizers production was used (Glabisz et al., 1992). In this process, as a result of the conversion reaction of potassium chloride with ammonium dihydrogen phosphate (from the ammonization process of wet phosphoric acid), a solid phase is obtained, with the main components $KH_2PO_4$ and $NH_4H_2PO_4$. Because of the decomposition of ammonium dihydrogen phosphate and ammonia desorption during the dehydration process, it was assumed that the ammonium ion would be substituted with sodium ion (as $Na_2CO_3$) or calcium ion (as $CaCO_3$ or $CaO$).

The first stage of the investigation included the production of potassium−sodium or potassium−calcium hydrophosphates (Grzmil and Kic, 1995). It was proved that under the most favorable conditions of the conden-

**Table 1. Condensation of the Suitable Hydrogen Phosphates to Pyrophosphates**

| | | content (%) and **fraction** (%) | | | | | | content of individual forms of $P_2O_5$ (%) and **fraction** (%) | | | |
| | | $P_2O_5$ | | K | | Na | | | | | |
| system | temp, °C | total | water-soluble | total | water-soluble | total | water-soluble | ortho | pyro | tripoly | higher condensed |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $K_2HPO_4$ | | | | | | | | | | | |
| 1 | 350 | 37.31 | 37.19 | 42.40 | 36.40 | | | 19.10 | 17.99 | 0.10 | 0.00 |
| | | | **99.68** | | **85.85** | | | **51.36** | **48.37** | **0.27** | **0.00** |
| 2 | 500 | 38.33 | 37.34 | 41.63 | 36.58 | | | 0.00 | 37.34 | 0.00 | 0.00 |
| | | | **97.42** | | **87.86** | | | **0.00** | **100.00** | **0.00** | **0.00** |
| $Na_2HPO_4$ | | | | | | | | | | | |
| 1 | 350 | 48.38 | 47.87 | | | 33.93 | 26.20 | 0.15 | 45.86 | 1.76 | 0.10 |
| | | | **98.95** | | | | **77.22** | **0.31** | **95.80** | **3.68** | **0.21** |
| 2 | 500 | 48.99 | 47.40 | | | 33.33 | 27.22 | 0.00 | 46.35 | 0.95 | 0.10 |
| | | | **97.84** | | | | **81.67** | **0.00** | **97.79** | **2.00** | **0.21** |
| $K_2HPO_4-Na_2HPO_4$ | | | | | | | | | | | |
| 1 | 350 | 42.75 | 41.86 | 26.16 | 22.93 | 15.03 | 13.29 | 1.26 | 35.98 | 4.20 | 0.42 |
| | | | **97.92** | | **87.65** | | **88.42** | **3.01** | **85.95** | **10.03** | **1.00** |
| 2 | 500 | 44.41 | 43.45 | 26.08 | 24.57 | 15.85 | 13.09 | 0.00 | 43.05 | 0.40 | 0.00 |
| | | | **97.84** | | **94.21** | | **82.59** | **0.00** | **99.08** | **0.92** | **0.00** |
| $K_2HPO_4-0.5Na_2HPO_4$ | | | | | | | | | | | |
| 1 | 350 | 43.25 | 43.10 | 31.92 | 31.77 | 10.53 | 10.05 | 4.82 | 37.26 | 0.51 | 0.51 |
| | | | **99.65** | | **99.53** | | **95.44** | **11.18** | **86.45** | **1.18** | **1.18** |
| 2 | 500 | 43.21 | 43.03 | 32.03 | 32.02 | 10.82 | 10.37 | 0.00 | 41.28 | 1.00 | 0.75 |
| | | | **99.58** | | **99.97** | | **95.84** | **0.00** | **95.93** | **2.32** | **1.74** |

**Table 2. Condensation of the Suitable Hydrogen Phosphates to Tripolypolyphosphates**

| | | content (%) and **fraction** (%) | | | | | | content of individual forms of $P_2O_5$ (%) and **fraction** | | | |
| | | $P_2O_5$ | | K | | Na | | | | | |
| system | temp, °C | total | water-soluble | total | water-soluble | total | water-soluble | ortho | pyro | tripoly | higher condensed |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $K_2HPO_4-0.5KH_2PO_4$ | | | | | | | | | | | |
| 1 | 350 | 46.59 | 45.97 | 41.53 | 41.25 | | | 3.75 | 4.22 | 37.53 | 0.47 |
| | | | **98.67** | | **99.33** | | | **8.16** | **9.18** | **81.64** | **1.02** |
| 2 | 500 | 46.82 | 45.67 | 41.38 | 41.34 | | | 0.92 | 2.83 | 42.45 | 0.46 |
| | | | **97.54** | | **99.90** | | | **2.01** | **6.20** | **92.95** | **1.01** |
| $Na_2HPO_4-0.5NaH_2PO_4$ | | | | | | | | | | | |
| 1 | 350 | 57.43 | 55.25 | | | 30.30 | 30.27 | 2.34 | 7.02 | 45.43 | 0.47 |
| | | | **96.20** | | | | **99.90** | **4.24** | **12.71** | **82.23** | **0.85** |
| 2 | 500 | 57.82 | 56.59 | | | 30.61 | 30.57 | 2.56 | 6.99 | 45.96 | 1.08 |
| | | | **97.87** | | | | **99.87** | **4.52** | **12.35** | **81.22** | **1.91** |
| $2K_2HPO_4-KH_2PO_4-Na_2HPO_4-NaH_2PO_4$ | | | | | | | | | | | |
| 1 | 350 | 52.39 | 51.50 | 21.27 | 20.50 | 14.73 | 14.00 | 1.00 | 8.00 | 40.00 | 2.50 |
| | | | **98.30** | | **96.38** | | **95.04** | **1.94** | **15.53** | **77.67** | **4.85** |
| 2 | 500 | 53.36 | 52.89 | 21.98 | 20.66 | 14.55 | 13.78 | 0.99 | 8.48 | 40.91 | 2.49 |
| | | | **99.12** | | **93.99** | | **94.71** | **1.87** | **16.03** | **77.35** | **4.71** |
| $2K_2HPO_4-KH_2PO_4-Na_2HPO_4-0.5NaH_2PO_4$ | | | | | | | | | | | |
| 1 | 350 | 51.05 | 49.60 | 28.82 | 26.77 | 11.52 | 10.41 | 0.48 | 4.85 | 42.48 | 0.97 |
| | | | **97.16** | | **92.87** | | **90.36** | **0.96** | **9.78** | **86.29** | **1.96** |
| 2 | 500 | 50.48 | 49.85 | 30.13 | 27.91 | 10.59 | 9.47 | 0.96 | 1.46 | 46.93 | 0.97 |
| | | | **98.75** | | **92.63** | | **89.42** | **1.94** | **2.93** | **94.14** | **1.95** |

**Table 3. Ranges of *d* Value Changes Dependent of the Initial Mixture Composition**

| substrate | product | *d*, Å | $I/I_0$, % | substrate | product | *d*, Å | $I/I_0$, % | $\Delta d$ max |
|---|---|---|---|---|---|---|---|---|
| $Na_2HPO_4$ | $Na_4P_2O_7$ | 2.695 | 70 | $K_2HPO_4$ | $K_4P_2O_7\ \alpha$ | 2.890 | 100 | −0.195 |
| | | | | | $K_4P_2O_7\ \beta$ | 2.915 | 90 | −0.220 |
| $2K_2HPO_4 + KH_2PO_4$ | $K_5P_3O_{10}$ | 2.967 | 100 | $2Na_2HPO_4 + NaH_2PO_4$ | $Na_5P_3O_{10}$ I | 2.755 | 100 | +0.212 |
| | | | | | $Na_5P_3O_{10}$ II | 2.695 | 85 | +0.272 |

sation reaction, it is possible to obtain potassium–sodium polyphosphates which are fully water-soluble and which are suitable for liquid PK fertilizer production. However, under the other conditions, condensated potassium–sodium or potassium–calcium phosphates with differentiated solubility were obtained, which could make a group of so-called fertilizers with controlled solubility, i.e., slow-release fertilizers.

In the next stage of the investigation, not only was $NH_4^+$ ion replaced by sodium ion (as $Na_2CO_3$) but also $H^+$ ion, to obtain neutral pyro- or tripolyphosphates, which—together with micronutrients—create complex compounds, with higher stability constants than for hydropolyphosphates (Ringbom, 1963).

EXPERIMENTAL PROCEDURES

The condensation of suitable potassium, ammonium, and sodium hydrophosphates was carried out in the temperature range of 350–500 °C in the system shown in Chart 1.

To reach the high reaction ratio, water has been added to substrates for preliminary partial dissolving of the components, to improve the condensation conditions. The weight ratio of the liquid phase to the solid phase was equal to 0.15, which corresponded to a moisture content in the solid product from the potassium chloride conversion process. The reaction mass (about 12 g) of a definite composition was first thoroughly mixed and then placed in a glass crucible and finally put into a furnace. The heating time of the reacting substances to the assumed temperature (in range of 350–500 °C) and the time of polycondensation at that temperature were equal to 1.0 h. The substrates were heated at the rate of about 5–8 °C/min (dependent on temperature) but without being mixed. The process was carried out in a vertical laboratory tubular furnace, equipped with an automatic control system. The reactor was purged by air at the rate of about 6 $dm^3$/h, for carrying away the gases ammonia, carbon dioxide, and steam emitting during the reaction.

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**Table 4. Collection of Regression Equation Coefficients and Their Statistical Evaluation**

| no. | solid soln comp | polynomial eq coeff | | | $R^2$ | F | $F_{0.05}$ |
| | | $b_1$ | $b_2$ | $b_3$ | | | |
|---|---|---|---|---|---|---|---|
| 1 | pyrophosphates | 0.2256 | $-2.9761 \times 10^{-3}$ | $7.8073 \times 10^{-6}$ | 0.982 | 348.99 | 4.67 |
| 2 | tripolyphosphates | 0.2203 | $-1.7137 \times 10^{-3}$ | $-5.3113 \times 10^{-6}$ | 0.997 | 1127.78 | 5.59 |
| 3 | pyrophosphates | 101.2348 | $-5.9395 \times 10^{+2}$ | $6.7167 \times 10^{+2}$ | 0.978 | 291.61 | 4.67 |
| 4 | tripolyphosphates | 94.9948 | $-2.8746 \times 10^{+2}$ | $-6.6423 \times 10^{+2}$ | 0.995 | 687.19 | 5.59 |
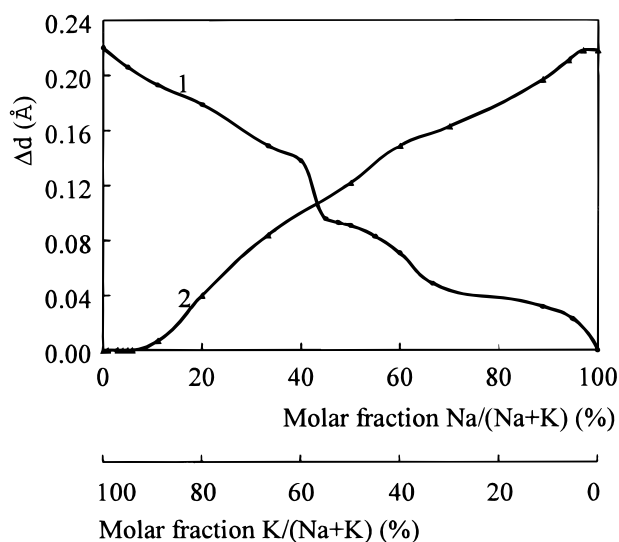


**Figure 1.** Relationship between displacement of diffraction lines and Na/(Na + K) molar fraction for sodium-potassium pyrophosphates (1) and K/(Na + K) for potassium−sodium tripolyphosphates (2).

The analytical control included the determination of the total and water-soluble $P_2O_5$ contents as well as the fractions of the particular forms of $P_2O_5$, i.e., ortho-, pyro-, and tripoly-

posphates and higher condensed phosphates in the products (Mateňko, 1975). For the determination of the phosphates, a colorimetric vanadium−molybdenum method was employed (Marczenko, 1979). The ammonium content was determined with an ion-selecting ammonium electrode (Orion Research, 1979). Gasometric analysis was used for the determination of the carbon dioxide content (Struszyňski, 1954) and a flame photometric technique for the estimation of water-soluble forms of potassium and sodium (Połuektov, 1969). X-ray diffraction analysis was used for the phase identification of crystalline condensation products.

## RESULTS AND DISCUSSION

In the studies on obtaining condensed potassium and sodium phosphates, the effects of process temperature and the composition of the initial mixture were determined in relation to the following: the water solubility of the final compositions in relation to the total $P_2O_5$ content; the fraction of ortho-, pyro-, and tripolyposphates and higher condensed forms of $P_2O_5$ in the products in relation to the water-soluble $P_2O_5$ content; and their phase compositions.

In the first stage of the investigation, the effect of temperature on the condensation degree of the suitable potassium and sodium hydrophosphates and their mixtures to neutral pyro- or tripolyphosphates was determined (systems 1−6). The obtained results have con-
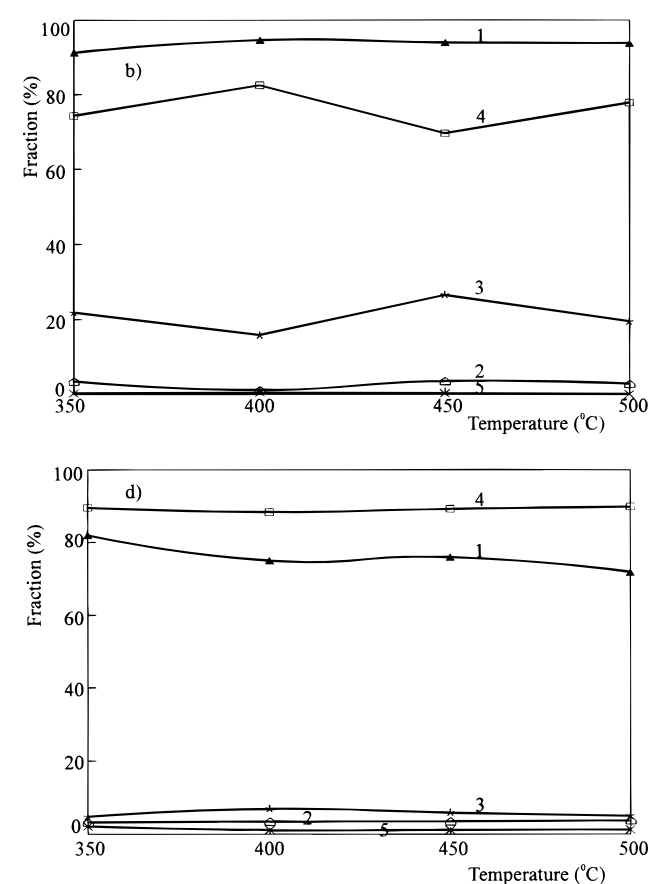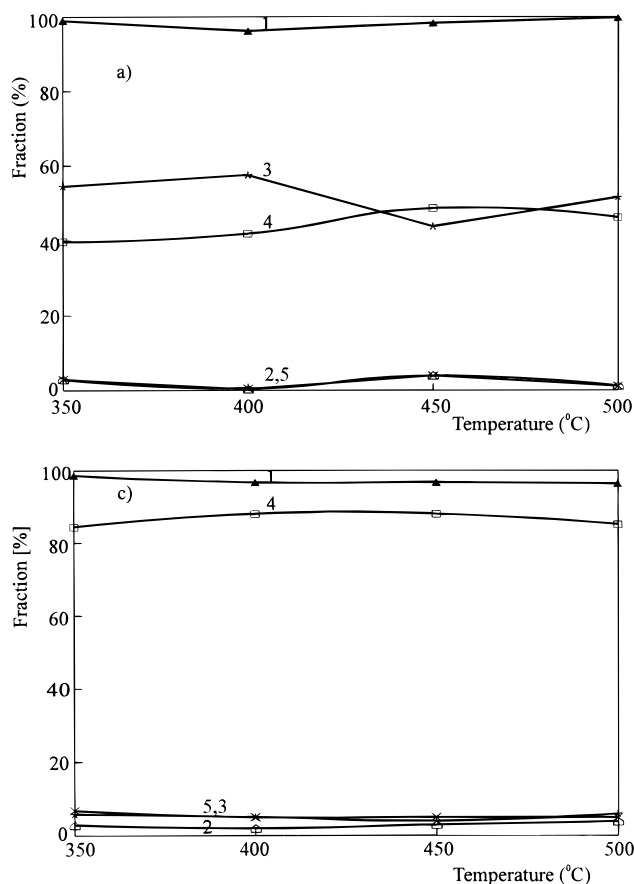


**Figure 2.** Influence of condensation temperature on the fraction of individual $P_2O_5$ forms of the products of systems (a) $KH_2PO_4-0.5Na_2CO_3$, (b) $NH_4H_2PO_4-Na_2CO_3$, (c) $KH_2PO_4-0.33Na_2CO_3$, and (d) $NH_4H_2PO_4-0.83Na_2CO_3$. 1, water-soluble $P_2O_5$; 2, orthophosphates; 3, pyrophosphates; 4, tripolyphosphates; 5, higher condensed phosphates.
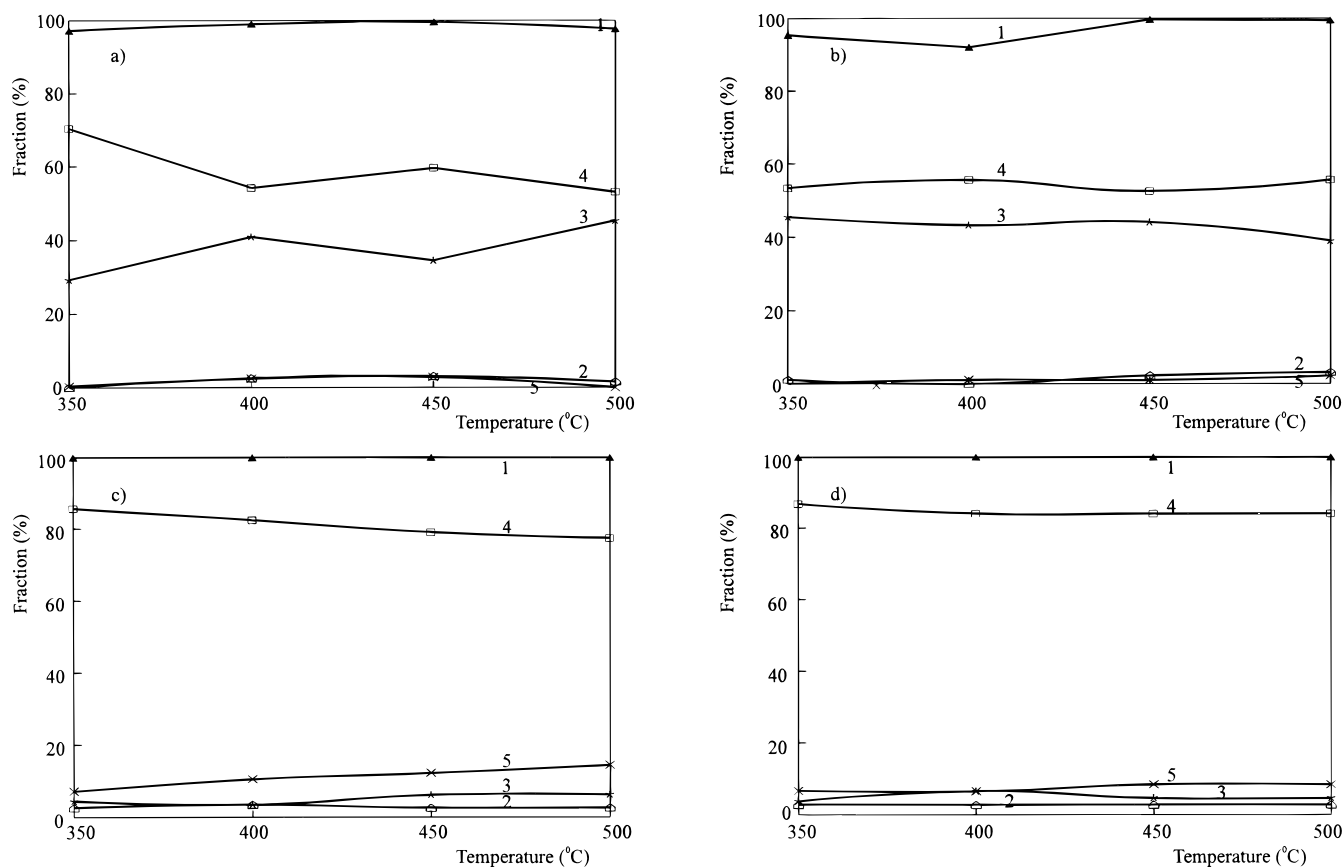
**Figure 3.** Influence of condensation temperature on the fraction of individual $P_2O_5$ forms of the products of systems (a) $KH_2PO_4-NH_4H_2PO_4-1.5Na_2CO_3$, (b) $KH_2PO_4-0.5NH_4H_2PO_4-Na_2CO_3$, (c) $KH_2PO_4-NH_4H_2PO_4-1.17Na_2CO_3$, and (d) $KH_2PO_4-0.5NH_4H_2PO_4-0.75Na_2CO_3$. 1, water-soluble $P_2O_5$; 2, orthophosphates; 3, pyrophosphates; 4, tripolyphosphates; 5, higher condensed phosphates.

firmed the earlier data (Frazier et al., 1972; Van Wazer, 1961; Prodan and Prodan, 1969), because the main crystalline phases—according to initial mixture composition—were pyrophosphates (systems 1 and 3), $\alpha$- and $\beta$-$K_4P_2O_7$, $K_4P_2O_7 \cdot 4H_2O$, $K_4P_2O_7 \cdot 3H_2O$, and $Na_4P_2O_7$, or tripolyphosphates (systems 2 and 4), $K_5P_3O_{10}$, $K_5P_3O_{10} \cdot 2H_2O$, and I- and II-$Na_5P_3O_{10}$. In the dehydration of the mixture of potassium and sodium hydrophosphates (systems 5 and 6), new crystalline phases were obtained, which corresponded probably to potassium–sodium pyro- or tripolyphosphate solid solutions: $(K,Na)_4P_2O_7$, $(K,Na)_5P_3O_{10}$. This statement is not based solely on the published data (Prodan and Prodan, 1969; Van Wazer, 1961). The diffraction patterns of the examined samples did not show the presence of crystalline phases, adequate for $Na_4P_2O_7$ or $\alpha$-,$\beta$-$K_4P_2O_7$ or $K_5P_3O_{10}$ or I-,II-$Na_5P_3O_{10}$, although the $P_2O_5$ fractions were high in the forms of pyro- (about 85–100%) or tripolyphosphates (about 84–90%), which was determined by means of ion-exchange column chromatography technique (Tables 1 and 2).

On the other hand, it was observed that along with the increasing sodium pyro- or tripolyphosphate fraction (assumed in the experiment) in the products, in comparison with the suitable potassium salts, a progressive change of the diffraction line positions, corresponding to the adequate characteristic grating constants from $\alpha$- or $\beta$-$K_4P_2O_7$ to $Na_4P_2O_7$ or from $K_5P_3O_{10}$ to I- or II-$Na_5P_3O_{10}$ (depending on the condensation process temperature), can be noticed. It could indicate that the progressive substitution of potassium ion with sodium ion in the crystal structure of potassium pyro- or tripolyphosphate takes place (ionic radius: $K^+$ 1.33 Å and $Na^+$ 0.98 Å).

The ranges of the changes of $\Delta d$ values, taken into consideration in this work, dependent on the initial mixture composition of the condensed sodium and potassium hydrophosphates and dependent on the process temperature, considering the formation of the suitable polymorphic forms potassium pyrophosphates or sodium tripolyphosphates, is shown in Table 3. $\Delta d$ is the difference between the grating constant for a solid solution $(K,Na)_4P_2O_7$ or $(K,Na)_5P_3O_{10}$ determined by the method of X-ray diffraction analysis and the grating constant for pure $Na_4P_2O_7$ or $K_5P_3O_{10}$.

The relationship between $|-\Delta d|$ and the molar fraction of sodium ion in relation to the sum of sodium and potassium ions in the initial mixture for the condensation products (obtained at 500 °C) in which pyrophosphates were the main fraction is shown in Figure 1. Also shown is a similar relationship between $|+\Delta d|$ and the molar fraction of potassium ion in relation to the sum of potassium and sodium ions, for tripolyphosphates.

The obtained dependences were expressed mathematically by an incomplete polynomial regression of the second order of one independent variable in the form

$$Y = b_1 + b_2X + b_3X^2$$

where $X$ is the molar fraction Na/(K + Na) or K/(Na + K) in the substrates (0−100%) and $Y$ is the difference of the grating constant absolute values $|\Delta d|$.

In Table 4 (positions 1 and 2) are compiled the equation coefficients, for particular systems and process temperatures, for the independent variable and their statistical estimation, where $R^2$ is the square of the multiple correlation coefficient, $F$ is the calculated value

**Table 5. Determination of Potassium–Sodium Pyro- and Tripolyphosphates Solid Solutions Compositions**

| init mixture comp | condensation temp, °C | $P_2O_5$ content, % | | | $\Delta d$, Å | K(Na)/(K + Na) molar fraction, % | | $x$ in $K_xNa_{5-x}P_3O_{10}$ or $Na_xK_{4-x}P_2O_7$ |
| | | total | pyro | tripoly | | total assumed | calcd, chem bonded with $P_3O_{10}^{5-}$ or $P_2O_7^{4-}$ | |
|---|---|---|---|---|---|---|---|---|
| KH₂PO₄−0.333Na₂CO₃ | | | | | | | | |
| 1 | 350 | 50.84 | 2.96 | 42.95 | 0.1080 | 60.02 | 56.20 | 2.81 |
| 2 | 400 | 51.57 | 2.57 | 45.38 | 0.1034 | 60.02 | 58.17 | 2.91 |
| 3 | 450 | 51.15 | 2.04 | 45.01 | 0.1069 | 60.02 | 56.67 | 2.83 |
| 4 | 500 | 50.86 | 3.01 | 43.32 | 0.1114 | 60.02 | 54.73 | 2.74 |
| KH₂PO₄−NH₄H₂PO₄−1.167Na₂CO₃ | | | | | | | | |
| 1 | 350 | 54.30 | 2.43 | 46.54 | 0.1576 | 29.99 | 33.19 | 1.66 |
| 2 | 400 | 54.32 | 1.90 | 44.80 | 0.1610 | 29.99 | 31.49 | 1.57 |
| 3 | 450 | 54.71 | 3.37 | 43.28 | 0.1601 | 29.99 | 31.94 | 1.60 |
| 4 | 500 | 54.91 | 3.46 | 42.54 | 0.1634 | 29.99 | 30.29 | 1.51 |
| KH₂PO₄−0.5NH₄H₂PO₄−0.75Na₂CO₃ | | | | | | | | |
| 1 | 350 | 55.00 | 2.06 | 47.42 | 0.1474 | 40.00 | 38.19 | 1.91 |
| 2 | 400 | 54.63 | 3.57 | 45.91 | 0.1487 | 40.00 | 37.56 | 1.88 |
| 3 | 450 | 54.99 | 2.55 | 45.95 | 0.1490 | 40.00 | 37.42 | 1.87 |
| 4 | 500 | 54.56 | 2.55 | 45.89 | 0.1476 | 40.00 | 38.09 | 1.90 |
| K₂HPO₄−0.5Na₂HPO₄ | | | | | | | | |
| 1 | 350 | 43.25 | 37.26 | 0.51 | 0.1339 | 33.33 | 33.74 | 1.35 |
| 2 | 400 | 42.64 | 39.96 | 2.60 | 0.1388 | 33.33 | 31.73 | 1.27 |
| 3 | 450 | 42.25 | 41.14 | 0.66 | 0.1344 | 33.33 | 33.54 | 1.34 |
| 4 | 500 | 43.21 | 41.28 | 1.00 | 0.1402 | 33.33 | 31.16 | 1.25 |
| K₂HPO₄−Na₂HPO₄ | | | | | | | | |
| 1 | 350 | 42.75 | 35.98 | 4.20 | 0.0791 | 50.00 | 58.45 | 2.34 |
| 2 | 400 | 42.11 | 41.00 | 0.56 | 0.0924 | 50.00 | 52.09 | 2.08 |
| 3 | 450 | 43.57 | 42.38 | 0.00 | 0.0820 | 50.00 | 57.05 | 2.28 |
| 4 | 500 | 44.41 | 43.05 | 0.40 | 0.0898 | 50.00 | 53.31 | 2.13 |
| 0.5K₂HPO₄−Na₂HPO₄ | | | | | | | | |
| 1 | 350 | 50.82 | 43.43 | 4.04 | 0.0744 | 66.67 | 60.76 | 2.43 |
| 2 | 400 | 51.46 | 44.78 | 2.40 | 0.0772 | 66.67 | 59.83 | 2.39 |
| 3 | 450 | 50.62 | 43.79 | 2.54 | 0.0743 | 66.67 | 60.81 | 2.43 |
| 4 | 500 | 50.78 | 44.55 | 1.98 | 0.0815 | 66.67 | 57.29 | 2.29 |

of Snedecor's $F$ test for the regression equation, and $F_{0.05}$ is the boundary value of the $F$ test for significance level $\alpha = 0.05$.

The values of the regression function coefficients were determined using Marquardt's method, by minimization of the squares of deviation sum. The correlation significance was verified with the use of Snedecor's $F$ test.

Next, the trial of utilizing the obtained results for describing the compositions of the forming solid solutions of pyro- or tripolyphosphates by approximate formula $(Na_xK_{4-x})P_2O_7$ or $(K_xNa_{5-x})P_3O_{10}$ was undertaken. To reach this, the dependences described above were inversed to the function of sodium or potassium ion molar fraction, in relation to their sum, on $\Delta d$. These dependences were also expressed mathematically by an incomplete polynomial regression of the second order of one independent variable in the form

$$Y = b_1 + b_2X + b_3X^2$$

where $X$ is the difference of the grating constant absolute values $|\Delta d|$ and $Y$ is the molar fraction Na/(K + Na) or K/(Na + K) in the parent substances (0−100%).

In Table 4 (positions 3 and 4) are compiled the equation coefficients, for particular systems and process temperatures, for the independent variable and their statistical estimation, where: $R^2$ is the the square of the multiple correlation coefficient, $F$ is the calculated value of Snedecor's $F$ test for the regression equation, and $F_{0.05}$ is the boundary value of the $F$ test for significance level $\alpha = 0.05$.

The values of the regression function coefficients were determined using Marquardt's method, by minimization of the squares of deviation sum. The correlation significance was verified with the use of Snedecor's $F$ test.

Next, the dehydration of potassium dihydrogen phosphate, with simultaneous substitution of $H^+$ ion with $Na^+$ ion, at two different mole ratios of reacting sub-

stances (system 7), was studied. In this case, besides the polycondensation process, decomposition of sodium carbonate with carbon dioxide emission from the reaction mixture in the range of 95.5−98.4% took place simultaneously. The prepared products, independent of the initial mixture composition and of the process temperature, were well water-soluble (96−100%).

In the produced compositions (Figure 2a,c), in the first case (for the initial mixture composition, adequate to obtain pyrophosphates), pyro- and tripolyphosphates were determined ($P_2O_5$ fraction adequately 43.7−54.4% and 39.7−48.6%), and in the second case, tripolyphosphates were determined ($P_2O_5$ fraction 84.5−88.0%). The identified crystalline phases were solid solutions of potassium−sodium pyro- and tripolyphosphates [(K,Na)₄P₂O₇ and (K,Na)₅P₃O₁₀].

In the next experiments, the effect of temperature on the condensation process of $NH_4H_2PO_4$, with simultaneous substitution of $NH_4^+$ and $H^+$ ions with $Na^+$ ion for obtaining neutral sodium pyro- or tripolyphosphates (system 8) was determined. Processes taking place parallel to the dehydration reaction, $NH_4H_2PO_4$ and $Na_2CO_3$ decomposition with ammonia and carbon dioxide desorption, influenced the properties and the compositions of obtained products. The water solubility was not complete—in the first case, the $P_2O_5$ fraction was in range of 91.3−94.6% and in the second case in range of 71.8−82.0% (Figure 2b,d). The decomposition ratio of sodium carbonate was also unsatisfactory, and it was in the range of 91.6−95.7% for the first system and about 94.0% for the second one. However, the ammonia desorption ratio was very high, because the ammonia content of the reaction products was determined at a very low level (less than 0.1%). Among the water-soluble phosphates, the main fraction comprised tripolyphosphates (69.6−82.5%) and pyrophosphates (15.8−26.5%)—for a higher $NH_4H_2PO_4/Na_2CO_3$ molar ratio in the initial mixture—and also tripolyphosphates (88.4−

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89.9%) and pyrophosphates (4.9−7.0%)—for a lower $NH_4H_2PO_4/Na_2CO_3$ molar ratio. $Na_4P_2O_7$ or $Na_5P_3O_{10}(I,II)$ and $NaPO_3II$ were identified as the main phases—dependent on the process temperature—by means of X-ray diffraction analysis.

In the last stage of the investigation, the effects of the temperature and the initial mixture composition on $KH_2PO_4$ and $NH_4H_2PO_4$ dehydration, at two different molar ratios of these substrates with sodium carbonate (system 9), to obtain sodium and potassium pyro- (higher $Na_2CO_3$ content of substrates) or tripolyphosphates (lower $Na_2CO_3$ content) were determined.

The compositions, obtained in the first case, were well water-soluble, independent of the process temperature. The content of residual carbon dioxide in the products was in the range of 0.79−0.23%, which corresponded to the degree of sodium carbonate decomposition in the range of 97−99%. A trace amount of ammonia was determined at the same time, what testified to the high degree of substrates reaction at the assumed process conditions. However, the water-soluble forms of $P_2O_5$ were pyrophosphates, the fraction of which was in the range of 29.3−45.5%, and tripolyphosphates, 79.4−52.5%, in the presence of small amounts orthophosphates and higher condensed phosphates (Figure 3a,c).

The condensed phosphates, produced in the second case and likewise in the first one, were 100% water-soluble. The degree of substrates reaction, determined on the basis of carbon dioxide (0.15−0.53% $CO_2$) and ammonia contents of the products, was high. In the obtained compositions, independent of the process temperature and initial mixture composition, mainly tripolyphosphates ($P_2O_5$ fraction 77.5−86.8%) and higher condensed phosphates (6.5−14.4%) were determined, in the presence of small amounts of residual ortho- and pyrophosphates (Figure 3b,d). The crystalline phases, which have been identified, were dependent on the initial mixture composition, solid solutions of potassium−sodium pyro- and tripolyphosphates or tripolyphosphates.

On the basis of the obtained diffraction patterns of the studied samples and using the regression equations, presented above, the existing crystalline phases, corresponding to the solid solutions of potassium−sodium pyro- or tripolyphosphates were described by approximate formulas. The results are compiled in Table 5.

CONCLUSIONS

Comparing the data, obtained as the results of pure $Na_2HPO_4$ condensation reaction and of the substance obtained indirectly, by ammonium ion substitution with sodium ion in $NH_4H_2PO_4$ condensation reaction, the presence in the reaction products mainly of pyrophosphates ($P_2O_5$ fraction 95−98%) in the first case and mainly of tripolyphosphates ($P_2O_5$ fraction 69−82%), with a small fraction of pyrophosphates in the second one, was found, independent of the process temperature. However, on the basis of the results of the $Na_2HPO_4$ and $NaH_2PO_4$ mixture or $NH_4H_2PO_4$ and $Na_2CO_3$ mixture condensation (at molar ratio $Na_2O/P_2O_5 = 1.67$), the condensed phosphates were created, and the differentiated solubility ratio was the only difference between them. The compositions, produced in the first system, were about 96% water-soluble and 71.8−82% obtained by the second system, although in both cases tripolyphosphates were the main form of $P_2O_5$.

Also, in the case of pyrophosphates obtained by $KH_2PO_4$ or its mixture with $NH_4H_2PO_4$ dehydration in the presence of sodium carbonate, a high fraction of tripoly-

phosphates of the products, besides the assumed pyrophosphates, was found, unlike the products, obtained by the $K_2HPO_4$ and $Na_2HPO_4$ mixture.

It was also found that the main fraction of the condensed phosphates, obtained independent of the initial mixture composition ($KH_2PO_4$ with $Na_2CO_3$; $KH_2PO_4$ and $NH_4H_2PO_4$ with $Na_2CO_3$), at the molar ratio $Me_2O/P_2O_5 = 1.67$ was tripolyphosphates, with a small fraction of the higher forms of $P_2O_5$.

The differences, presented above, between the results, obtained for the particular systems are the consequence of the incomplete reaction of sodium carbonate, under the process conditions, which caused the creation of condensed phosphates at a lower $Me_2O/P_2O_5$ molar ratio, than was assumed.

The aim of the present work was the investigation of the process of neutral potassium−sodium pyro- or tripolyphosphates produced from potassium and ammonium dihydrogen phosphates mixture. It was proved that under the assumed conditions of the phosphates mixture polycondensation reaction, water-soluble condensed phosphates were obtained as the products. The main fractions of these compositions were pyro- and tripoly- or tripolyphosphates, which belong to micronutrients complexing agents. And the created crystalline phases were suitable solid solutions of potassium−sodium pyro- and tripolyphosphates: $(K,Na)_4P_2O_7$, $(K,Na)_5P_3O_{10}$. The approximate chemical compositions these solid solutions using X-ray diffraction analysis were determinated.

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