1. Introduction

Condensed phosphates of alkali metals have been widely applied in different sectors of industry, such as food, cosmetic, pharmaceutical, chemical, construction, etc. Depending on the conditions of application and the requirements put forward to the properties, individual polyphosphates and mixtures of variable composition are utilized. Ammonium polyphosphate is used as a fertilizer and a fire retardant. Polyphosphates of calcium, potassium, and ammonium improve the taste qualities of food products. Among the polyphosphates of alkali metals, the most commonly used are sodium polyphosphates, which possess considerable restructuring properties and rather high solubility in water.

Sodium polyphosphates are actively used in water pre-treatment and anticorrosive protection of the conduits of circulating water supply. The inhibition of corrosion by polyphosphates makes it possible to substantially increase the period of operation of heating and cooling systems and in power engineering. The use of sodium phosphates in the polymeric form is promising in modern processes of the hot working of metals by pressure. By applying the molten phosphates as components of technological lubricants, it is possible to substantially intensify the processes of the hot working of metals, as well as improve ecological conditions of labor. Polyphosphate mixtures contribute to reduction in the deformation forces; substantially increase the lifecycle of tools and productivity of the presses of rolling mills.

Thus, the development of technologies for obtaining the inorganic polymeric phosphates with the assigned composition and predicted physical-chemical properties is a relevant task of contemporary chemical science.

2. Literature review and problem statement

The basic properties that determine commercial use of polyphosphates are cheapness, ecological safety and biodegradability. Polyphosphates bind into complexes the cations of different metals. The possibility to form hydrogenous bonds predetermines the capability of polyphosphates to retain significant amount of water [1].

Polyphosphates are used as fertilizers [2], non-halogen, highly effective and nontoxic inorganic fireproofing com-
Phosphates and polyphosphates are applied in the field of treatment of the surface of metals. Steel structures being the most common construction material possess low anticorrosive durability. In this regard, a steel surface requires additional protection. Depending on the operating conditions and requirements to the physical-mechanical properties of surface of steel constructions, galvanic [8, 9], varnish-and-paint or conversion coatings are used. It is well known that the modification of composition of the paint and varnish coatings with anticorrosive pigments may improve the resistance of protective coatings to exfoliation. Polyphosphates of zinc and aluminum are the promising reagents, which can be utilized for this purpose [10, 11]. Conversion coatings based on phosphates ensure high protective properties [12, 13]. Polymeric phosphates are applied in the production of technological greases, used in the processes of metal working at high temperatures [14, 15].

As can be seen from the scientific literature data, polyphosphates have a rather extensive scope of application. Depending on the requirements put forward to the properties of polyphosphates, compounds with different structure and variable length of the polymer chain are used. The synthesis of polyphosphates of the assigned structure in each particular case requires a specific technique and selection of optimum conditions for conducting the process.

Thus, the mixed polyphosphate Na$_2$Mg$_2$(PO$_4$)$_3$.P$_2$O$_5$ was obtained by authors of [16] by the stepwise heating of a mixture of magnesium oxide, soda and ammonium orthophosphate monosubstituted to 900 °C with the subsequent cooling of reaction mixture under assigned temperature mode. By using the method of solid-phase recovery, there was received the new compound Pb$_4$[Li$_x$(P$_2$O$_7$)$_7$(P$_2$O$_5$)$_9$] (P$_2$O$_7$)$_3$, containing in its structure several polyphosphate groups [17]. In [18], a method of spontaneous crystallization was applied to synthesize polyphosphate, which contains two different polyphosphate anions. Centrally symmetrical and asymmetrical polyphosphate structures were synthesized by the high-temperature melting by authors of article [19]. The compound Cs$_5$Mg$_2$(PO$_4$)$_3$ was synthesized from CsF, MgF$_2$, and NH$_3$.H$_2$PO$_4$ through the solid-phase interaction of reagents. Under the analogous conditions, the polyphosphate compound Cs$_5$MgZn$_2$(PO$_4$)$_3$ was obtained from a mixture of CsF, MgF$_2$, ZnO and NH$_3$.H$_2$PO$_4$. The basic method of obtaining the condensed sodium phosphates in the crystalline and powdered-like state is the thermal dehydration of acid orthophosphates. Thus, the high-temperature treatment of sodium orthophosphate monosubstituted monohydrate was applied in [20] to synthesize polyphosphates with a variable length of the polymer chain. The synthesis was carried out at 700 °C and 775 °C and duration of thermal treatment from 30 minutes to 9 hours. In the process of high-temperature dehydration, depending on the temperature and duration of the process, various forms of polymeric phosphates are created.

3. The aim and tasks of research

The aim of present work is to establish special features of thermal dehydration of sodium orthophosphate monosubstituted with the formation of polymeric phosphates of variable composition. This will make it possible to purposefully control the process of the synthesis of polyphosphates, ensuring the controlled qualitative ratio of the obtained products.

To accomplish the set aim, the following tasks were to be solved:

- to explore the effect of temperature of dehydration of sodium orthophosphate monosubstituted on the composition of the obtained polymeric phosphates and to establish the chemical scheme of conversion;
- to examine the effect of temperature and duration of the process on the composition of salt mixtures of polyphosphates, which are formed at different temperature regimes of conducting the dehydration of sodium orthophosphate monosubstituted.

4. Materials and methods for examining the high-temperature dehydration of sodium orthophosphate monosubstituted

Obtaining the polymeric phosphates from sodium orthophosphate monosubstituted was carried out on the laboratory installation whose schematic is shown in Fig. 1.
Obtaining the polymeric phosphates was accomplished in several stages – the synthesis of sodium orthophosphate monosubstituted and its thermal treatment. Sodium orthophosphate was obtained in the cylindrical reactor – crystallizer 1, equipped with jacket 3 and stirring device 2. In the reactor we loaded the calculated quantity of 85% of phosphoric acid and, at the enabled mixer 2, we neutralized it with soda ash to pH 3.5–4.0. The exothermic process of neutralizing the phosphoric acid was accompanied by the creation of supersaturation due to the progress of irreversible chemical reaction of forming the crystals of sodium orthophosphate from the solution. The pulp of sodium orthophosphate was cooled in the reactor-crystallizer to the temperature of 25–30 °C, by feeding the cooling water to jacket 3, with subsequent separation of crystals on Buchner funnel 6. Drying the obtained sample of sodium orthophosphate was performed in the muffle furnace SNOL (Lithuania) 9 with the accuracy of temperature registration ±2 °C at temperature 25–30 °C to a constant mass. The obtained product met the standard “pure for analysis” in line with GOST 245-76. We experimentally established that the crystalline hydrate of sodium orthophosphate monosubstituted contained 1.3 molecules of H₂O, which can be linked to the crystallization mono- and dihydrates from the solution of the mixture. The thermal treatment of sodium orthophosphate was carried out in muffle furnace 9 at different temperatures.

The thermograms were recorded on the derivatograph Q-1500 D (Hungary), Paulik system, in the air atmosphere in the range of temperatures 20–1000 °C at the heating rate of the sample NaH₂PO₄·1.3H₂O equal to 0.17 to K/s. The radiographs were recorded on the diffractometer DRON 3.0 (Russia) using the CuKα-emission. The interplanar spacing on the radiographs of dehydration products was compared to the data in the catalog of ASTM (American Society for Testing and Materials).

Quantitative composition of the dehydration products was established by the method of eluent ion exchange chromatography, which is the most effective for the separation of various forms of phosphates. The chromatographic separation of phosphates was conducted employing the following procedure. As a chromatographic column we used a glass column of diameter 15 mm and length 90 mm, and as an ion-exchange resin – the anionite IF-23 (Ukraine). Determining a mass fraction of P₂O₅ in the samples was conducted according to GOST 20291-80, with the help of the photoelectric colorimeter FEK-56M (Russia) at wavelength 440 nm.

The selection of optimum conditions for conducting the chromatography of the mixture of phosphates was carried out experimentally. It is established that the relationship (or ion-exchange potential) of phosphates to the resin IF-23 (Ukraine) increases with an increase in the polarizability of anions, which is characteristic for the highly alkaline ion exchangers.

We examined a dependence of the washing-out rate of ions of ortho, pyro-, triply, and metaphosphate from the ion-exchange column on the eluent pH. Fig. 2 shows the curves of elution of standard solutions of ions (optical density characterizes the ion concentration in separate portions of eluent) depending on the concentration and volume of eluent.

Results of the studies testify to the fact that the maximum separation of the mixture of ortho-, pyro-, triply- and metaphosphates can be reached at the eluent pH 5.6–5.8 (Fig. 2, curve 2). It is necessary to sequentially increase the eluent concentration from 0.1 mol/l to 0.4 mol/l (Fig. 2). The passage rate of eluent through the column must not exceed 2 ml per 1 minute.

It was established that when using the neutral or weak-alkaline solutions of eluent, it is not possible to reach the complete separation of ortho-, pyro- and tripolyphosphates (Fig. 2, curve 1). The reason for this is the increased value of the coefficient of anion confinement at such pH. The use of eluent solutions with pH lower than 4 (Fig. 2, curve 3) leads to an increase in the volume of eluent that must be used for the complete washing out of the analyzed ions, which considerably increases the duration of analysis.

Metrological characteristics of determining the ortho-, tri- and metaphosphates by the method of ion exchange chromatography are given in Table 1.

<table>
<thead>
<tr>
<th>Defined anion</th>
<th>Introduced, mg</th>
<th>Found (±δ), mg</th>
<th>Sr*</th>
</tr>
</thead>
<tbody>
<tr>
<td>orthophosphate</td>
<td>5.00</td>
<td>5.04±0.12</td>
<td>0.02</td>
</tr>
<tr>
<td>pyrophosphate</td>
<td>5.00</td>
<td>4.97±0.28</td>
<td>0.05</td>
</tr>
<tr>
<td>triplyphosphate</td>
<td>5.00</td>
<td>5.04±0.18</td>
<td>0.03</td>
</tr>
<tr>
<td>metaphosphate</td>
<td>5.00</td>
<td>5.05±0.10</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Note: * n – the number of measurements; P – confidence probability; Sr – relative standard deviation

The low values of relative standard deviation of the analytically determined amount of anion from the true values testify to sufficient sensitivity of the procedure and reproducibility of the results.

5. Results of examining the thermal dehydration of crystalline hydrate of sodium orthophosphate monosubstituted

The process of high-temperature dehydration of sodium orthophosphate is described by complicated chemical reactions. It is experimentally established that the isothermal
treatment of sodium orthophosphate at a temperature lower than 180 °C is accompanied only by removal of crystallization water from the sample, which agrees well with the results of thermogravimetric studies [15].

Fig. 3 shows that a number of endo-effects is observed at a temperature lower than 130 °C. In this case, obviously, there occurs the removal of the physically sorbed moisture from the sample, the melting of mono sodium phosphate (MSP) crystalline hydrate in the crystallization water and the loss of the crystallization water.

It was experimentally established that the obtained model of MSP contains crystallization water in the amount of 1.3 molecules of H$_2$O.

The radiographs of the model sample, thermostatically controlled at t=130 °C (Fig. 4), registered the maxima at $d_{\text{HKL}}=6.65$, 3.83, 3.35 and 3.20 Å. The latter relate to the interplanar spacing of the waterless sodium orthophosphate monosubstituted NaH$_2$PO$_4$.

Dehydration in the temperature interval of 130–220 °C is accompanied by the endo-effect, which corresponds to 188 °C. In this case, there occurs the splitting of 0.5 mole of water and formation of the sodium dihydroxyphosphate Na$_2$H$_2$P$_2$O$_7$. This is confirmed by the existence of maxima in the radiograph of the sample (Fig. 6) at $d_{\text{HKL}}=6.70$, 3.42, 3.85 and 3.07 Å.

The thermochemical transformations, which take place in the range of temperatures from 300 °C to 420 °C, are accompanied by the absorption of heat at 342 °C, by the removal of 0.5 moles of water and by the formation of Na$_3$P$_3$O$_9$. Essential inhibition of dehydration is caused by the emergence of a dense film at the surface of the product, which hampers dehydration. The formation of Na$_3$P$_3$O$_9$ is confirmed by the existence of maxima in the radiograph of the sample (Fig. 7) at $d_{\text{HKL}}=6.70$, 3.42, 3.85 and 3.07 Å.
6. Discussion of results of examining the thermal dehydration of crystalline hydrate of sodium orthophosphate monosubstituted

A composition of the products of high-temperature dehydration depends on both the temperature and the duration of process. The quantitative composition of dehydration products, which corresponds to the specific time of thermal treatment, was determined by the method of eluent ion exchange chromatography.

Fig. 8 shows a time dependence of the percentage of various forms of polymeric phosphates (ω, % by weight), obtained from MSP at temperature 220 °C.

![Graph showing time dependences of the distribution of phosphate forms at t=220 °C: 1 – NaH₂PO₄·1.3H₂O; 2 – Na₃H₂P₂O₇](image)

It was experimentally established that at 220 °C the process of isothermal dehydration of sodium orthophosphate monosubstituted proceeds with high selectivity and the formation of only sodium dihydropyrophosphate (NaH₂P₂O₇).

Fig. 8 shows that during the first 10 minutes, the content of NaH₂PO₄·1.3H₂O sharply decreases, while the content of Na₃H₂P₂O₇ grows by the exponential dependence. Subsequently, an increase in the content of Na₃H₂P₂O₇ and reduction in the amount of NaH₂PO₄·1.3H₂O proceed at lower speed, which is, apparently, related to an increase in the diffusion resistance to the removal of water through a layer of the reaction product.

Complete transformation of sodium orthophosphate monosubstituted into dihydropyrophosphate at 220 °C finishes in 40 minutes. Thus, with the variation of time of conducting the process, it is possible to obtain a mixture of polymeric phosphates with the required content of NaH₂PO₄·1.3H₂O and Na₃H₂P₂O₇.

The dehydration of MSP at 420 °C (Fig. 9) is characterized by the more complicated chemistry of the process.

*Fig. 9. Time dependences of the distribution of phosphate forms at t=420 °C: 1 – NaH₂PO₄; 2 – Na₃H₂P₂O₇; 3 – Na₅P₃O₁₀* 

Thus, at temperature 420 °C, there forms a salt mixture, which contains Na₅P₃O₁₀, Na₃H₂P₂O₇, and NaH₂PO₄. The ratio of components changes depending on the time of thermal treatment of the reaction mixture. The obtained salt systems could be used as phosphate components when rolling the pipes in automatic mills.

Fig. 10 shows a time dependence of the percentage of various forms of polymeric phosphates, obtained from MSP at temperature 650 °C. The process of formation of Na₅P₃O₁₀ is superimposed with side reactions, which proceed with the formation of Na₃H₂P₂O₇ and Na₅P₃O₁₀ (sodium tripolyphosphate). In the first 2.5 min. the content of Na₃H₂P₂O₇ in the sample reaches a maximum and it is lowered over time to 8 %, which is associated with its transition into Na₅P₃O₁₀ and Na₅H₃P₃O₁₀.

Sodium tripolyphosphate forms in the course of two parallel reactions:

\[ \text{NaH}_2\text{PO}_4 \rightarrow 1/3 \text{Na}_3\text{H}_2\text{P}_2\text{O}_7 + 2/3 \text{H}_2\text{O}, \quad (4) \]

\[ \text{NaH}_2\text{PO}_4 + \text{Na}_3\text{H}_2\text{P}_2\text{O}_7 \rightarrow \text{Na}_5\text{H}_3\text{P}_3\text{O}_{10} + \text{H}_2\text{O}. \quad (5) \]

The formation of Na₅H₃P₃O₁₀ proceeds by reaction (2).

High-temperature dehydration of NaH₂PO₄·1.3H₂O proceeds predominantly with the formation of Na₅P₃O₁₀ by reaction:

\[ \text{NaH}_2\text{PO}_4 \cdot 1.3\text{H}_2\text{O} \rightarrow \text{Na}_5\text{P}_3\text{O}_{10} + 2.3\text{H}_2\text{O}. \quad (6) \]
A composition of the salt system obtained at 650 °C during 10–30 minutes remains unchanged: 76% Na₃PO₄, 8% Na₃H₂P₂O₇, 8% Na₃H₂PO₄, 8% NaH₂PO₄.

Such salt systems might be used as the basic phosphate component of technological lubricants for the hot rolling of pipes in the reeler machines.

References


