

УДК 546.185:[544.77.022.822+544.77.022.823]

**A.I. Sumich**, assistant lecturer (BSTU); **L.S. Eshchenko**, D.Sc. (Engineering), professor (BSTU)

### COMPOSITION OF PHOSPHATES FORMED BY THE INTERACTION OF LIQUID GLASS WITH ORTHOPHOSPHORIC ACID SOLUTIONS

The chemical and phase composition of products formed by interaction of liquid glass with 20–80%  $\text{H}_3\text{PO}_4$  is investigated. It is shown that the products of the synthesis include hydrated silicon and phosphorus containing phases. The silicon containing phase is a mixture of amorphous silica gel and nonstoichiometric sodium silicates. The phosphorus containing phase is sodium hydrophosphate  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ . It is established that the crystalline phase is formed irrespective of a mixing method and acid concentration. It is suggested that the cause of formation of acid salt of phosphoric acid even at a large excess of water glass is replacement of protons  $\text{H}^+$  of silanol  $\equiv\text{Si-OH}$ -groups of silicic acid by cations of  $\text{Na}^+$  and formation of sodium silicates which act as a connecting bridge between adjacent globules of the formed hydrogel.

**Introduction.** At present methods based on mixing of chemically active reagents namely neutralizing substances with liquid proton-containing reagents are of special relevance in field of detergent processing all over the world [1–3]. These methods are less energy consuming in contrast to a process comprising the drying of detergent slurry in a boiling layer, and allow to synthesize necessary components of detergents, especially surface active, complex agents at the stage of mixing. This excludes the need to enter the above components in the detergent composition in a form of individual compounds and can reduce the product cost. Carbonates and alkali metal silicates are used as neutralizing agents and organic and inorganic acids are used as proton-containing reagents. Among the great diversity of these reagents liquid glass and orthophosphoric acid are of particular interest because the products of their interaction in combination with surface active agents possess high detergent capacity as noted in several works [4–6]. Due to the lack of data on research of physical and chemical transformations that occur when mixing these reagents the purpose of this work is investigation of products composition in particular sodium phosphates formed by reacting liquid glass with a solution of  $\text{H}_3\text{PO}_4$ .

**Main part.** Thermal phosphoric acid and technical liquid glass with a molar ratio  $\text{SiO}_2 : \text{Na}_2\text{O}$ , equal to 3 (mass content  $\text{SiO}_2$  is equal 31.1 wt%,  $\text{Na}_2\text{O}$  is equal 10.6 wt%,  $\text{pH} = 11$ ) were used as the starting reagents. Products of synthesis were obtained in several ways:

1) phosphoric acid solution was poured into liquid glass with continuous stirring – the direct mixing;

2) liquid glass was added to phosphoric acid solution – inverse mixing;

3) the reactants were simultaneously added into the reaction vessel and their flow rate was being controlled.

Changing the pH medium was recorded with a HANNA HI 221 pH-meter. The concentration of phosphoric acid and the molar ratio between the reagents in terms of  $\text{Na}_2\text{O} : \text{P}_2\text{O}_5$  were variable parameters. Synthesis was performed at room temperature.

Composition of hardening products was calculated based on the material balance of the process of obtaining and the phase composition was identified by X-ray phase analysis on a Bruker D8 Advance diffractometer (Germany).

Phase and colloid-chemical transformations associated with formation of a supersaturated solution of the sodium phosphates and their crystallization, polymerization of silicic acid which causes appearance of a sol and its transition into gel occur when liquid glass and solution of phosphoric acid are mixed. It was established that by direct mixing of reagents physicochemical transformations occur at a constant pH value of 10.8–10.9. This is probably due to ability of a sol of poly-silicon acids to form buffer systems [7]. Hardening and forming of powder-like products occurs at molar ratios of the reagents in terms of  $\text{Na}_2\text{O} : \text{P}_2\text{O}_5$  components (5-7): 1 and the content of  $\text{H}_3\text{PO}_4$  in a solution of 20-80 wt %.

In the inverse mixing of reagents pH value is gradually increased to 3.0 – 3.5 and then a jump is observed (Fig. 1), which is probably related with the formation of sodium dihydrogen phosphate. The system is coagulated into gel. Powder-like product is formed by achieving a molar ratio of reagents in terms of  $\text{Na}_2\text{O} : \text{P}_2\text{O}_5$  equal to (1.0–2.5) : 1.0.

In the case of simultaneous mixing of reagents, the form of the final product depends on the ratio of the starting reagents which is set by the regulating their flow rates. It was determined that the formation of sol, gel and hardening of the system occurs at a molar ratio of  $\text{Na}_2\text{O} : \text{P}_2\text{O}_5$  corresponding both the direct and reverse mixing.

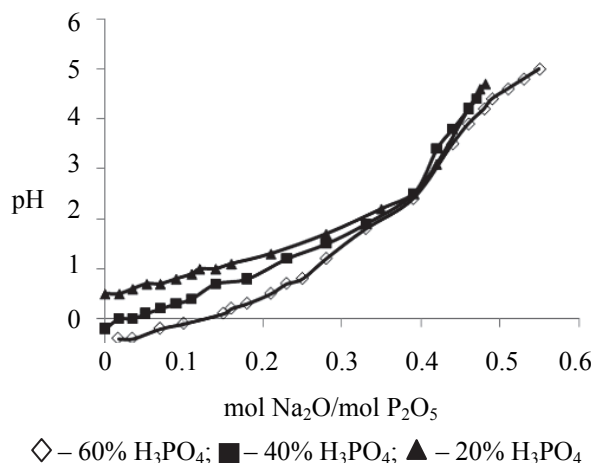


Fig. 1. pH of the medium vs. the  $\text{Na}_2\text{O}/\text{P}_2\text{O}_5$  molar ratio in inverse mixing

Products of synthesis are wet powder of empirical formula  $x\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot y\text{SiO}_2 \cdot n\text{H}_2\text{O}$  where  $x = 2.5\text{--}7.25$ ,  $y = 7.5\text{--}21.7$ ,  $n = 45.0\text{--}188.9$  in the direct mixing and  $x = 1.33\text{--}2.5$ ,  $y = 4.0\text{--}7.5$ ,  $n = 30.0\text{--}218.3$  in the inverse. These products include hydrated silicon- and phosphorus-containing phases the ratio between, whose relative amounts depend on the synthesis conditions. The hydrated silicon-containing phase is X-ray amorphous silica gel, which is a porous matrix with  $15\text{--}75\text{-}\mu\text{m}$  pores (Fig. 2). The presence of a certain amount of non-stoichiometric sodium silicates produced as a result of the partial hydrolysis of liquid glass is also possible.

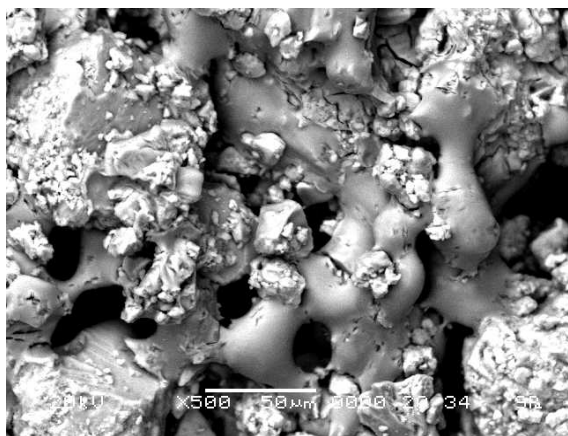
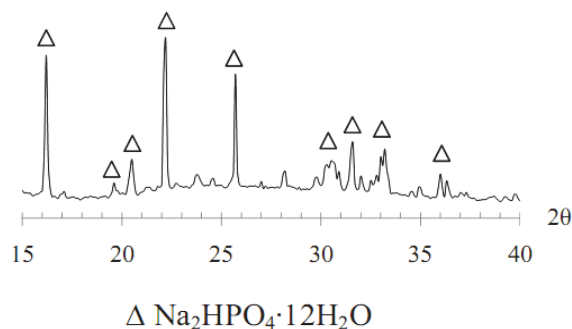


Fig. 2. Micrograph of powder-like product obtained by reacting  $\text{H}_3\text{PO}_4$  with liquid glass

It was found that regardless of the mixing method and the ratio of the initial reagents acid salt of orthophosphoric acid of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  (Fig. 3) is formed. Diffractogram of hardening products obtained both at a molar ratio of  $\text{Na}_2\text{O} : \text{P}_2\text{O}_5 = 3$  and at  $\text{Na}_2\text{O} : \text{P}_2\text{O}_5 = 6$  are identical. As can be seen

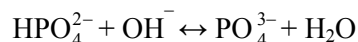
from the electron microscopic studies (Fig. 2) the crystalline phase of hydrophosphate dodecahydrate sodium is formed on a porous matrix of silica gel in the form of  $20\text{--}50\text{-}\mu\text{m}$  particles aggregates of ir-



regular shapes.

Fig. 3 X-ray diffraction pattern of the hardening products obtained by mixing of liquid glass and  $\text{H}_3\text{PO}_4$

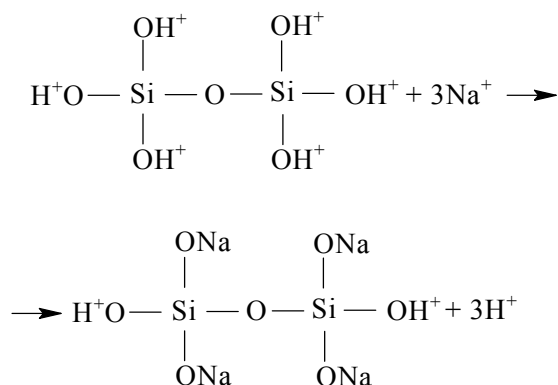
Of particular interest is the formation of an acid salt of orthophosphoric acid (hydro-phosphate sodium) regardless of the mixing method and proportions of starting reagents. It is known [8] 20 for 15 20 25 30 35 40 ely  $\text{Na}_3\text{PO}_4$ ,  $\text{Na}_3\text{PO}_4 \cdot 0.5\text{H}_2\text{O}$ ,  $\text{Na}_3\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{Na}_2\text{HPO}_4$ ,  $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{Na}_2\text{HPO}_4 \cdot 8\text{H}_2\text{O}$ ,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ,  $\text{Na}_2\text{HPO}_4 \cdot \text{NaH}_2\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4 \cdot 2\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{NaH}_5(\text{PO}_4)_2$  is possible in  $\text{Na}_2\text{O} - \text{P}_2\text{O}_5 - \text{H}_2\text{O}$  system. As can be seen from the phase diagram [8] a salt with a different number of substituted protons  $\text{H}^+$  by  $\text{Na}^+$  depends on the molar ratio of  $\text{Na}_2\text{O} : \text{P}_2\text{O}_5$  and the number of moles of crystalline hydrate water depends on the total water content in the system. From the analysis of the phase equilibria in the system that the formation of average salt of orthophosphoric acid is possible at molar ratios  $\text{Na}_2\text{O} : \text{P}_2\text{O}_5 \geq 2.5$ , i.e. when there is large excess of alkali and equilibrium



is shifted to the right. In this connection the production of sodium orthophosphate is performed in two stages: the first, orthophosphoric acid is neutralized with sodium carbonate to sodium hydrogen phosphate and the second it is neutralized with solution  $\text{NaOH}$ . The excess alkali is 10–12% [9].

At the same time, as shown by the results of studies of hardening products the di-substituted sodium salt of orthophosphoric acid is crystallized in the system of liquid glass –  $\text{H}_3\text{PO}_4 - \text{H}_2\text{O}$  even at ratios of reactants in terms of  $\text{Na}_2\text{O} : \text{P}_2\text{O}_5$  equal to 7.6. This fact can be explained on the basis of the secondary colloid-chemical interactions of the electrolyte (sodium phosphate solution) and polymers, in particular silicic acid di-

mers. According to [10], liquid glass comprises sol particles of polysilicic acid (3D structures), sodium silicate chains (1D structures) and a NaOH alkaline solution. Neutralization of NaOH, formation the corresponding salt of the acid and oligomers including dimers of silicic acid are occurred when adding a solution of phosphoric acid to liquid glass. Along with dissociation of sodium salt incomplete dissociation of silicic acid is observed. As a result of ion exchange the protons of silanol groups  $-\text{Si}\equiv\text{O}-\text{H}$  are partially replaced by the cations of  $\text{Na}^+$  by the following scheme



This forms a dimer of sodium silicate which acts as a connecting bridge between adjacent globules of the forming gel. One can assume that the larger ratio of the liquid glass to phosphoric acid in the system the higher the content of the resulting sodium silicate. As a result, the required for the formation of sodium orthophosphate stoichiometric ratio between  $\text{Na}_2\text{O}$  and  $\text{P}_2\text{O}_5$  is not reached and sodium hydrogen phosphate is crystallized in the system. The occurring of similar phenomena has also been noted in [11], however, the authors consider the reduction of  $\text{Na}^+$  concentration in the liquid phase from the point of view of the sorption by active hydrogel.

The formation of crystalline sodium hydrogen phosphate with a number of moles of crystalline hydrate water equal to 12 is due to the high content of water in the system. As calculations represented in the table have shown, hardening prod-

ucts obtained by mixing the liquid glass with 50–80% solution  $\text{H}_3\text{PO}_4$  contain 55–60 wt % of water and when using more dilute solutions of acids (less 50 wt % of  $\text{H}_3\text{PO}_4$ ) they contain about 65–70 wt % of  $\text{H}_2\text{O}$ .

The content of the silicon-containing phase and dodecahydrate of sodium hydro-phosphate in powder-like products depends upon the method of mixing. Thus, in the direct mixing the mass fraction of silicon phase is 25–30 wt %  $\text{SiO}_2$  and 10–35 wt %  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  whereas in the inverse mixing of reagents it is 15–25 wt %  $\text{SiO}_2$  and 20–55 wt %  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ . The composition of the products of interaction of the liquid glass and orthophosphoric acid obtained by simultaneous mixing depends upon the molar ratio  $\text{Na}_2\text{O} : \text{P}_2\text{O}_5$  given by the flow of reactants. This allows to adjust the ratio between the silicon phase and  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  within wide limits.

#### Conclusion.

1. The physicochemical and colloidal transformations occurring in the interaction of liquid glass with 20–80%  $\text{H}_3\text{PO}_4$  are investigated. Range of  $\text{Na}_2\text{O} : \text{P}_2\text{O}_5$  molar ratios when the system hardens completely is founded.

2. It is shown that the hardening products are crumbly powder composed of a porous matrix of silica gel with 15–75- $\mu\text{m}$  pores and on its surface the irregularly shaped 20–50- $\mu\text{m}$  aggregates of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  are located.

3. It was determined that the formation of disodium salt of orthophosphoric acid regardless of the mixing method of the reactants is due to the fact that the molar ratio of  $\text{Na}_2\text{O} : \text{P}_2\text{O}_5$  in a liquid phase corresponding to the formation of the average salt is not obtained. This is due to substitution of protons  $\text{H}^+$  of silanol  $\equiv\text{Si}-\text{OH}$ -groups of silicic acid by  $\text{Na}^+$  cations and the formation of sodium silicates which act as a connecting bridge between adjacent globules of the forming hydrogel.

**Water content in products of interaction of liquid glass and  $\text{H}_3\text{PO}_4$**

Composition of initial reactants wt %					Total water content * in hardening products obtained at molar ratio $\text{Na}_2\text{O} : \text{P}_2\text{O}_5 = 3$ , wt %
orthophosphoric acid		liquid glass			
$\text{H}_3\text{PO}_4$ content in solution	total content of $\text{H}_2\text{O}$ in solution (including constitution)	content			
		$\text{Na}_2\text{O}$	$\text{SiO}_2$	$\text{H}_2\text{O}$	
80	42.1 (22.1)	10.6	31.1	58.3	56.3
50	63.8 (13.8)				59.3
20	85.6 (5.6)				68.0

\* Calculated on basis of mixing material balance of starting reactants.

### References

1. Verfahren zur Herstellung von Wash- oder Reinigungsmitteln: DE 102005005499 Deutschland, C 11 D 11/00 / A. Rene-Andres, S. Claudio, P. Fulvio, R. Wilfried, A. Frosinone, B. Luca, D. Stefano, P. Vittorio, P. Ferentino; Henkel KGaA; заявл. 04.02.2005; опубл. 17.08.2006.
2. Detergent builder composition: US 20020155982 USA, C 11 D 3/02 / H. Bauer, J. Holz, G. Schimmel; Clariant GmbH; заявл. 14.11.2000; опубл. 24.10.2002.
3. Particulate laundry detergent compositions containing nonionic surfactant granules: US 6262010 C 11 D 17/00 / W. Emery, T. Instone, R. Kohlus, J. Langeveld, S. Liem; Unilever Home & Personal Care USA; заявл. 20.11.1999, опубл. 17.07.2001.
4. Моющее и чистящее средство: пат. 11807 Респ. Беларусь, МПК(2006) C 11D 7/02 / Л. С. Ещенко, Г. М. Жук, А. И. Сумич; заявитель Белорус. гос. технол. ун-т. – № а 20070987; заявл. 02.08.2007; опубл. 28.01.2009.
5. Сулейманова, С. В. Исследование моющих гелеобразующих систем / С. В. Сулейманова // Новые исследования в материаловедении и экологии: сб. науч. ст. / Петербург. гос. ун-т путей сообщ. – 2006. – Вып. 6. – С. 76.
6. Современные моющие средства на основе кремнегелей и утилизация отработанных моющих растворов / Е. И. Макарова [и др.] // Современные проблемы экологии: докл. Всерос. науч.-техн. конф., Тула, 18 апр. 2006 г.: в 2 кн. – Тула, 2006. – Кн. 2. – С. 26–28.
7. Айлер, Р. К. Химия кремнезема. В 2 ч. Ч. 1. Растворимость, полимеризация, коллоидные и поверхностные свойства, биохимия / Р. К. Айлер; пер. с англ. Л. Т. Журавлева; под ред. В. П. Прянишникова. – М.: Мир, 1982. – 416 с.
8. Wendrow, B. The alkali orthophosphates. Phase equilibria in aqueous solutions / B. Wendrow, K. A. Kobe // Chemical Reviews. – 1954. – N 6. – P. 891–924.
9. Никандров, М. И. Разработка технологии концентрированных динатрий- и тринатрий-фосфатов: автореф. дис. ... канд. техн. наук: 05.17.01 / М. И. Никандров; РХТУ им. Д. И. Менделеева. – М., 2005. – 16 с.
10. Чукин, Г. Д. Химия поверхности и строение дисперсного кремнезема / Г. Д. Чукин. – М.: Типография Паладин: ООО «Принта», 2005. – 172 с.
11. Сорбенты на основе силикагеля в радиохимии / под ред. Б. Н. Ласкорина. – М.: Атомиздат, 1977. – 302 с.

Received 27.02.201



