УДК 661.185.6:543.32

A.I. Sumich, assistant lecturer (BSTU);
L. S. Eshchenko, D. Sc. (Engineering), professor (BSTU);
A.D. Alekseyev, PhD (Chemistry), assistant professor (BSTU);
O.Yu. Fedorova, student (BSTU)

REAGENT PRECIPITATION OF HARDNESS IONS BY CARBONATE-CONTAINING BUILDERS

Phase composition of carbonate containing builders obtained by neutralization of proton containing reagents with sodium carbonate is investigated. It is shown that the builders are a mixture consisting mainly of $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, $Na_2CO_3 \cdot H_2O$ and salts of the corresponding acids. The mixture is able to reduce total water hardness with 3.9 to 1.6–1.7 mmol-eq·l^{-1}. It is found that the builders containing $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, $Na_2CO_3 \cdot H_2O$ and $CH_3COONa \cdot 3H_2O$ remove hardness as well as Na_2CO_3, $Na_3PO_4 \cdot 12H_2O$ and STPP at the same flow rate.

Introduction. Synthetic detergents (SD) are multi-component composition containing up to 90 w.% of builder [1–3]. The builder consists of a number of organic and inorganic salts. These salts must maintain a specified pH of detergent solution, remove total water hardness, reduce critical micelle concentration and possess surface-active, dispersing and emulsifying properties. The reduction of the hardness salts concentration in washing solution providing high detergency is one of the most important requirements to the builders [4–6].

Builder can be obtained by mechanical mixing of components. However thus generated mixture is not uniform, not granular and it is disposed to caking. The ways of obtaining of the builders and detergents on their basis through the neutralization of proton-containing reagents using the neutralizers [7–9] are widely applied in the last ten years. These ways require relatively less investments and they are less power-intensive in contrast to the spray drying. The carbonates or silicates of alkali metals are used as the neutralizers, and the water solutions of organic, inorganic acids or their acid salts are used as proton-containing reagents. Such a method for detergent production allows to adjust the obtained mixture composition that determines the degree of water hardness removal.

In this connection we have analyzed in the present study the influence of the builder composition obtained in the system "proton-containing reagent – sodium carbonate – water" to the residual concentration of the hardness salts at water softening.

Main part. The solutions of orthophosphoric, citric and acetic acids were used as the proton-containing reagents, the neutralizing reagent being Na_2CO_3. The samples of carbonate-containing builders were made in the PHILIPS high-speed blender (power – 700 W). At the continuous mixing the particles of sodium carbonate were sprayed by the solution of proton-contained reagent (H_xAn_y, where x is number of H^+ cations and y is number of anions in formula unit of acid; An is acid anion) at the fixed molar ratios Na_2CO_3 / H_xAn_y and content of H_xAn_y in the solution.

Crystalline phases have been identified using the X-ray phase analysis on 08 Advance diffractometer of "Bruker" AXS company (Germany). The water hardness was determined by the standard procedure of trilonometric method [10]. The tap water with the total hardness 3.9 mmol-Eq·l^{-1} was used for the research. Water softening was made at the room temperature. Builder sample was dissolved in the water under study, then kept during 15 min., after what the formed sediment was filtered to determine the residual hardness. The hardness removal degree has been calculates under the following formula:

$$D = \frac{H_0 - H}{H_0} \cdot 100\%,$$

where H_0 is initial hardness of water, 3.9 mmol-Eq·l^{-1}; H – water hardness after treatment by reagent, mmol-Eq·l^{-1}.

The production conditions and phase composition of builders at different molar ratios Na_2CO_3 / H_xAn_y and H_xAn_y content in the solution are given in Table 1. As you can see from the provided data, the builders, obtained on the basis of sodium carbonate and of orthophosphoric, citric and acetic acids, are the mixture of carbonate-containing phases and salts of appropriate acids. At that the carbonate-containing phase is mainly concentrated sodium sesquicarbonate ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) and $Na_2CO_3 \cdot H_2O$ (samples No 1–4, 7–17). $Na_2CO_3 \cdot H_2O$ is not contained in the salt mixture (sample No 6) obtained at molar ratio Na_2CO_3 / H_3PO_4 equal to 6.0, and at content in solution 20 wt. % of H_3PO_4. As to samples No 5, 8, 12, 14 the presence of sodium bicarbonate was registered.

The salts of orthophosphoric, citric or acetic acids are the part of builders in the form of crystalline hydrates. Thus when spraying the acetic acid solution on powdery sodium carbonate, we generate $CH_3COONa \cdot 3H_2O$ (samples No 1–4), and when spraying citric acid, we get $Na_3C_6H_5O_8 \cdot 2H_2O$ (samples No 15–17). In case of orthophosphoric acid application, it is typical the presence of phosphates with different number of H^+ protons substituted by Na^+.

It was established that when reducing the content of H_3PO_4 in solution from 33 up to 22 wt. %, the content of orthophosphates in terms of anhydrous salt increases, while the content of sodium hydrophosphate reduces. The builders (samples No 13, 14) obtained from 33% H_3PO_4 at molar ratio Na_2CO_3 / H_3PO_4 equal to 4.5–6.0 include $Na_2HPO_4 \cdot 2H_2O$, $Na_2HPO_4 \cdot 7H_2O$, while when using 20% H_3PO_4 the phosphate-containing phase is presented by the sodium orthophosphate with the $Na_3PO_4 \cdot 8H_2O$ composition.

Considering that the obtained builders include such compounds as sodium citrates, carbonates and phosphates, which are usually applied in detergents for water softening, there is the question about the efficiency of these mixtures as reagents reducing the hardness salts concentration. The degree of the hardness removal by individual compounds widely used in the detergents formulations: zeolites, sodium tripolyphosphates, sodium metasilicates and others was determined to make a comparative evaluation. The results of the research are given in Table 2.

As it is evident from the provided data, the sodium tripolyphosphates and $Na_3PO_4 \cdot 12H_2O$ remove the water hardness the most in full. The level of the hardness removal at these reagents consumption of 0.50 $g \cdot l^{-1}$ H_2O is within the range 60–67%, while this range for other reagents at the same consumption is 51–52% and less.

Thus, after dilution of 0.50 gr of $C_6H_8O_7 \cdot 2H_2O$ in 1 liter of water, the hardness salts concentration did not change. Only when the consumption of citric acid was increased up to 2.0–3.5 $gr \cdot (l\ H_2O)^{-1}$, the removal degree rose up to 20–35%. As to the water glass the low degree of hardness removal makes 7.6% at the consumption 0.50–1.00 $gr \cdot (l\ H_2O)^{-1}$. It is also to be mentioned that the sodium carbonate and sodium sesquicarbonate soften the water practically equally, in spite of the different chemical compositions.

Table 1

The production conditions and phase composition of builders

Sample	Production conditions: Na_2CO_3 / H_xAn_y molar ratio	Production conditions: Content of H_xAn_y in solution, wt. %	Phase composition
$H_xAn_y = CH_3COOH$			
1	1.5	90	$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, $Na_2CO_3 \cdot H_2O$, $CH_3COONa \cdot 3H_2O$
2	2.5	40	
3	3.5	32	
4		24	
$H_xAn_y = H_3PO_4$			
5	4.0	20	$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, $Na_2CO_3 \cdot H_2O$, $NaHCO_3$, $Na_2HPO_4 \cdot 7H_2O$, $Na_2HPO_4 \cdot 12H_2O$, $Na_3PO_4 \cdot 12H_2O$
6	6.0		$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, $Na_3PO_4 \cdot 12H_2O$
7	7.5		$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, $Na_2CO_3 \cdot H_2O$, $Na_3PO_4 \cdot 8H_2O$
8	10.5		$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, $Na_2CO_3 \cdot H_2O$, $NaHCO_3$, $Na_3PO_4 \cdot 8H_2O$
9	4.0	25	$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, $Na_2CO_3 \cdot H_2O$, $Na_2HPO_4 \cdot 7H_2O$, $Na_3PO_4 \cdot 12H_2O$
10	4.5		$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, $Na_2CO_3 \cdot H_2O$, $Na_2HPO_4 \cdot 7H_2O$, $Na_3PO_4 \cdot 8H_2O$
11	6.0		
12	4.0	33	$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, $Na_2CO_3 \cdot H_2O$, $NaHCO_3$, $Na_2HPO_4 \cdot 2H_2O$, $Na_2HPO_4 \cdot 7H_2O$, $Na_3PO_4 \cdot 12H_2O$
13	4.5		$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, $Na_2CO_3 \cdot H_2O$, $Na_2HPO_4 \cdot 2H_2O$, $Na_2HPO_4 \cdot 7H_2O$
14	6.0		$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, $Na_2CO_3 \cdot H_2O$, $NaHCO_3$, $Na_2HPO_4 \cdot 2H_2O$, $Na_2HPO_4 \cdot 7H_2O$
$H_xAn_y = C_6H_8O_7$			
15	6.0	40	$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, $Na_2CO_3 \cdot H_2O$, $Na_2CO_3 \cdot 7H_2O$, $Na_3C_6H_5O_8 \cdot 2H_2O$
16		50	$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, $Na_2CO_3 \cdot H_2O$, $Na_3C_6H_5O_8 \cdot 2H_2O$
17		60	

Table 2

Research results for the process of hardness salts removal from the water

Reagent	Consumption, $g \cdot (l\,H_2O)^{-1}$	H*, mmol-Eq $\cdot l^{-1}$	D, %	Presence of sediment
Na_2CO_3	0.50	1.8	53.8	+
$Na_3PO_4 \cdot 12H_2O$	0.50	1.5	61.5	+
	1.00	0.6	84.6	+
Sodium tripolyphosphate	0.50	1.3	66.7	–
$C_6H_8O_7 \cdot 2H_2O$	0.50	3.9	0	–
	1.00	3.4	12.8	–
	2.00	3.1	20.5	–
	3.35	2.5	35.9	–
$Na_3H(CO_3)_2 \cdot 2H_2O$	0.50	1.9	51.3	+
Crystalline sodium metasilicate	0.50	3.0	23.1	+
	1.00	1.9	51.3	+
	2.00	0.9	76.9	+
	3.35	0.3	92.3	+
Zeolite NaY	0.50	3.4	12.8	+
	1.00	2.9	25.6	+
	2.00	2.3	41.0	+
	3.35	1.9	51.3	+
Water glass**	0.50	3.6	7.6	–
	1.00	3.6	7.6	–

* Initial water hardness (before removal) is 3.9 mmol-Eq$\cdot l^{-1}$;
** Silica modulus (SiO_2 / Na_2O) is equal 3.

As appears from the Table 2, the degree of the hardness removal using these reagents is at the level of 50–54%. The crystalline sodium metasilicate shows activity at rather high consumption. When increasing the sample mass from 0.50 up to 3.35 gr$\cdot$(l $H_2O)^{-1}$, the hardness salts concentration reduces accordingly from 3.0 down to 0.3 mmol-Eq$\cdot l^{-1}$, while the removal degree of cations Ca^{2+} and Mg^{2+} increases from 23 up to 92%. As it follows from the test data (Table 2) the zeolite NaY showed the low capacity for the hardness removal.

The sedimentation at dilution of the carbonate, sodium sesquicarbonate and dodecahydrate of sodium orthophosphate in hard water is caused by the formation of insoluble calcium carbonates and orthophosphates. The higher degree of the hardness removal for sodium orthophosphate, as against the sodium carbonate and sodium sesquicarbonate, is connected with the relatively lower value of solubility product of calcium and magnesium orthophosphates. According to [11], $SP(CaCO_3) = 492 \cdot 10^{-9}$, $SP(MgCO_3) = 6.82 \cdot 10^{-6}$, while $SP(Mg_3(PO_4)_2) = 1.04 \cdot 10^{-24}$, and $SP(Ca_3(PO_4)_2) = 2.07 \cdot 10^{-33}$. The water softening under the action of sodium tripolyphosphate and citric acid dehydrate is determined by formation of soluble polyphosphate and citrate complexes of calcium and magnesium respectively. Absence of the sediment has been also fixed when using the water glass with the consumption equal to 0.50–1.00 gr$\cdot l^{-1}$ H_2O.

The results of the water hardness removal using the builders are shown in Table 3.

Table 3

Hardness removal by builders

Number of the sample according to the Table 1	Hardness* after removal, mmol-Eq$\cdot l^{-1}$	D, %	Presence of sediment
1	1.8	53.8	+
2	1.7	56.4	+
3	1.6	58.9	+
4	1.7	56.4	+
5	2.0	48.7	+
6	2.2	43.5	+
7	2.3	41.0	+
8	2.7	30.8	+
9	2.1	46.1	+
10	1.0	51.3	+
11	2.1	46.1	+
12	1.9	51.3	+
13	1.8	53.8	+
14	1.9	51.3	+
15	3.5	10.3	+
16	3.0	23.1	+
17	2.6	33.3	+

* Consumption of salt mixture for hardness removal was 0.50 gr$\cdot$(l $H_2O)^{-1}$.

As you can see from the provided data, the acetate and carbonate containing builders remove the hardness salts more in full as against the phosphate-, citrate carbonate containing builders at the same their consumption. The degree of the hardness removal using samples No 1–4 is at the level of 54–59%, while samples No 5–14 remove the hardness by 40–54%, and samples No 15–17 – by 10–33%. Different degree of water hardness removal is obviously caused by different content of main substances softening water in the builders.

Thus, the content of carbonate-ions in the acetate- and carbonate-containing builders is rather high taking into account their chemical and phase composition; which ensures the solubility process of calcium and magnesium carbonates. The part of the phosphate-ions in builders containing series of sodium phosphate crystalline hydrates (Table 1) is at the level of 6–13 wt. %, that requires considerable consumption of builders for fixation of Ca^{2+} and Mg^{2+} cations into the sparingly soluble orthophosphates. The rather low degree of hardness removal using the citrate carbonate containing builders (samples No 15–17) is connected with the low water-softening action of the citrates them-selves, especially of citric acid (Table 2).

Conclusion. The builders consisting mainly of $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, $Na_2CO_3 \cdot H_2O$ and salts of corresponding acids are obtained by neutralization of different proton-containing reagents (acetic, orthophosphoric and citric acids) using the neutralizer, sodium carbonate in particular. Influence of the chemical and phase composition of the builders on the degree of water hardness removal is determined. It is shown that the increase of crystalline hydrate water moles number in the composition of the builders causes the reduction of reactants content and that of the hardness removal degree. It is observed that the obtained builders can be used in the compositions of powder-like synthetic detergents.

References

1. Florescu S., Golgojan A., Leca M. The performance of a particular builder system in the detergency process: Proceedings of the 4th World Conference on Detergents, Montreux, 4–8 October 1998 / Switzerland, editor A. Cahn. AOCS Press., 1998. P. 249–254.

2. Louis Ho Tan Tai. Formulating detergents and personal care products. New York: AOCS PRESS, 2000. 555 p.

3. Appel P. W. Modern methods of detergent manufacture // J. of Surfactant and Detergents. 2000. Vol. 3, No. 3. P. 395–405.

4. Laundry detergents / E. Smulders [et al.]; Weinheim: Wiley-VCH Verlag GmbH, 2002. 261 p.

5. Powdered detergents / ed. by M. S. Showell. New York: Marcel Dekker, Inc., 1998. 345 p.

6. Handbook of detergents / ed.-in-chief U. Zoller. Part F: Production Israel: CRC Press, 2009. 579 p.

7. Borchers G. Design and manufacturing of solid detergent products // J. of Surfactant and Detergents. 2005. Vol. 8, No. 2. P. 123–128.

8. Verfahren zur Herstellung von Wash- oder Reinigungsmitteln: пат. 102005005499 DE, C 11 D 11 / 00. Rene-Andres A., Claudio S., Fulvio P., R. Wilfried, A. Frosinone, B. Luca, D. Stefano, P. Vittorio, P. Ferentino; Henkel KGaA; заявл. 04.02.2005; опубл. 17.08.2006.

9. A cogranule for use in solid detergent compositions: пат. 08150939 EP, C 11 D 17 / 00, 7 / 12, 7 / 23, 17 / 06, 7 / 14 / Sch. Frank, J. Cecilia, S. Ajse; заявитель Kamira Oyj; заявл. 01.02.2008; опубл. 06.08.2008.

10. Общая химическая технология: лаб. практикум / Л. С. Ещенко [и др.]; под общ. ред. Л. С. Ещенко. Минск: БГТУ, 2004. 83 с.

11. Волков А. И., Жарский И. М. Большой химический справочник. Минск: Современная школа, 2005. 608 с.

Received 14.03.2013