УДК 648.18:661.185.6

L. S. Yeshchanka, A. D. Alekseev, A. I. Sumich, G. M. Zhuk
Belarusian State Technological University

BUILDER COMPOSITION DEVELOPMENT FOR LOW-PHOSPHATIC DETERGENTS

The effect of a content of sodium metasilicate, water glass, and the "matrix" / sodium carbonate mass ration in composition of builder on hygroscopicity, surface activity and detergency of the low-phosphatic detergents are investigated. In order to optimize the composition of the builder 3 factorial experiment based on close to D-optimal plan Kono has been used. The optimal values of the investigated factors for each criterion optimization are determined, equations of private utility functions are obtained and values of the generalized optimization criterion in each row of the experimental design are calculated. As a result, the second-degree polynomial as the dependence of the generalized criterion optimization on three variables − the content of sodium metasilicate (x_3), water glass (x_2) and the mass ratio of the "matrix" / carbonate solution (x_1) the following type $W = 0.7367 + 0.0798x_1 – 0.1310x_2 – 0.3410x_3 – 0.0015x_1x_2 + 0.0021x_1x_3 + 0.0050x_2x_3 – 0.0009x_1^2 + 0.0096x_2^2 + 0.0110x_3^2$ is derived. It is shown that the optimum value of hygroscopic point, detergency and surface activity is achieved at two different compositions of the builder. Based on the totality of the data, the optimal composition of the builder comprising 4 wt % of water glass, 4 wt % of sodium metasilicate, and the resulting mass ratio "matrix" / sodium carbonate equal to 43.60 is offered.

Key words: detergent, builder, sodium metasilicate, liquid glass, sodium sesquicarbonate, optimization, mathematical planning.

Introduction. Detergents (SD) are a complex mixture consisting of a number of components (at least 10−15), each of them has a certain function during the washing. Detergents manufactured in the Republic of Belarus and countries of former USSR have low competitiveness because of the traditional character of their formula (high content of phosphates, expensive foreign ingredients – trilone B, citrates, zeolites etc.) and ways of production not providing a proper quality, in particular, according to granulometric composition, caking, packed density, dusting and other (obtaining by mechanic intermixture) or energy-consuming (obtaining by spray drying).

At the department of inorganic materials technology and genereal chemical technology there are studies carried out for several years aimed at the development of low phosphates and phosphates free salt compositions and ways of their obtaining. Rational utilization of secondary raw materials (salt mixture) forming at OJSC "BMP" (Zhlobin) as a result of evaporation of the solution obtained by desalting of waste water by reverse osmosis method as comparatively cheap sourse of sulphate and sodium chloride is indicated in this article [1]. It has been also pointed out [2, 3], that during water solutions spraying of proton-containing reagents onto the surface of neutralizing substances powder products are formed with humidity not higher than 8–9 wt % that include derivatives of proton-containing reagents (of salt) and carbonate-containing compounds, in particular, sodium sesquicarbonate. Obtained products are attractive as a base for production of multicomponent builders for powder detergents.

The aim of this article is the development of optinal composition of multicomponent builders for low phosphate detergents obtaining on the base of proton-containing reagent (ortho-phosphoric acid), sodium carbonate and salt mixture forming at OJSC "BMP".

Main part. Thermal ortho-phosphoric acid, sodium carbonate, sodium hydrocarbonate, salt mixture, liquid glass (wt %: Na_2O – 11.7; SiO_2 – 33.8), carbamide and technical sodium metasilicate have been taken as initial reagents. In accordance with technical analysis salt mixture includes, wt %: Na_2SO_4 – 55.0; NaCl – 38.2; Na_2CO_3 – 0.6; unsolved sediment – 0.5; free water − 5.7. Salt composition was obtained in high speed blender with power of 700 Vt in two stages: obtaining of «matrix» by mixing of wet salt mixture with sodium carbonate and sodium hydrocarbonate at mole ratio of $H_2O:NaHCO_3:Na_2CO_3$, providing fixation of free water into crystallohydrated and equal 0.75:1.0:0.5 [1]; introduction of sodium metasilicate into "matrix" and additional amount of sodium carbanate and spraying on the forming mixture of ortho-phosphoric acid solution, containing carbamide at mole ratio of Na_2CO_3/H_3PO_4 = 6.0 and H_2O/Na_2CO_3 = 4.0 [4]. Phase composition of of salt composition has been determined with the help of X-ray phase analysis by diffractometer "Bruker" AXS (Germany).

Detergent on the base of the obtained builder has been prepared by means of introduction of NaCMC into it, optical brightener, enzymes, fragrance and spraying of diluted liquid glass and surface-active agent. Detergency of the tested samples of detergents has been determined in accordance with NSS 22567.15−95, hydroscopic point – by desiccant method, surface activity has been calculated in accordance with the date on surface tension, determined by stalagmometric method [5].

For optimization of builder composition three-factor experiment based on the plan close to D-optimal Kono has been used [6, 7]. Independent variables were x_1 – mass ratio "matrix"/sodium carbonate; x_2 – mass fraction of liquid glass in relation to the whole mixture; x_3 – mass fraction of sodium metasilicate in relation to the whole mixture. Table 1 presents levels of factor variation in coded and natural expressing. At the moment of calculation of optimal variable values Y_1 – hygroscopic point, %; Y_2 – surface activity, mJ · м$^{-2}$; Y_3 – detergency, % were the criterias of optimization. Planning matrix based on 14 experiments has been developed. According to this matrix, the samples of builders and detergents on their base have been developed (Table 2).

After computer processing of experimental data in electronic tables of Microsoft Excel, maths models describing Y_1, Y_2, Y_3 dependence out of their composition, have been obtained:

$$Y_1 = 68.19 + 0.68x_1 + 0.17x_2 - 0.9x_3 - 0.16x_1x_2 + 0.28x_1x_3 + 0.5x_2x_3 - 0.3x_1^2 + 0.53x_2^2 - 1.03x_3^2;$$

$$Y_2 = 170.45 - 11.24x_1 - 2.99x_2 - 0.26x_3 - 3.07x_1x_2 + 2.45x_1x_3 - 5.3x_2x_3 - 20.05x_1^2 - 0.55x_2^2 + 37.63x_3^2;$$

$$Y_3 = 162.08 - 3.42x_1 - 7.06x_2 - 8.99x_3 - 3.95x_1x_2 + 14.17x_1x_3 + 3.03x_2x_3 - 42.79x_1^2 + 21.86x_2^2 - 1.64x_3^2.$$

Negative coefficients point out that increase of value of corresponding factor decreases the value of controlling parameter.

Table 1

Levels of factor variation

Units of factor measurement	Levels of factor variation								
	x_1 – mass ratio "matrix"/Na_2CO_3			x_2 – content of liquid glass, wt %			x_3 – content of sodium metasilicate, wt %		
Coded units	–1	0	+1	–1	0	+1	–1	0	+1
Physical units	60 : 30	60 : 45	60 : 60	4	8	12	4	8	12

Table 2

Experiment planning

Number of sample	Factors			Optimization criteria		
	Mass ratio "matrix"/sodium carbonate	Content, wt %		Hygroscopic point, %	Surface activity, mJ · m^{-2}	Detergency, %
		of liquid glass	of sodium metasilicate			
1	60 : 30	4	4	68.1	191.0	163.0
2	60 : 60	4	4	69.1	182.5	150.5
3	60 : 30	12	4	67.5	214.5	165.5
4	60 : 60	12	4	68.4	163.0	115.0
5	60 : 30	4	12	65.1	203.0	125.0
6	60 : 60	4	12	67.5	180.0	142.4
7	60 : 30	12	12	66.3	180.0	122.8
8	60 : 60	12	12	68.0	165.0	161.3
9	60 : 60	8	12	66.7	183.0	109.3
10	60 : 45	12	12	67.9	204.0	149.2
11	60 : 30	8	12	64.8	203.0	93.3
12	60 : 45	4	12	65.1	221.0	182.7
13	60 : 60	12	8	68.6	143.0	112.0
14	60 : 45	8	8	68.7	160.0	176.8

Comparative analysis of the obtained regression equations shows that hygroscopic point, surface activity and detergency of the detergents dubiously change depending on their composition. Optimal values of physico-technical properties have samples of different compositions: detergent composing of $x_1 = +1$, $x_2 = -1$, $x_3 = -1$ is characterized by a maximum hygroscopic moisture; detergents composing of $x_1 = 0$, $x_2 = -1$, $x_3 = +1$ are characterized by surface-active and detergent properties.

It was necessary to find a compromise. So, the task is to find such values of mass ratio of "matrix"/sodium carbonate, sodium carbonate content, liquid glass and sodium metasilicate, at which the best combination of properties Y_1, Y_2 и Y_3 can be reached.

To determine optimal values of the testing factors for each criterion of optimization equations of ratio utility (d_i) have been obtained and values of generalized criterion of optimization (W_i) have been calculated according to the following formula:

$$d_i = e^{-e^{(b_0+b_i y_i)}};$$

$$W_i = (d_{1i} d_{2i} d_{3i})^{1/3},$$

where b_0 and b_1 − coefficients, determining by the curves $W_i = f(y_i)$ [6]. According to the data from Table 3 coefficients of composite polynomial approximant have been established

$$W_i = 0.7367 + 0.0798x_1 - 0.1310x_2 - 0.3410x_3 - 0.0015x_1x_2 + 0.0021x_1x_3 + 0.0050x_2x_3 - 0.0009x_1^2 + 0.0096x_2^2 + 0.0110x_3^2.$$

According to regression equation, response surface has been built, which is presented in the Figure. Saddle-shaped of response surface for W_i at fixed value of d_3 proves that optimal composition of samples of salt compositions can be achieved at least while dealing with two different compositions. With the help of iteration method optimal factor values at maximal values of generalized criterion of optimization have been calculated. As a result the optimal composition of the builder and ratio between reagents at obtaining of the builder: content of sodium metasilicate – 4 wt %, liquid glass – 4 wt %, mass ratio of "matrix"/sodium carbonate 43.6 have been suggested. Detergent based on this builder has hygroscopic point equals to 69%, surface activity and detergency of 1% water solution – 201 mJ · m^{-2} and 200%, respectively.

Conclusion. Influence of the builder forming as a result of mixing of sodium carbonate and sodium hydrocarbonate with salt mixture – secondary raw material, forming at OJSC "BMP", with the solution of orthophosphoric acid, sodium metasilicate and liquid glass at obtaining of light phosphate detergent (SD) on hygroscopic point, surface activity and detergency is studied.

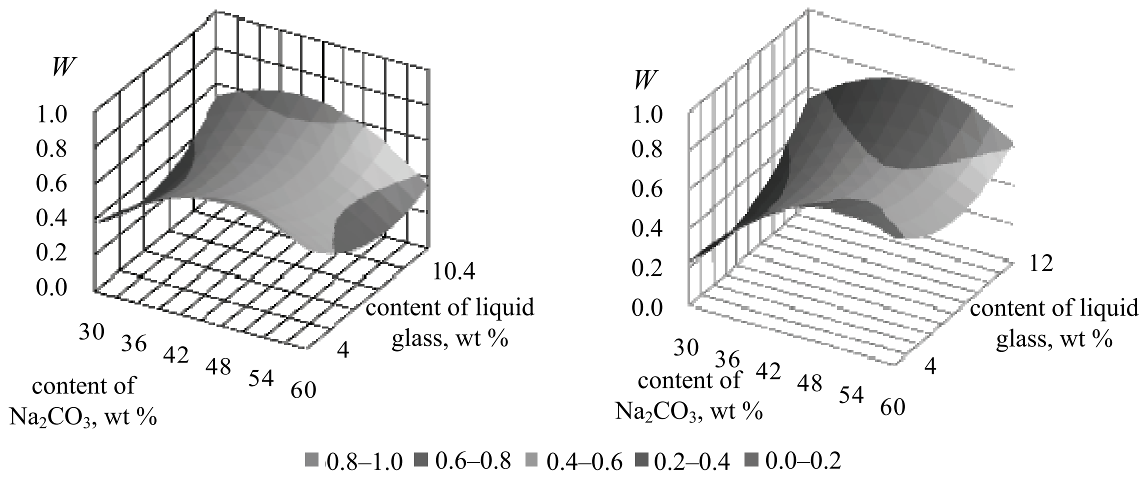
With the help of maths method of experiment planning dependence of physico-technical properties data on the content of sodium metasilicate, liquid glass and mass ratio of "matrix"/sodium carbonate in the form of regression equations is established.

According to the equations of ratio utility functions values of generalized criterion of optimization have been calculated and optimal builder has been suggested; based on this builder the detergent with detergency of 200%, hygroscopic point of 69% and surface activity of 1% solution equals to 201 mJ · m^{-2} has been obtained.

Table 3

Plan of experiment with a view to generalized criterion of optimization

Number of sample	Factors			Values of ratio utility functions			Values of generalized criterion of optimization W_i
	X_1, "matrix"/sodium	X_2, wt %	X_3, wt %	$d_1(Y_1)$	$d_2(Y_2)$	$d_3(Y_3)$	
1	60 : 30	4	4	0.8819	0.7826	0.8799	0.8468
2	60 : 60	4	4	0.8009	0.6826	0.9500	0.8038
3	60 : 30	12	4	0.8939	0.9305	0.8058	0.8752
4	60 : 60	12	4	0.3275	0.3479	0.9093	0.4697
5	60 : 30	4	12	0.4925	0.8771	0.1137	0.3662
6	60 : 60	4	12	0.7255	0.6472	0.7991	0.7213
7	60 : 30	12	12	0.4572	0.6472	0.4974	0.5280
8	60 : 60	12	12	0.8730	0.3863	0.8700	0.6645
9	60 : 60	8	12	0.2354	0.6893	0.6081	0.4621
10	60 : 45	12	12	0.7902	0.8830	0.8623	0.8442
11	60 : 30	8	12	0.0500	0.8771	0.0500	0.1299
12	60 : 45	4	12	0.9500	0.9500	0.1232	0.4809
13	60 : 60	12	8	0.2782	0.0500	0.9246	0.2343
14	60 : 45	8	8	0.9351	0.2910	0.9286	0.6322



a *b*

Surface response for generalized criterion of optimization W_i at content of sodium metasilicate: *a* – 8 wt %; *b* – 12 wt %

References

1. Yeshchanko L. S., Sumich A. I., Alekseev A. D., Pavlovich V. L., Gannochenko K. I. *Sostav dlya chistki tverdoy poverkhnosti* [Composition for cleaning of solid surface]. Patent BY, no. a 20121001, 2012.

2. Sumich A. I., Yeshchanko L. S., Alekseev A. D. [Obtaining low-phosphatic and phosphate-free multifunctional detergents]. *VI Mizhnarodna naukovo-tekhnichna konferentsiya Novitni energo- ta resursozberigajuchi khimichni tekhnologii' bez ekologichnykh problem* [VI International Scientific Conference New energy- and resource-saving chemical technologies without environmental problems]. Odessa, 2013, vol. 1, pp. 207–208 (in Russian).

3. Sumich A. I. [On the "dry" producing process of multicomponent inorganic materials for detergents]. *Materialy mezhdunarodnoy nauchno-tekhnicheskoy konferentsii* [Materials of the International Scientific and Technical Conference]. *Tehnologiya-2013* [Technology-2013], Severodonetsk, 2013, vol. 1, pp. 137–138 (in Russian).

4. Sumich A. I. Features of sodium sesquicarbonate formation in the Na_2CO_3 – H_3PO_4 – H_2O. *IV Vseross. konf. po khimich. tekhnol., Vseross. molodezhnaya konf. po khimich. tekhnol., Vseross. shkola po khimich. tekhnol. dlya molodykh uchenykh i spetsialistov, Vseros. simpozium po khimii i tekhnol. ekstraktsii I sorbtsii* [IV All-Russian Conference on Chemical Engineering, National Youth Conference on Chemical Technology, All-Russian School of Chemical Engineering for Young Scientists and Specialists, Russian Symposium on Chemistry and Technology of extraction and sorption]. Moscow, 2012. vol. 1, pp. 217–218.

5. Zimon A. D. *Kolloidnaya khimiya* [Colloid chemistry]. Moscow, Agar Publ., 2003. 320 p.

6. Repin S. V., Shepin S. A. *Matematicheskie metody obrabotki statisticheskoy informatsii s pomoshch'yu EVM* [Mathematical methods of statistical information on a computer]. Minsk, University Publ., 1990. 128 p.

7. Uempen F., Peir D. *Excel 97. Seriya "Enter".* [Excel 97. Series "Enter"]. Rostov-on-Don, Feniks Publ., 2007. 592 p.

Information about the authors

Yeshchanka Lyudmila Semenovna – D. Sc. Engineering, professor. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: yeshchanko@belstu.by

Alekseev Anatoliy Dmitrievich – Ph. D. Chemistry, assistant professor. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: ada@belstu.by

Sumich Andrey Ivanovich – assistant lecturer, Department of Inorganic Materials Technology and General Chemical Technology. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: sumich@belstu.by

Zhuk Galina Mikhaylovna – researcher, Department of Inorganic Materials Technology and General Chemical Technology. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: galm@belstu.by

Received 19.03.2015