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PHYSICAL AND CHEMICAL PROPERTIES OF THE PRODUCTION TECHNOLOGY OF INDIVIDUAL UREA-FORMALDEHYDE COMPOUNDS AND MULTIFUNCTIONAL COMPOUNDS ON THE BASIS OF THOSE COMPOUNDS AND ZINC ACETATE

Abstract. Optimum parameters of drying process of the thin layers of low-molecular urea-formaldehyde compounds - monomethylolurea, dimethylolurea and methylene dicarene, as well as multifunctional compounds on the base of those compounds and zinc acetate, were determined. The input parameters were: pH 6.5-7.4, temperature 70-95 ^{o}C and drying process time 2-40 minutes. Output parameters: the content of methylol, methylene formaldehyde, free urea.

The optimum drying parameters were: pH of solutions 6.5-7.0, temperature 70-90 ^{o}C, drying time of solutions 2-10 min. The data of the conducted studies allow us to recommend a spray dryer for the production of solid urea-formaldehyde compounds, as well as multifunctional compounds based on them and zinc acetate.

Key words: urea-formaldehyde compounds, drying process, phase composition changes, polycondensation process, spray dryer.

Introduction. For the physical and chemical justification of the technology for obtaining low-molecular urea-formaldehyde compounds (UFC) – monomethylol ureas, dimethylol urea and methylene-diuria, as well as multifunctional compounds based on them and zinc acetate, studies were conducted in order to determine the change in their phase composition as a function of pH, temperature, duration drying process in thin layers.

To carry out the experiment, model saturated solutions of UFC (table 1) were prepared and their composition is defined by the conditions of their synthesis [1-3].

Table 1 – Composition of model solutions of individual UFC

Compound	Composition, mass. %			
	UFC	formaldehyde	Urea	Water
$H_2NCONHCH_2OH$	40,0	0	0	60,0
	38,0	0,67	1,33	60,0
$HOCH_2NHCONHCH_2OH$	40,0	0	0	60,0
	34,0	3,0	3,0	60,0
$H_2NCONHCH_2NHCONH_2$	30,0	0	0	70,0

EXPERIMENTAL PART

Experiment methodology. Model solutions of UFC were applied in a thin layer on a surface having a temperature of 70, 90 and 95 °C, and the products were dried for 2, 5, 10, 15, 20, 25, 30 minutes.

At the first stage of the study, experiments on drying solutions of UFC in thin layers were carried out at pH 6.5-7.4, in the temperature range 70-95 °C for a constant time equal to two minutes.

RESULTS AND DISCUSSION

It is established (table 2) that in the case of using a solution of monomethylolurea that does not contain free urea and unreacted formaldehyde having a pH of 6.5, with thin-layer UFC drying in the temperature range 70-95 °C, it is

Table 2 – Composition of drying product obtaining from monomethylolurea solution

Composition of drying product of monomethylolurea, mass %	Experiment conditions		Composition of product, mass %		
	pH	temperature, °C	Monomethylourea	Condensation product	Free urea
Monomethylourea – 40,0 Formaldehyde – 0 Urea – 0 Water – 60,0	6,5	70	86,0	12,0	2,0
		90	76,0	22,2	1,8
		95	72,0	26,8	1,2
	6,8	70	100	0	0
		90	98,2	1,8	0
		95	92,5	7,5	0
	7,0	70	100	0	0
		90	100	0	0
		95	98,4	1,6	0
	7,4	70	100	0	0
		90	100	0	0
		95	99,2	0,8	0
Monomethylourea – 38,0 Formaldehyde – 0,67 Urea – 1,33 Water – 60,0	6,5	70	97,2	1,1	1,7
		90	95,0	3,8	1,2
		95	89,1	10,2	0,7
	6,8	70	97,5	0	2,5
		90	69,4	2,1	1,5
		95	91,2	7,8	1,0
	7,0	70	96,62	2,5	3,38
		90	96,62	2,5	3,38
		95	95,3	3,0	1,7
	7,4	70	92,62	0	7,38
		90	92,65	0	7,35
		95	92,7	6,0	1,3

impossible to obtain a stable product due to the polycondensation reaction of monomethylolurea with the formation, according to paper chromatography analysis, of monomethylolmethylene compounds of urea.

When the pH of the monomethylolurea solution is increased to 6.8, the product of stable composition can only be obtained at a temperature of 70 °C, increasing the temperature to 90 ° C promotes the formation of condensation products, as well as formation and release of free urea.

When the pH of the monomethylolurea solution is 7.0-7.5, the product does not undergo polycondensation in the drying temperature range from 70 to 90 °C, and with rising the temperature to 95 °C, observed a slight formation of condensation products about 0.8-1.6%. In case of using a solution of monomethylolurea containing 0.67% formaldehyde and 1.33% urea at pH 6.5 at the temperature range from 70 to 90 °C, the polycondensation process takes place forming monomethylolmethylene derivatives of urea. An increase in pH to 6.8 makes it possible to obtain a stable product only at 70 °C. At a solution pH value about 7.0-7.4 and temperature range from 70 to 90 °C, condensation don´t occur and obtained product contains 96.62% monomethylolurea and 3.38% urea. However, increase the drying temperature to 95 °C promotes formation of the condensation products. In this case, the products contain less urea, which is defined by its interaction with formaldehyde and methylol derivatives of urea [4, 5]. Thus, the optimum condition for obtaining a stable monomethylolurea of stable composition by drying in thin layers are : aeration process about 2 minutes with a minimum content of condensation products; pH of solution 6.8-7.4 and temperature range from 70 to 90 °C.

At the next stage of the experiment, carried out determination the change in the phase composition of the products depending on the drying time (interval 2-30 minutes) in the model solutions of monomethylolurea. At the same time, the constant factors of the drying process were the temperature 75 °C and the pH of

Table 3 – Characteristics of monomethylourea in relation to the time of heat treatment

Composition of drying product of monomethylolurea, mass %	Duration drying process, minute	Drying temperature, °C	Composition of the product, mass %		
			monomethylolurea	Condensation product	Free urea
Monomethylolurea – 40 Formaldehyde – 0 Urea – 0 Water – 60,0	2	75	100	0	0
	5		100	0	0
	10		100	0	0
	20		99,5	0,5	0
	30		91,2	6,7	2,1
Monomethylolurea – 38 Formaldehyde – 0,67 Urea – 1,33 Water – 60,0	2	75	96,62	0	3,38
	5		96,62	0	3,38
	10		96,62	0	3,38
	20		96,62	Traces neglibile	3,37

the solution 7.0. From the data obtained (table 3) it follow that at the temperature 75 °C in a neutral medium, a product of stable composition can be obtained with a drying time about 2-10 minutes. When the heat treatment time is increased to 20-30 minutes, takes place formation of condensation products up to 0.5-6.7% in the system.

Experimental data on the change in the phase composition of the drying products of dimethylolurea solutions in thin layers, depending on pH 6.5-7.4 and temperature 70-95 °C are presented in table 4.

Table 4 – Composition of the drying product of dimethylolurea solution

Composition of drying product of monomethylolurea, mass %	Experiment conditions		Composition of the product, mass %		
	pH	tempe-rature, °C	Dime-thylolurea	Condensation product	Free urea
Monomethylolurea – 40 Formaldehyde – 0 Urea – 0 Water – 60,0	6,5	70	82	15,8	2,2
		90	73	21,9	5,1
		95	65	26,3	8,7
	6,8	70	100	0	0
		90	83	13,7	3,3
		95	75	19,8	5,2
	7,0	70	100	0	0
		90	100	0	0
		95	95,4	3,0	1,6
	7,4	70	100	0	0
		90	100	0	0
		95	96,5	2,7	0,8
Dimethylolurea 34 Formaldehyde – 3,0 Urea – 0 Water – 60,0	6,5	70	85,2	2,6	12,2
		90	70,3	13,6	16,1
		95	65,2	15,5	19,3
	6,8	70	91,9	0	8,1
		90	79,1	9,4	11,5
		95	75,0	11,7	13,3
	7,0	70	91,9	0	8,1
		90	91,9	0	8,1
		95	85,0	4,2	10,8
	7,4	70	91,9	0	8,1
		90	91,9	0	8,1
		95	85,9	3,7	10,4

The drying time of the products was constant - 2 minutes. Drying process for model solutions of dimethylolurea with a pH of 6.5 at the temperature range from 70 to 95 °C does not make it possible to obtain a stable product. The amount of condensation product is 15.8-26.3%. In this case, 2.2-8.7% of free urea is formed. According to the paper chromatography analysis, dimethylolmethylene and methylene compounds of urea are formed in the product. With an increase the pH of the solution to 6.8, the product of stable composition can be obtained only at the temperature about 70 °C. At pH 7.0-7.4 in the temperature range from 70 to 90 °C there is no condensation of dimethylolurea. An increase the temperature to 95 °C leads to the formation of a 2.7-3.0% condensation product in the system; thus forming free urea in an amount about 0.8-1.6%.

Using a solution of dimethylolurea containing free urea and unreacted formaldehyde, when drying the salt, such patterns of the composition of the products are observed depending on the pH and temperature of the process (table 4), as in the case of a solution of dimethylolurea that does not contain impurities.

However, in this case, the formaldehyde presence in the solution of dimethylolurea is dried out during the drying process of the product into the gas phase and must be disposed. When the pH of the solutions is 7.0-7.4, condensation of the product is excluded in the temperature range of 70-90 °C.

Increasing the temperature to 95 °C promotes the formation about 3.7-4.2% condensation product in the system.

The results of the studies to determine the change in the composition of the products during the drying process of solutions of dimethylolurea in the range of 2-30 minutes at a constant temperature of 75 °C and pH 7.0 showed (table 5) that the composition of the product is stable in the drying time of 2-10 minutes, 10-30 minutes condensation of dimethylolurea takes place with the formation of urea in dimethylolmethylene compounds (7.1-18.0%).

Table 5 – Composition of the drying product of dimethylolurea as a function of the time of heat treatment

Dimethylolurea pulp composition, mass %	Duration of drying process, minutes	Drying temperature, °C	Composition of the product, mass %		
			Monomethylolurea	Condensation product	Free urea
Monomethylolurea – 40 Formaldehyde – 0 Urea – 0 Water – 60,0	2	75	100	0	0
	5		100	0	0
	10		100	0	0
	20		98,5	1,5	0
	30		88,3	7,1	4,6
Dimethylolurea 34 Formaldehyde – 3,0 Urea – 0 Water – 60,0	2	75	91,9	0	9,1
	5		91,9	0	9,1
	10		91,9	0	9,1
	20		88,9	2,0	9,1
	30		77,0	18,0	5,0

The studies carried out to determine the change in the composition of the products of drying of methylenedimourea pulp in thin layers in the temperature range 70-95 °C, the pH of solutions of 6.5-7.4 and the process time of 2-30 minutes have shown the possibility of obtaining a solid product of stable composition that is not condensed.

Thus, optimal conditions for the preparation of solid individual low-molecular-weight UFC - monomethylol-, dimethylolurea, methylene-diureas of stable composition were determined: the pH of UFC solutions was 6.8-7.4, the temperature was 70-90 °C, the drying time of UFC solutions in thin layers was 2-10 minutes. For drying solutions of UFC to obtain solid products, a spray dryer is recommended.

For the justification of the technology of preparation of multifunctional action compounds, based on low molecular weight UFC and zinc acetate, studies have also been carried out to change the composition of the preparations depending on the temperature, pH and drying time in thin layers of saturated solutions of double salts.

To carry out the research, solutions of 20% concentrationof polyfunctional action preparations - double compounds based on monomethylol-, dimethylol ureas and 20% pulps based on methylene-diureas were used. The experiments were carried out as follows. Model solutions of double UFC compounds with zinc acetate were deposited in a thin layer on the surface at a temperature of 70, 90, 95 °C and the products were dried for 2-30 minutes.

In the first stage of the experiment drying of solutions of double compounds in thin layers was carried out in the temperature range 70-95 °C, pH of solutions 5.5-7.0 for a constant time equal to 2 minutes.

The results of studies of products based on monomethylol- and dimethylol ureas are presented in tables 6 and 7. When drying solutions of a double compound based on monomethylol urea and zinc acetate (Table 6) at pH 5.5-6.0 in the temperature range 70-95 °C, stable product, the amount of methylol formaldehyde was 65-92%, and methylene 8-35%.

At the pH value 6.5-7.0 of solutions at the temperature range from 70 to 90 °C there is no hydrolysis of the double compound and the formation of condensation products, as indicated by a 100% content in the final product of methylol formaldehyde. Increasing the drying temperature to 95 °C promotes the polycondensation of monomethylolurea in the composition of the double salt. This is evidenced by a decrease in the amount of methylol formaldehyde to 90-92% and the formation of 8.0-10.0% methylene formaldehyde in the product.

Thus, during the drying process 2 minute of a solution of a double compound based on monomethylolurea and zinc acetate at the temperature range from 70 to 90 ^{o}C and pH 6.5-7.0, hydrolysis of the product and condensation of monomethylolurea does not occur. Conditions obtaining a preparation of multifunctional action of stable composition.

Table 6 – Content of methylol and methylene formaldehyde in the product of drying of a double compound based on monomethylolurea and zinc acetate

Experiment conditions		Fragment forms of formaldehyde in the product,% mass	
pH	temperature, °C	methylol	Methylene
5,5	70	86	14
	90	72	28
	95	65	35
6,0	70	92	8
	90	86	14
	95	76	24
6,5	70	100	0
	90	100	0
	95	90	10
7,0	70	100	0
	90	100	0
	95	92	8

The next stage of the experiment, the composition of the products, depending on the drying time of model solutions of a double compound based on monomethylolurea and zinc acetate in the time interval from 2 to 40 minutes, at isothermic condition (75 °C) and pH 7.0 were determined.

Table 7 – Containing the methylol and methylene forms of formaldehyde in the product after drying of a double compound based on dimethylolurea and zinc acetate

Experiment conditions		Fragment forms of formaldehyde in the product,% mass	
pH	temperature, °C	methylol	Methylene
5,5	70	81	19
	90	69	31
	95	62	38
6,0	70	86	14
	90	82	18
	95	73	27
6,5	70	100	0
	90	100	0
	95	83	17
7,0	70	100	0
	90	100	0
	95	86	14

It was found that at a drying temperature of solutions which prepared at 75 °C and pH 7.0, a product of stable composition can be obtained during the drying time from 2 to 10 minutes. Increasing the time of heat treatment of solution of the double compound to 20-30 minutes leads to the condensation of monome-thylolurea to 5.8% of the total formaldehyde content. During the drying time from 40 minute, the amount of condensation product of the latter was 10.8%.

Table 7 presents the obtained data on the change in the composition of the drying products of solutions of a double compound based on dimethylolurea and zinc acetate depending on pH and temperature. The drying time of the products was conducted during 2 minutes.

From the data obtained, it follows that the patterns of variation in the composition of the double compound by methylol and methylene formaldehyde are similar to those for a double compound based on monomethylol urea and zinc acetate. However, the amount of formed methylene formaldehyde in the product is greater. This indicates a less stable product at high temperatures of 90-95 ^{o}C.

Conclusion. The optimal conditions of drying process to preparation products of stable composition based on dimethylol urea and zinc acetate are pH 6.5-7.0, temperature 70-90 ^{o}C. The studies carried out to determine the change in the composition of the products during the drying process of the solutions of the preparation for 2-40 minutes at a constant temperature 75 °C and pH of solution 7.0. It show that during the drying time from 2 to10 minutes at temperature 75 °C, the products are stable and do not undergo hydrolysis and polycondensation in the future . Drying the samples for 20-40 minutes lead to formation of of methylene formaldehyde in the products about 7.0-12.0%.

Studies on drying solutions of a double compound based on dimethylenourea and zinc acetate in thin layers the temperature range from 70 to 90 °C, pH solutions 5.5-7.0 and drying time about 2 to 20 minutes have shown the possibility of obtaining a product of stable composition which does not undergo to polycondensation.

Thus, the optimal conditions for the preparation of solid compounds based on monomethylol-, dimethylol- and methylenedimourenes of stable composition at pH solutions about 6.5 to 7.0, the temperature from 70 to 90 °C, drying time of solutions of double compounds based on UFC 2-10 minutes have been determined. These studies allow the recommendation for spray drying and drying of solutions of compounds based on UFC and zinc acetate to obtain solid products.

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REFERENCES

[1] Usmanov S., Ugaj D.P., Ermahanova F.R. Razrabotka tehnologii stimuljatorov rosta rastenij na osnove nizkomolekuljarnyh mochevino-formal'degidnyh soedinenij i acetatov dvuhvalentnyh metallov. Soobshhenie 1. Politerma rastvorimosti sistemy $H_2NCONHCH_2OH$-$Zn(CH_3COO)_2$-H_2O / Deponir. v VINITI 1991 g., № 1218-V91., Tashkent.

[2] Usmanov S., Ermahanova F.R., Bogdanov A.V., Rudnik O.D. Sistema dimetilolmochevina – acetat cinka- voda / Deponir. v Uz NIINTI 1992 g., № 153-A92., Tashkent.

[3] Usmanov S., Ermahanova F.R., Bogdanov A.V., Rudnik O.D. Sistema metilendimochevina – acetat cinka – voda pri 25˚S / Deponir. v Uz NIINTI 1992 g., № 154-A92.

[4] Usmanov S., Ermahanova F.R., Bogdanov A.V., Isakov H., Rudnik O.D. Issledovanie tehnologii nizkomolekuljarnyh mochevino-formal'degidnyh soedinenij v raspylitel'noj sushilke / Deponir. v Uz NIINTI 1992 g., № 148-A92., Tashkent.

[5] Usmanov S., Ermahanova F.R., Bogdanov A.V., Bandurina O.Fiziko-himicheskie osnovy tehnologii nizkomolekuljarnyh mochevino-formal'degidnyh soedinenij i stimuljatorov rosta rastenij // Tezisy dokladov Mezhdunarodnoj nauchno-prakticheskoj konferencii «Nauka i tehnologija – 93», Shymkent, Kazahstan, 1993. Shymkent, 2015. P. 467.

Резюме

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ЖЕКЕ МОЧЕВИНО-ФОРМАЛЬДЕГИДТІК ҚОСЫЛЫСТАР МЕН ОЛАРДЫҢ НЕГІЗІНДЕ МЫРЫШ АЦЕТАТЫМЕН ПОЛИФУНКЦИОНАЛДЫ ӘРЕКЕТТІ ПРЕПАРАТТАР АЛУДЫҢ ФИЗИКА-ХИМИЯЛЫҚ ТЕХНОЛОГИЯ НЕГІЗДЕРІ

Төменмолекулалы мочевино-формальдегидті қосылыстар – монометилолмочевина диметилолмочевина және метилендимочевинаның, сонымен қатар олардың негізінде мырыш ацетатымен полифункционалды әрекетті препараттарды жұқа қабатта кептірудің оңтайлы параметрлері анықталды. Кіріс параметрлері: pH 6,5–7,4, температурасы 70-95 °С кептіру ұзақтығы 2-40 мин. Шығыс параметрлері: метилолды, метиленді формальдегидтер мазмұны, еркін мочевина.

Кептірудің оңтайлы параметрлеріне жатады: pH-6,5–7,0 ерітінділер, температура 70–90 ^{o}С, кептіру ұзақтығы 2-10 минут. Жүргізілген зерттеулер деректері қатты мочевиноформальдегидті қосылыстар, сонымен қатар олардың негізінде мырыш ацетатымен полифункционалды әрекетті препараттар алу үшін бүркеуші кептіргішті ұсынуға мүмкіндік береді.

Түйін сөздер: мочевино-формальдегидті қосылыстар, кептіру, фазалық құрам өзгерістері, поликонденсация, бүркеуші кептіргіш.

Резюме

Ф. Р. Ермаханова, С. Усманов, Г. Т. Омарова

ФИЗИКО-ХИМИЧЕСКИЕ ОСНОВЫ ТЕХНОЛОГИИ ПОЛУЧЕНИЯ ИНДИВИДУАЛЬНЫХ МОЧЕВИНО-ФОРМАЛЬДГИДНЫХ СОЕДИНЕНИЙ, ПРЕПАРАТОВ ПОЛИФУНКЦИОНАЛЬНОГО ДЕЙСТВИЯ НА ИХ ОСНОВЕ И АЦЕТАТА ЦИНКА

Определены оптимальные параметры сушки в тонких слоях низкомолекулярных мочевино-формальдегидных соединений – монометилолмочевины, диметилолмочевины и метилендимочевины, а также препаратов полифункционального действия на их основе и ацетата цинка. Входными параметрами были: pH 6,5–7,4, температура 70–95 ^{o}С и продолжительность сушки 2-40 мин. Выходные параметры: содержание метилольного, метиленового формальдегида, свободной мочевины.

Оптимальными параметрами сушки явились: pH растворов 6,5–7,0, температура 70–90^{o}С, продолжительность сушки растворов 2–10 мин. Данные проведенных исследований позволяют рекомендовать распылительную сушилку для получения твердых мочевино-формальдегидных соединений, а также препаратов полифункционального действия на их основе и ацетата цинка.

Ключевые слова: мочевино-формальдегидные соединения, процесс сушки, изменения фазового состава, процесс поликонденсации, распылительная сушилка.