N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2019.2518-1491.72**
Volume 6, Number 438 (2019), 42 – 48

UDK 541.64+678

Zh.B. Rakhimberlinova[1], G.A. Mustafina[2], A.T. Takibayeva[1], I.V. Kulakov[3], A.R. Iskakov[1],O.G. Nazarova[1]

[1]Karaganda State Technical University, Karaganda, Kazakhstan;
[2]LP «KAZ-OPTIMUM», Karaganda, Kazakhstan;
[3]Tyumen State University, Tyumen, Russia
E-mail:kargtu_tss@mail.ru

SYNTHESIZING NITRILE-CONTAINING GLYCONITRILE (CO) POLYMERS

Abstract. The article presents the results of studying the production of new nitrile-containing monomers by acylation of unsaturated N- and N,N′ - α-aminoacetonitrile chlorides (meta) acrylic acids using acrylamide. The initial unsaturated N- and N,N′ - α-aminoacetonitriles were synthesized by interaction of glycolic acid nitrile (glyconitrile) with amines of various classes. The ability of new monomers to radical (co)polymerization was studied, namely, the possibility of producing polyacrylamides based on N,N′ nitrile derivatives of (meta) acrylamide and vinyl ester (N - acetonitrile) monoetholamine (VEEAN) with acrylamide in bulk in the presence of radical initiators and organic solvents with formation of carbochain polymers. The formation of nitrile-containing polyacryamides is confirmed by the data of the elemental analysis, viscometry, IR spectroscopy. Viscometric data [ή] = 0.10 - 0.29 dl/g of polymers indicate low reactivity of the synthesized nitrile acrylamides compared to acrylamide that is associated with the steric effect of the chain length. The synthesized copolymers were studied as modifiers of urea-formaldehyde binders (UFB) used to strengthen unstable rocks. The samples strengthened with UFB solutions without a modifier showed low strength indices for 62 and 77 % concentrations, respectively, while introduction of nitrile-containing copolymers in the amount of 1-5 % wt. improved strength characteristics of the samples by 1.2-1.8 times. The good strength results for mine rocks are explained by the increased flexibility and elasticity of the urea-formaldehyde binder chains with new functional groups responsible for the resin adhesion to the rock.

Keywords:α-aminoacetonitriles, glycolic acid nitrile (glyconitrile), monoethanolamine vinyl ester, acrylamide, polyacrylamide, N,N'- acrylamide nitrile derivatives, copolymers, urea-formaldehyde binder modifiers.

Introduction

Recently the scientific and practical interest in the directed synthesis of nitrile-containing polyfunctional polymers has been steadily growing. This is caused by a wide range of useful properties of these (co)polymers that can be further used as promising flocculants, coagulants, polyelectrolytes, modifiers for urea binders, semi-synthetic soil structures. Great prospects in this direction are opened by studying the interaction of glyconitrile with various compounds cuased by its extremely high reactivity and associated with it rich possibility of obtaining a wide variety of organic compounds. Among the variety of compounds synthesized from glyconitrile, the most interesting are its N- and N,N'-α-amino derivatives, which is associated with the ease of their preparation, the possibility of chemical transformations and their practical significance. Many of them can be proposed as polyfunctional monomers for polymerization or polycondensation, which will allow obtaining new types of interesting polymers both in practical and in scientific terms.

Nitrile-containing polyfunctional polymers described in the article were obtained by joint radical (co)polymerization of monomers of nitrile derivatives N,N'- (meta) acrylamide that were synthesized by acylation of unsaturated N- and N,N'- α-aminoacetonitriles (meta) acrylic acids, acrylates.

The obtained (co)polymers based on derivatives of glycolic acid nitrile are assigned to carbochain polymers of linear structure with long side groups. New nitrile-containing (co)polymers are characterized by a low molecular weight and a significant number of functional groups capable of further transformations and predetermining various fields of their application [1-2].

Experimental Part

Synthesizing α-aminoacetonitriles (I-VI)

Aminoacetonitrile NH_2CH_2CN (I). 16 ml of the 70% aqueous glyconitrile solution (0.2 mol) are added dropwise to 13.6 ml of the 23% aqueous ammonia solution (0.2 mol) with cooling at the temperature of 0-5 °C so that the temperature of the reaction mixture does not exceed 10 °C. After that, the synthesis temperature is raised to the room temperature and held within 1.5 hours. 20 ml of concentrated HCl (0.2 mol) are added to the reaction mixture. The mixture containing aminoacetonitrile in the form of hydrochloric acid salt is evaporated. $HCl{\cdot}NH_2$-CH_2-CN crystals are washed with ester and dried.

N-methylaminoacetonitrile CH_3NHCH_2CN (II). The synthesis is carried out analogously to (I) with 2 moles of amine. At the end of the synthesis, the reaction mixture is saturated with sodium sulfate and extracted repeatedly with diethyl ester. The solvent is distilled off, the residue is subjected to vacuum distillation.

N-allylaminoacetonitrile CH_2=CH-CH_2-NH-CH_2CN (III). To 22.8 ml of the 50 % aqueous solution of allylamine (0.2 mol) there are added dropwise 16 ml of the 70 % aqueous solution of glyconitrile (0.2 mol) while the reaction mixture is cooled to 5 °C. Upon completion of adding the glyconitrile solution, the mixture is heated to 35 °C and kept at this temperature within 2 hours. The separated oil layer of aminonitrile is separated from the aqueous solution using a separatory funnel. An additional amount of aminonitrile is extracted from the aqueous layer with diethyl ester. The ester extract and the organic layer are mixed, dried over anhydrous sodium sulfate, diethyl ester is distilled off, the residue is subjected to vacuum fractional distillation.

*Vinyl ester of (-N-acetonitrile)-ethanolamine CH_2=CH-O-CH_2CH_2NH-CH_2CN (IV).*The synthesis is carried out similarly to (III) with 0.2 moles of amine at 35-40 °C.

N-benzylaminoacetonitrile $C_6H_5CH_2NHCH_2CN$ (V-VI). The synthesis is carried out similarlyto (III) with 0.2 moles of amine at 35-40 °C (Table 1).

Table 1 - Synthesizing α – aminoacetonitrile – $RHNCH_2CN$

Compounds	R	Yield, %	T_{boil}, °C	d_4^{20}	n_D^{20}
I	H	80	T_{mel}165-166	-	-
II	CH_3	65	45/0.4	0.9300	1.4199
III	CH_2=CH–CH_2	78	85-88/0.4	0.9281	1.4486
IV	CH_2=CH–CH– –O–CH_2–CH_2	90	91-93/0.4	1.0060	1.4691
V	$C_6H_5CH_2$	90	130-133/0.4	1.0460	1.5388
VI	C_6H_5	50	145/1	-	-

Synthesizing N,N′-derivatives of glycolic acid nitrile (VII-XI)

N,N′-substituted acrylamides: a) a mixture of 200 ml of benzene (diethyl ester or acetone), 7 g of dry K_2CO_3 and 0.2 mol of α-aminoacetonitrile is cooled to 8-10 °C, a solution of 0.2 mol of acrylic acid chloride is added dropwise in 60 ml of benzene (diethyl ester or acetone) at such a rate that the temperature of the reaction mixture does not exceed 10 °C. After 45 minutes, another 7 g of dry $K_2CO_3$are added and stirred within 1 hour at 10 °C, then 1 hour at the room temperature. The inorganic precipitate is filtered off, washed twice with 60 ml of hot benzene (diethyl ester or acetone). The solvent is distilled off, the residue containing nitrile-substituted acrylamide is subjected to fractional vacuum distillation in the presence of the copper chip polymerization inhibitor (Table 2).

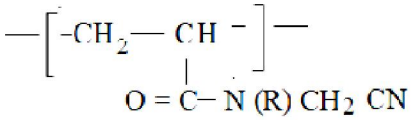
b) In the aqueous medium synthesizing N,N′-substituted acrylamides is carried out according to the following procedure: an equimolar amount of acrylic acid chloride in benzene and the 50 % aqueous

NaOH solution are added from two dropping funnels to the reaction mixture of α-aminoacetonitriles obtained by the above procedure II-VI with vigorous stirring and cooling (-5 °C). Then the reaction mixture is kept within 1 hour at the room temperature. The final product is extracted with benzene, the solvent is distilled off, nitrile-substituted acrylamide is subjected to vacuum distillation. Their characteristics are given in Table 2.

Table 2 –Characteristics of N,N′-substituted acrylamides

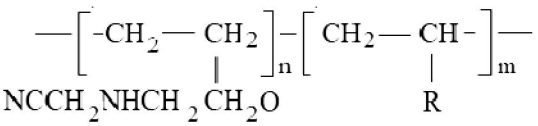
Compound No.	R	R′	Yield, g	T_{boil}, °C; 0,4 MPa
VII	CH_3	H	15.0 (54)	115-118
VIII	CH_3	CH_3	19.0 (75)	117-120
VIII	CH_3	CH_3	20.3 (80)*	117-120
IX	CH_2=CH-O-CH_2CH_2	H	19.0 (62)	140-142
X	CH_2=CH-O-CH_2CH_2	CH_3	30.6 (90)	147-149
XI	CH_2=CH-O-CH_2CH_2	CH_3	28.0 (85)*	147-149
*-in the aqueous medium				

Homopolymer of N,N′-derivatives of acrylamide (XII)



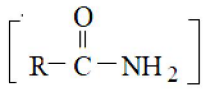
The synthesis is carried out by radical polymerization in bulk or in dimethylformamide (DMF) in the presence of radical initiators: dinitrile azobisisobutyric acid (DAA) or benzoyl peroxide in the amount of 0.5-1 % of the total weight of the monomer at 70 % within 6-10 hours, in argon atmosphere. The copolymers obtained are reprecipitated from solutions in dioxane, acetone, dimethylformamide (DMF), water or methanol and dried at the room temperature in a vacuum oven to the constant weight.

(-N-acetonitrile) ethanolamine vinyl ester copolymers (XIII)



a) with alkyl acrylates (R = -OR ′, where R′-CH_3-; C_2H_5-; C_4H_9-) are obtained in bulk in the presence of 0.5 % DAA at various ratios of monomers, the synthesis temperature is 70 °C, and the duration is 6 hours. The copolymers are reprecipitated according to procedure (1);

b) with acrylamide:



is obtained by copolymerization of components in DMF, in the presence of DAA in the amount of 0.5 % of the monomer weight at the temperature of 70 °C within 6 hours, the ratio of the starting reagents is equimolar. The copolymers are reprecipitated according to procedure (1).

Urea-formaldehyde binders UFB modifications (XIV–XV). Synthesized copolymer (XII) was diluted with water-dioxane (2:1) to the 50 % concentration, the specific gravity of the solution was 1.078 g/cm^3, and copolymer (XIII) was diluted to the 70 % concentration with the specific gravity of 1.073 g/cm^3.

Resultsanddiscussion

The subject of our studies were copolymers and polymers of nitrile derivatives of N,N'(meta) acrylamide with acrylamide that were studied as new modifiers for urea binders used to strengthen unstable rocks, semi-synthetic soil structures, foaming agents in flotation concentration of sulfide copper ores.

Unsaturated N- and N,N'- α-aminoacetonitriles were used as starting monomers for synthesizing the above polymers. The synthesis of α-aminoacetonitriles is based on the reaction of glycolic acid nitrile (glyconitrile) interaction with amines of various classes according to the scheme:

$$RR'NH + HOCH_2CN \rightarrow RR'NCH_2CN + H_2O,$$

where R and R' are alkyl, aryl, alkenyl, heterocycle.

The specific structure of glyconitrile, namely, the close proximity of OH and CN - groups determines the features of its interaction with primary and secondary amines. The synthesis of glyconitrile with amines was studied at the equimolar ratio of the starting reagents, various temperatures, durations, solvents, and the concentration of the starting reagents. The optimum process parameters were found (40-60 °C, 1-2 hours, amine concentration 50-100 %, glyconitrile concentration 50-70 %, water). Above 60 °C side reactions begin to occur with participation of C≡N and NH - groups of products of imines or resins formation. In organic solvents the yield of final products is significantly reduced.

Their structure is confirmed by the data of the elemental analysis, IR and NMR spectra. IR spectra of aminonitriles are characterized by the presence of a number of absorption bands, groups: 2250 - 2240 cm^{-1} - C≡N; 3400 - 3320 cm^{-1} – NH; 1640 cm^{-1} – CH_2═ CH- .

The new N,N' derivatives of acrylamide were synthesized by acylation of unsaturated R-α-aminoacetonitriles obtained by the above procedure with (meta) acrylic acid chlorides:

$$RNHCH_2CN + CH_2 = CR_1\text{-}COCL \longrightarrow CH_2{=}CR_2\text{-}\underset{\underset{O}{\|}}{C}\text{-}\underset{\underset{R'}{|}}{N}CH_2CN \qquad 1)$$

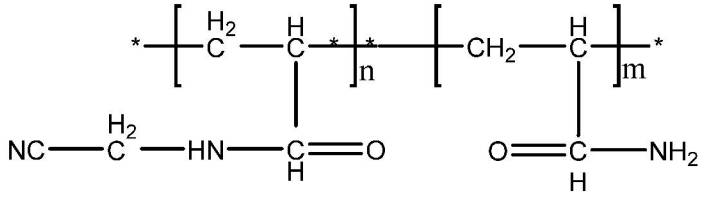
where R = H, - NH-CH_2CH_2OCH═CH_2; R' = H, - CH_3.

The physical-and-chemical constants of the obtained N,N'-derivatives of acrylamide are presented in Table 2. Their composition and structure were confirmed by the elemental analysis, IR and NMR spectra.

The IR spectra of these compounds contain absorption bands in the region of 2300 cm^{-1} (nitrile group), 1650–1680 cm^{-1} (amide group), 1800–1860 cm^{-1} (vinyl group). The NMR spectra show absorption bands of methylene protons of the – CH_2CN group (region 4.26–4.67 ppm) and vinyl protons at 5.9–6.9 ppm and 5.25-6.03 ppm.

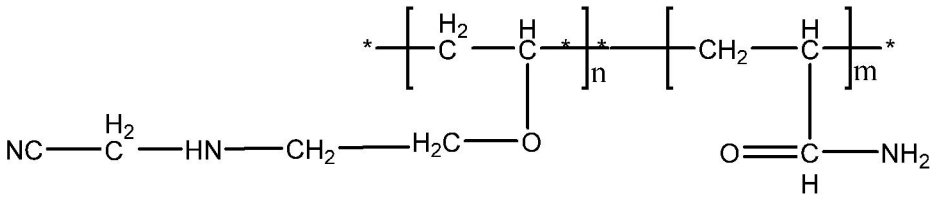
We investigated the possibility of producing polymers based on N,N'- nitrile derivatives of (meta) acrylamide and vinyl ester (N - acetonitrile) - monoetholamine (VEEAN) with acryamide with formation of carbochain polymers of the following structure:

- copolymers of N,N'- nitrile derivatives (meta) of acrylamide with acrylamide:



(2)

- copolymer of vinyl ester (N-acetonitrile)-ethanolamine with acrylamide



3)

The viscometric data [ή] = 0.10 - 0.29 dl/g of polymers indicate low reactivity of the synthesized nitriacryamides compared to acrylamide that is associated with the steric effect of the long chain and the nature of the R_1 substituent. For the obtained polymers, an anomalous dependence of viscosity on solution concentration is observed, which is associated with the presence of ionogenic groups in the composition. It allows attributing them to polyelectrolytes.

The synthesized copolymers were investigated as modifiers for urea binders (UFB) used to strengthen unstable rocks.

Modification was carried out by combining aqueous solutions of UFB with the copolymers taken in the amount of 1-5 % of the UFB weight. It was noted that copolymers combine well with UFB and do not stratify over time. The presence of active functional groups (CO =, C≡N, NH2, -C-O, $CONH_2$) in the modifiers contributed to increasing the adhesive ability.

In order to establish the modifying effect of the copolymers based on synthesized (co)polymers for compressive strength, the mixtures with a hardener, oxalic acid, and with a filler, ground mine rock, represented by medium strength mudstone, were compiled. The resin to rock ratio was 1: 6, the mixture was loaded into molds and pressed at 10 atm within 3 minutes. Testing the strengthened samples for compressive strength was carried out after 7 and 21 days of storage in the air at 15 °C. The results of testing the rock samples reinforced with modified solutions of UFB depending on the concentration of resin and modifier are presented in Table 3.

Table 3 - The use of polymers based on copolymers of nitrile derivatives of N,N'(meta) acrylamide with acrylamide as bindersfor mine rocks

No.	Modifier	Concentration, %	Modifier concentration %	Compression strength of the samples, kp/cm^2	
				Storage time	days
				7	21
	UFB without a modifier	77	0	18.4	31.1
XIV	(N-acetonitrile)-ethanolamine vinyl ester copolymer with acrylamide	77	1	26.9	41.0
		77	3	-	38.2
		77	5	-	39.6
		62	5	19.8	26.9
XV	Methylacetonitrile acrylamide copolymer with acrylamide	77	-	-	53.8
		77	3	-	56.6
		77	5	-	56.6
		62	5	-	26.2

From the data of Table 3 it follows that the samples strengthened with UFB solutions without a modifier have low strength indicators for 62 and 77 % concentration, respectively. The introduction of nitrile-containing copolymers in the amount of 1-5 % wt. increases the strengthened samples strength by 1.2-1.8 times in comparison with the samples strengthened with unmodified UFB. It has been shown that with decreasing the concentration of UFB in the binder, the samples strength decreases. Increasing the modifier concentration from 1 to 5 % wt. does not lead to a substantial increase in strength properties.

Conclusions

Thus, as a result of studies performed, by the acylation reaction of N- and N,N'- α- aminoacetonitrile chlorides of (meta)acrylic acids with acrylamide, new monomers of (meta)acrylamide were obtained and characterized. The initial unsaturated N- and N,N'- α- aminoacetonitriles were synthesized by the interaction of glycolic acid nitrile (glyconitrile) with amines of various classes. The ability of new monomers to radical (co)polymerization in bulk and in organic solvents with formation of nitrile-containing polyacrylamides has been shown.

According to the results of laboratory tests, the synthesized copolymers have shown that they are good binders for mine rocks, providing relatively high mechanical strength compared to unmodified binders. The strengthening effect of modifiers is caused by increasing the flexibility and elasticity of urea-formaldehyde binder chains (UFB) with the advent of new functional groups CO =; C≡N; CONH2; C-O-C that are responsible for the resin adhesion to the rock.

Ж.Б. Рахимберлинова[1], Г.А. Мустафина[2], А.Т. Такибаева[1], И.В. Кулаков[3], А. Р. Искаков[1], О.Г. Назарова[1]

[1]Қарағанды мемлекеттік техникалық университеті, Қарағанды, Қазақстан;
[2] ЖШС «KAZ-OPTIMUM», Қарағанды, Қазақстан;
[3]Тюмень мемлекеттік университеті, Тюмень, Ресей

НИТРИЛ ҚҰРАМДЫ ГЛИКОНИТРИЛ СО ПОЛИМЕРЛЕРІНІҢ СИНТЕЗІ

Аннотация. Мақалада N - и N,N′ - α - аминоацетонитрилдерді хлорангидридтермен (мета) акрил қышқылдарымен, акриламидпен ацилдеу жолымен жаңа нитрил бар мономерлерді алуды зерттеу нәтижелері келтірілген. Бастапқы күтпеген N - және N,N′ - α - аминоацетонитрилдер әртүрлі класты аминдермен гликоль қышқылы (гликонитрил) нитрилінің өзара әрекеттесуімен синтезделген. Жаңа мономерлердің радикалды (со)полимерлеуге қабілеттілігі зерттелді, атап айтқанда N,N′ – нитрил туынды (мета) акриламид пен винил эфирі (N – ацетонитрил) моноэтоламин (ВЭЭАН) негізінде радикалды бастамашылардың қатысуымен және карбоцепті полимерлер түзілетін органикалық еріткіштерде акриламидпен полиакриламид алу мүмкіндігі зерттелді. Құрамында нитрил бар полиакриламидтердің түзілуі элементтік талдау, вискозиметрия, ИК – спектроскопия деректерімен расталған. [ή] = 0,10 - 0,29 дл/г полимерлердің вискозиметриялық деректері синтезделген нитрилакриламидтердің акриламидпен салыстырғанда реакциялық қабілетінің төмендігін көрсетеді, бұл тізбек ұзындығының стерильді әсерімен байланысты. Синтезделген сополимерлер тұрақсыз тау жыныстарын нығайту үшін пайдаланылатын мочевино-формальдегидті байланыстырғыш (МФС) модификаторлар ретінде зерттелді. Модификаторсыз МФС ерітіндісімен бекітілген үлгілер 62 және 77% концентрацияға арналған төмен беріктік көрсеткіштерін көрсетті, 1-5% салмақ мөлшерінде нитрил бар сополимерлерді енгізу. үлгілердің беріктігін 1,2-1,8 есеге жақсартты. Шахталық жыныстар үшін беріктік көрсеткіштері бойынша жақсы нәтижелер шайырдың жыныска адгезиясына жауапты жаңа функционалдық топтармен несепнәрформальдегидті байланыстырушы тізбектерінің икемділігі мен икемділігінің артуымен түсіндіріледі.

Түйін сөздер: α –аминоацетонитрилдер, гликоль қышқылының нитрилі (гликонитрил), моноэтаноламин винил эфирі, акриламид, полиакриламид, N, N' – нитрил туынды акриламид, сополимерлер, мочевин-формальдегидті байланыстырғыштардың модификаторлары.

Ж.Б. Рахимберлинова[1], Г.А. Мустафина[2], А.Т. Такибаева[1], И.В. Кулаков[3], А. Р. Искаков[1], О.Г. Назарова[1]

[1]Карагандинский государственный технический университет, Караганда, Казахстан;
[2]ТОО «KAZ-OPTIMUM», Караганда, Казахстан;
[3]Тюменский государственный университет, Тюмень, Россия

СИНТЕЗ НИТРИЛСОДЕРЖАЩИХ (СО) ПОЛИМЕРОВ ГЛИКОНИТРИЛА

Аннотация. В статье приведены результаты исследований получения новых нитрилсодержащих мономеров путем ацилирования непредельных N- и N,N′ - α – аминоацетонитрилов хлорангидридами (мета) акриловых кислот, акриламидом. Исходные непредельные N- и N,N′ - α – аминоацетонитрилы синтезированы взаимодействием нитрила гликолевой кислоты (гликонитрила) с аминами различного класса. Изучена способность новых мономеров к радикальной (со)полимеризации, а именно возможность получения полиакриламидов на основе N,N′ – нитрилпроизводных (мета) акриламида и винилового эфира (N – ацетонитрил) моноэтоламина (ВЭЭАН) с акриламидом в массе в присутствии радикальных инициаторов и органических растворителях с образованием карбоцепных полимеров. Образование нитрилсодержащих полиакриамидов подтверждено данными элементного анализа, визкозиметрии, ИК – спектроскопии. Вискозиметрические данные [ή] = 0,10 – 0,29 дл/г полимеров свидетельствуют о невысокой реакционной способности синтезированных нитрилакриламидов по сравнению с акриламидом, что связано с стерическим влиянием длины цепи. Синтезированные сополимеры были исследованы в качестве модификаторов мочевино-формальдегидных связующих (МФС), используемых для укрепления неустойчивых горных пород. Образцы, укрепленные растворами МФС без модификатора, показали низкие прочностные показатели для 62 и 77% концентрации соответственно, введение же нитрилсодержащих сополимеров в количестве 1-5% вес. улучшили прочностные характеристики образцов в 1,2-1,8 раза. Хорошие результаты по прочностным показателям для шахтных пород объясняется увеличением гибкости и эластичности цепей

мочевиноформальдегидных связующих новыми функциональными группами, ответственных за адгезию смолы к породе.

Ключевые слова: α – аминоацетонитрилы, нитрил гликолевой кислоты (гликонитрил), виниловый эфир моноэтаноламина, акриламид, полиакриламид, N,N' – нитрилпроизводные акриламида, сополимеры, модификаторы мочевин-формальдегидных связующих.

Information about the authors:

Rakhimberlinova Zh.B. – Candidate of Chemical Sciences, Karaganda State Technical University, e-mail:kargtu_tss@mail.ru, orcid.org/0000-0002-3326-0998

Mustafina G.A. - Candidate of Chemical Sciences, LTD «KAZ-OPTIMUM», e-mail: gmustafina@list.ru, orcid.org/0000-0001-7265-2524

Takibayeva A.T. – Candidate of Chemical Sciences, Karaganda State Technical University, e-mail: altynarai81@mail.ru, orcid.org/0000-0003-0536-0817

Kulakov I.V. – Candidate of Chemical Sciences,Tyumen State University, e-mail:ivanku1@mail.ru, orcid.org/0000-0001-5772-2096.

Iskakov A.R. – Master student, Karaganda State Technical University, e-mail:arnur2397@mail.ru, orcid.org/0000-0003-4303-0894

Nazarova O.G. - Master student, Karaganda State Technical University, e-mail:nazarova_olga_pochta@mail.ru, orcid.org/0000-0003-4166-0905

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