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Д.В. Сокольский атындағы
«Жанармай, катализ және электрохимия институты» АҚ

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Z.M. Muldakhmetov, A.M. Gazaliev, A.Kh. Zhakina*, Ye.P. Vassilets, O.V. Arnt

LLP "Institute of Organic Synthesis and Coal Chemistry of the Republic
of Kazakhstan", Kazakhstan, Karaganda.
E-mail: alzhakina@mail.ru

SYNTHESIS AND STUDY OF THE STRUCTURE OF THE N-DERIVATIVE OF HUMIC ACIDS BASED ON COAL MINING WASTE

Abstract. The article presents the results of a study of directed chemical structural modification of humic acids. Considering the multifunctionality of humic acids, it seemed interesting to study the method of their chemical structural modification with an amine-containing compound. Research in this direction opens the way for the synthesis of new N-derivatives of humic acids with desired properties and expands the boundaries of their further application. Humic acids isolated from the coal waste of the Shubarkol deposit and hexamethylenetetramine were used as raw materials. The synthesis was carried out by the interaction of humic acid with hexamethylenetetramine in an aqueous solution in the presence of a catalyst at various ratios of the initial reagents, temperature and pH. The optimal parameters of the amination reaction have been found. The main factor influencing the yield and degree of addition of the amine is the pH. The highest yield of the product was 76% at pH=5. The reaction was controlled by the added amine and the content of acid groups, using an elemental analyzer and a conductometer. The structure of the N-derivatives of humic acids was confirmed by the data of IR-spectroscopy, elemental and conductometric analysis. Acetic acid was found to be the most active as a catalyst, maintaining the pH of the medium in the range of 5-6. The resulting product can be widely used in industry and agriculture.

Key words: coal waste, humic acids, hexamethylenetetramine, modification, amination.

З.М. Молдахметов, А.М. Ғазалиев, А.Х. Жакина*, Е.П. Василец, О.В. Арнт

«Қазақстан Республикасының органикалық синтез және көмір химиясы Институты» ЖШС, Қазақстан, Қарағанды.
E-mail: alzhakina@mail.ru

КӨМІР ӨНДІРУ ҚАЛДЫҚТАРЫ НЕГІЗІНДЕГІ ГУМИН ҚЫШҚЫЛДАРЫНЫҢ N-ТУЫНДЫСЫНЫҢ СИНТЕЗІ ЖӘНЕ ҚҰРЫЛЫМЫН ЗЕРТТЕУ

Аннотация. Мақалада гумин қышқылдарының бағытталған химиялық құрылымдық модификациясын зерттеу нәтижелері келтірілген. Гумин қышқылдарының көп функционалдылығына байланысты олардың химиялық құрылымдық модификациясының әдісін құрамында амин бар қосылыспен зерттеу қызықты болды. Осы бағыттағы зерттеулер берілген қасиеттері бар жаңа N-туынды гумин қышқылдарын синтездеу жолдарын ашады және оларды одан әрі қолдану шекарасын кеңейтеді. Бастапқы шикізат ретінде Шұбаркөл кен орнының көмір қалдықтарынан бөлінген гумин қышқылдары және гексаметилентетрамин пайдаланылды. Синтез бастапқы реагенттердің, температура мен pH-ның әртүрлі арақатынастарында катализатордың қатысуымен су ерітіндісінде гумин қышқылының гексаметилентетраминмен әрекеттесуі арқылы жүзеге асырылды. Аминдеу реакциясының оңтайлы параметрлері табылды. Аминнің шығуы мен қосылу дәрежесіне әсер ететін негізгі фактор pH болып табылады. Өнімнің ең жоғары шығымы pH=5 кезінде 76% құрады. Реакцияны бақылау элементтік анализатор мен кондуктометрді қолдана отырып, амин қосылған және қышқыл топтарының құрамы бойынша жүргізілді. Гумин қышқылдарының N-туындыларының құрылымы ИҚ-спектроскопия, элементтік және кондуктометриялық талдау деректерімен расталды. Катализатор ретінде қоршаған ортаның pH 5-6 аралығында сақтайтын сірке қышқылы ең белсенді екендігі анықталды. Алынған өнім өнеркәсіпте және ауыл шаруашылығында кеңінен қолданыла алады.

Түйін сөздер: көмір қалдықтары, гумин қышқылдары, гексаметилентетрамин, модификация, аминдеу.

З.М. Мулдахметов, А.М. Газалиев, А.Х. Жакина*, Е.П. Василец, О.В. Арнт

ТОО «Институт органического синтеза и углехимии Республики Казахстан», Казахстан, Караганда.
E-mail: alzhakina@mail.ru

СИНТЕЗ И ИЗУЧЕНИЕ СТРУКТУРЫ N-ПРОИЗВОДНОГО ГУМИНОВЫХ КИСЛОТ НА ОСНОВЕ ОТХОДОВ УГЛЕДОБЫЧИ

Аннотация. В статье представлены результаты исследования направленной химической структурной модификации гуминовых кислот. В связи с многофункциональностью гуминовых кислот представлялось интересным изучить метод их химической структурной модификации с аминосодержащим соединением. Исследования в этом направлении открывают пути синтеза новых N-производных гуминовых кислот с заданными свойствами и расширяют границы дальнейшего их применения. В качестве исходного сырья использованы гуминовые кислоты, выделенные из углеотходов Шубаркольского месторождения, и гексаметилентетрамин. Синтез осуществлен путем взаимодействия гуминовой кислоты с гексаметилентетрамином в водном растворе в присутствии катализатора при различных соотношениях исходных реагентов, температуре и pH. Найдены оптимальные параметры реакции аминирования. Основным фактором, влияющим на выход и степень присоединения амина, является pH. Наиболее высокий выход продукта составил 76% при pH=5. Контроль реакции осуществляли по присоединенному амину и содержанию кислотных групп, с использованием элементного анализатора и кондуктометра. Структура N-производных гуминовых кислот подтверждено данными ИК-спектроскопии, элементного и кондуктометрического анализа. Найдено, что наиболее активна как катализатор уксусная кислота, поддерживающая pH среды в пределах 5-6. Полученный продукт может найти широкое применение в промышленности и в сельском хозяйстве.

Ключевые слова: углеотходы, гуминовые кислоты, гексаметилентетрамин, модификация, аминирование.

Introduction. Currently, coal mining waste should be attributed to promising natural resources that can be used as raw materials for processing into various products (Panishev et al., 2015:8; Zhakina et al., 2015:3; Zhakina et al., 2017). Utilization of carbon waste containing natural compounds makes their value increase one of the most promising approaches to the development of important products based on them (Chugh et al., 2014:14; Feng et al., 2021:9; Kuzmina et al., 2016:5; Li et al., 2019:8). Their use allows not only to solve environmental problems, but also to increase the raw material base of the Republic. In connection with intensive research in the field of carbon chemistry, the chemical modification of humic substances is an urgent direction.

One of the main and most reactive components of humic substances is humic acids (HA). Extraction of humic acids does not present great economic and technological difficulties (Fatima et al., 2021:15; Huculak-Mączka et al., 2018:13; Khalikov et al., 2017:7; Sarlaki et al., 2019:12; Sarlaki et al., 2021:18; Yan et.al., 2021:10). However, the problem of studying the structure and properties of modified humic acids is still very difficult. This is facilitated by the complex structure of humic acids, the variability of composition, the presence of a large number of different functional groups, the tendency to form difficult to separate complexes with various mineral and organic compounds.

It is known that the number of functional groups in the structure of humic acid macromolecules is an important characteristic that determines their reactivity and physicochemical properties. As for the multifunctionality of humic acids, in this regard, it is promising to develop methods for structural modification of humic acids as products of coal mining waste processing and, consequently, affordable and cheap natural substances by introducing new functional fragments into their macromolecules, studying their composition and physio-chemical properties. Research in this direction opens the way for the synthesis of new humic acid derivatives and expands the boundaries of knowledge about their structure, properties and applications.

There are many works devoted to the methods of isolation and modification of humic acids, as well as their application (Dzhusipbekov et al., 2018:5; Fatima et al., 2021:15; Huang et al., 2021:13; Jindo et al., 2020:32; Klučáková et al., 2017:5; Sarlaki et al., 2019:12; Sarlaki et al., 2021:18; Wang et al., 2013:9; Zhao et al., 2022:14). However, the synthesis of amino-containing humic acids and the study of their structure is a little-studied area.

The purpose of this work is the synthesis of N-derivatives of humic acids, the study of their structures and the determination of the possibility of their further application.

Research materials and methods. Humic acids were isolated from samples of oxidized coals of the Shubarkol deposit (Central Kazakhstan) during alkaline impregnation caused by intercalation of sodium hydroxide into it. The method of alkaline impregnation included the following stages: mixing of dried coal with an aqueous solution of alkali with a concentration providing a given ratio of NaOH / substrate; heating (100°C, 2 h) with stirring and holding at room temperature; separation of the liquid phase from the residual coal with further bringing to pH = 1-2 with mineral acid. The precipitate was filtered out, washed to a neutral medium, dried to an air-dry state. The product yield was 75%. Humic acids from oxidized Shubarkol coals have the following average characteristics, %: humidity (W^a) – 12.1, ash content (A^a) – 22.0, carbon (C^g) – 36.3, hydrogen (H^g) – 3.73, nitrogen (N^g) – 0.70, sulfur (S^g) – 1.02, oxygen (O^g) – 58.9, the total content of acid groups ($\Sigma(COOH+OH)$) is 5.0±0.2 mmol-eq/g. Elemental analysis for the content of carbon, hydrogen, nitrogen, sulfur and oxygen are determined on the Elementar Unicube elemental analyzer.

Hexamethylenetetramine (urotropine, Ur) was used as an aminating agent for the study.

The synthesis of the N-derivative of humic acid was carried out by reacting humic acid with hexamethylenetetramine in an aqueous solvent at different ratios of the initial reagents in the presence of a catalyst, temperatures and pH of the medium. The product yield was 76%. The reaction was controlled by the attached amine, which was determined using the Elementar Unicube elemental analyzer, as well as direct and reverse conductometric titration of samples with sulfuric acid, and by the content of acid groups. The structure of the obtained N-derivatives of humic acids is confirmed by the data of IR spectroscopy, elemental and conductometric analysis. It was found that acetic acid, which maintains the pH of the medium within 5-6, is the most active as a catalyst.

The morphology of the surface of the synthesized substance was studied using a MIRA 3 scanning electron microscope (TESCAN). The scanning electron microscope (SEM) is equipped with a system of detectors that register various signals formed as a result of the interaction of an electron beam with the sample surface. The secondary electron detector allows you to obtain images with topographic contrast. And the X-ray energy-dispersive microanalysis system X-Act (Oxford Instruments) allows you to locally determine the elemental composition on the sample surface.

Results. One of the rational methods of using coal industry waste is the extraction of humic substances from their composition. Extraction of humic acids from oxidized coals of the Shubarkol deposit by alkaline extraction with further precipitation with mineral acid does not present great economic and technological difficulties. HA are allocated according to the methodology previously developed by us. The main disadvantage of alkaline activation of coal during the release of humic acids, which hinders its industrial implementation, is the use of significant amounts of activator, which entails large volumes of wastewater during the release of activated material. Therefore, taking into account the applied orientation of alkaline activation to the production of technical products, the process was transferred from reagent quantities to those close to catalytic ones, which made it possible to dramatically enhance the technological and environmental attractiveness of the process. It should be noted that the range of small activator/substrate ratios in terms of the development of the porous structure is practically not studied, although it is important to understand the mechanisms of alkaline activation, to search for conditions of catalytic influence on the processes that cause the pore formation of the surface of the reaction product and to develop approaches to control the characteristics of the porous structure.

Humic acids of coals contain a sufficient number of donor oxygen atoms of alcohol, carboxyl, ketone, phenolic and quinoid groups capable of forming donor-acceptor bonds. The introduction of nitrogen atoms into the composition of humic acids, which are more prone to the formation of donor-acceptor bonds, will increase both the complexing properties of HA and at the same time give them polyampholytic properties.

To obtain N-derivatives of humic acids and replenish our knowledge in the field of the structure, composition and properties of humic acid isolated from oxidized coals of the Shubarkol deposit, we investigated the reaction of humic acid with a nitrogen-containing compound (hexamethylenetetramine). The simplest method of introducing nitrogen into humic acid is the method of direct interaction of humic acid with hexamethylenetetramine. The ongoing reaction will explain the mechanism of interaction of the nitrogen-containing compound with individual structural elements of humic acid and will expand knowledge about its chemical properties.

The results of chemical studies of the reaction of the interaction of humic acid with hexamethylenetetramine are confirmed by IR spectroscopy data. Figure 1 shows the IR spectrum of the synthesized sample and the humic acid used as a raw material. The spectra were taken on an IR Fourier spectrometer FSM-1201 in KBr tablets. The spectrum of the initial humic acid (spectrum line 1, Figure 1) is characterized by the presence of a number of absorption bands corresponding to certain atomic groupings. Condensed aromatic systems are characterized in the spectra by the presence of an absorption band at 1628 cm^{-1} (planar vibrations of the skeleton C=C), as well as absorption bands in the region of 750-900 cm^{-1} (deformation vibrations of OH aromatic groups). Absorption bands of hydrocarbon groupings are observed in the spectra. Thus, the absorption bands at 2924, 2910, 2850 cm^{-1} (valence vibrations C–H) and at 1380-1470 cm^{-1} (deformation vibrations) indicate the content of aliphatic and alicyclic CH_2 and CH_3 groups. The absorption band at 1709 cm^{-1} can be attributed to fluctuations of C=O in carbonyl, carboxyl and other groups. A relatively wide band with a maximum at 1200 cm^{-1} includes the absorption of C–O valence and OH deformation vibrations in carboxyl groups and phenolic hydroxyls. Absorption bands in the regions of 1020, 1081, 1160 cm^{-1} and 1200-1300 cm^{-1} can be caused by C–O valence and OH deformation vibrations in alcohol groupings. The wide absorption band with a maximum at 3400 cm^{-1} is due to the presence of hydroxyl groups bound by hydrogen bonds.

In the IR spectrum of the N-derivative of humic acids (HA-Ur) (spectrum line 2, Figure 1), the absorption bands caused by fluctuations of urotropine molecules are little shifted during the formation of AHA. The methylene groups of urotropine molecules remain virtually unchanged. At the same time, there is a shift in the bands caused by valence fluctuations of C–N bonds from 1048 and 1007 cm^{-1} in the spectrum of free urotropine to 1002 and 924 cm^{-1}, respectively. This may indicate the coordination of urotropine molecules. As a result of the study of the reaction of the interaction of humic acids with a nitrogen-containing compound by IR spectroscopy, it was shown that, basically, the reactions of humic acid proceed along the carbonyl group, and the amount of the attached amino compound to the HA depends on basicity, the presence of substituents in the amine and stereochemical factors.

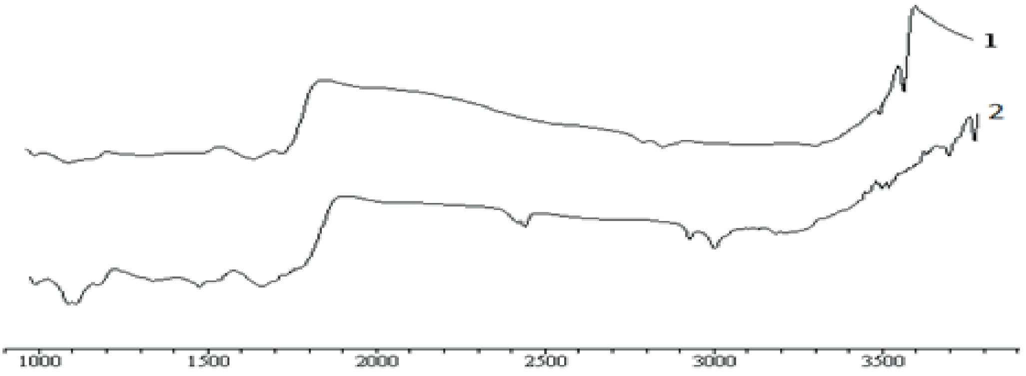


Figure 1. IR-spectrum of humic acid (1), N-derivative of humic acid (2)

Table 1 shows some characteristics of the N-derivative of humic acid in comparison with the initial humic acid. As can be seen from Table 1, with the introduction of an aminating agent into the composition of humic acid, the carbon content increases by 4.4% and nitrogen by 4.93%. The content of hydrogen and sulfur remain within the same limits. Amination of HA is accompanied by a decrease in the content of acidic groups and an increase in nitrogen content. The content of carboxyl groups was carried out using the ANION 4100 conductometer. The content of carboxyl groups in the amino derivative of HA is less than in the HA itself, which is explained by the formation of Schiff bases between the carboxyl groups of HA and the nitrogen atom of the aminating agent.

Table 1 – Characteristics of the synthesized N-derivative of humic acid

Sample of substance	W^a, %	A^a, %	C^g, %	H^g, %	N^g, %	S^g, %	O^g, %	Yeild, %	Σ(COOH+OH) mmol-eq/g
HA	12.1	22.0	36.3	3.73	0.70	1.02	58.3	75.01	5.0±0.2
HA-Ur	7.0	13.2	40.7	4.13	5.63	0.88	48.6	76.50	4.8±0.4

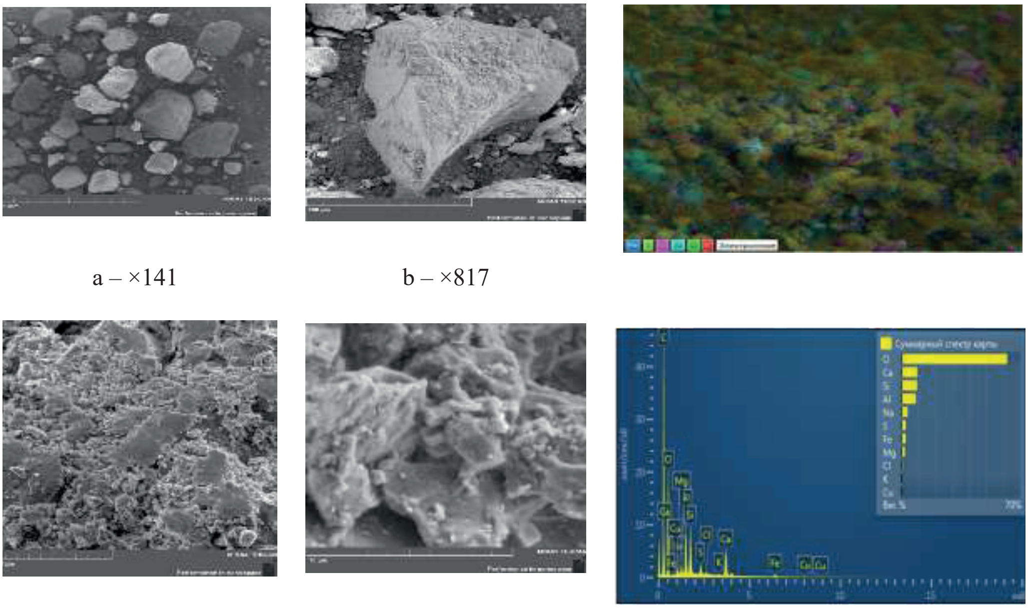
The kinetics of the amination reaction was studied at different amine concentrations and temperature for a certain period of time. The results of the study are shown in Table 2. As can be seen from Table 2, the optimal synthesis temperature is 60°C, since the highest yield of the product is achieved at this temperature. An increase in temperature to 100°C leads to the decomposition of humic acid and, consequently, to a decrease in the amount of attached amine and the yield of the product. The concentration of the aminating agent (urotropine) practically does not affect the sum of acidic groups, it remains unchanged with an error of ±0.3 mmol-eq/g.

Table 2 – Influence of various factors on the process of obtaining an N-derivative of humic acid

Amine	Solution concentration, %	Temperature, °C and synthesis time, min	Yield, %	The total content of acidic groups, mmol-eq/g
Urotropine	1	100°C, 60 min	79.3	4.9±0.2
	2,5		76.1	5.0±0.2
	5		72.2	4.8±0.3
	1	60°C, 60 min	76.6	4.8±0.2
	2,5		76.5	5.0±0.3
	5		80.0	4.7±0.2

The morphology of the surface of the resulting product was studied using a MIRA 3 scanning electron microscope (TESCAN), at an accelerating voltage of 20 kV. X-ray energy dispersion microanalysis was carried out by quartering in various areas of the sample surface. When performing the determination, it was taken into account that the study was conducted on carbon tape and the carbon content was not taken into account. The average value of the conducted studies was taken as the result.

One of the main methods of studying the structure of substances is electron microscopy. The current level of development of this direction allows you to increase objects by several thousand times and consider the particle sizes. The results of the surface morphology study and topographic images of the synthesized N-derivative of humic acid by direct amination are shown in Figure 2.



a – ×141

b – ×817

c – ×5 760

d – ×20 300

Figure 2. Topographic images of the surface, the EDS-map and the total spectrum of the map of the N-derivative of humic acid.

On the micrograph, you can see the loose surface of the sample, on which there are both small and large particles. With an increase of 20300 times, it is possible to examine in detail a separate HA particle – it is irregular in shape, has a rough surface and rather pronounced chips on some faces. The surface of the particle is uneven, the structure consists of various shapes of plates, some of which are connected into aggregates. The elemental composition and the multilayer EDS-map confirm the composition of the product, and the distribution of chemical elements on the microstructure confirms the presence of elements that are part of the HA (carbon, oxygen, also inclusions of aluminum, silicon), and the element that is part of hexamethylenetetramine (carbon, nitrogen).

Discussion. The obtained results on the synthesis of the N-derivative of humic acids can be interpreted based on the general laws of acid catalysis of the nucleophilic addition reaction to the carbonyl group of nitrogen-containing compounds. Under the conditions of acid catalysis, simultaneously with the acid activation of the carbonyl compound, the nucleophilic reagent is protonated, resulting in the formation of a non-reactive NH_3-form of the amino compound, in which the free electron pair is blocked by the attached proton. Therefore, with an increase in the acidity of solutions, the concentration of acid-activated carbonyl compound molecules and the proportion of protonated amine simultaneously increases. This may explain the fact that the interaction of carbonyl compounds with nucleophilic reagents with an increase in the acidity of solutions initially increases (due to acid catalysis), reaches a maximum at some optimal pH value and then decreases (due to prisonization of amine). The optimal pH value is in the region in which the concentration of the protonated form of the carbonyl compound is sufficiently high, and the attacking nucleophile has an unshared pair of electrons capable of attacking the carbonyl group. The conducted studies on the reaction of the interaction of humic acid with amines show that, basically, the reaction of humic acid proceeds by oxo groups, with the formation of Schiff bases.

Conclusion. Thus, a new functionalized N-derivative of humic acids was obtained by direct amination based on the product of processing of hydrocarbon raw materials – humic acid with a nitrogen-containing compound (hexamethylenetetramine). The influence of various factors on the process of its production has been established. The structure, composition, physio-chemical properties of the resulting substance have been proven by modern physio-chemical methods. The resulting functionalized N-derivative of humic acids is a representative of one of the most extensive classes of compounds with a variety of chemical properties, capable of entering into donor-acceptor and ionic interactions, participating in redox processes, which in the future allows them to be used in the creation of cheap and effective sorbents, fertilizers, bases for the production of drugs and other areas of application.

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Information about authors:

Muldakhmetov Zeinulla Muldakhmetovich – Academician of the National Academy of Sciences of the Republic of Kazakhstan, Doctor of Chemical Sciences, director of LLP "Institute of Organic Synthesis and Carbon Chemistry of the Republic of Kazakhstan", e-mail: iosu@mail.ru, ORCID: https://orcid.org/0000-0001-9497-2545;

Gazaliev Arstan Maulenovich – Academician of the National Academy of Sciences of the Republic of Kazakhstan, Doctor of Chemical Sciences, Deputy Director for Research of LLP "Institute of Organic Synthesis and Carbon Chemistry of the Republic of Kazakhstan", e-mail: iosu@mail.ru, ORCID: https://orcid.org/0000-0003-2161-0329;

Zhakina Alma Khasenovna – Candidate of Chemical Sciences, Assoc. Professor, Head of the Laboratory of Polymer Chemistry of LLP "Institute of Organic Synthesis and Carbon Chemistry of the Republic of Kazakhstan", e-mail: alzhakina@mail.ru, ORCID: https://orcid.org/0000-0001-5724-2279;

Vassilets Yevgeniy Petrovich – Master, researcher at the Laboratory of Polymer Chemistry of LLP "Institute of Organic Synthesis and Carbon Chemistry of the Republic of Kazakhstan", e-mail: vassilets88@mail.ru, ORCID: https://orcid.org/0000-0003-2242-486X;

Arnt Oxana Vasilievna – Master, researcher at the Laboratory of Polymer Chemistry of LLP "Institute of Organic Synthesis and Carbon Chemistry of the Republic of Kazakhstan", e-mail: oxana230590@mail.ru, ORCID: https://orcid.org/0000-0002-8996-4572.

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