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FORMATION OF LOW FREEZING TEMPERATURE OILS ON THE BASIS OF ETYLEN AND HEXEN-1

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The article examines the methods of preparation of low-freezing oils. Due to their high viscosity-temperature properties, ethylene-hexane oils are used in industrial compressors, vacuum, etc. can be used as oils. sooligomerization of ethylene with 1-hexane in the presence of a catalytic system in an intermittent apparatus (Al + IPX + C_2H_4*) was studied. This catalyst accelerates the process of sooligomerization of ethylene with 1-hexane and an oil-type oligomer is obtained. The effect of various parameters (temperature, reaction time, amount of IPX (isopropyl chloride) in the reaction zone and ethylene in the liquid phase) on the process and the characteristics of the fat fraction was studied, optimal conditions for the synthesis of a good oil base were determined. When studying the effect of temperature on the process of so oligomerization of ethylene with 1-hexane in the range of 80-150*^{0}*C, it was found that the induction period for the formation of the active catalytic complex decreases sharply: from 120 minutes to 3 minutes. However, there is an increase in the total yield of oligomeric products and their fat fractions. It was determined that the optimal temperature for the production of oils with viscosity-temperature properties is 100-120*^{0}*C. Above this temperature, the properties and quality of the oil deteriorate. At temperatures of 80*^{0}*C and below, sooligomerization reactions proceed very slowly. As the content of IPX increases, the formation time of the catalytic complex decreases sharply, the reaction rate and the total output of the salinometer increase, the yield per 1 g of IPX decreases per minute. However, more than 10 g / l in the reaction zone of IPX has a negative effect on the properties of fat fractions. Thus, rational conditions for the application of oils have been identified. It has been determined that the oils obtained can be used as medicinal and perfumed oils.*

Keywords: *ethylene and hexene-1, lubricants, traditional methods, viscosity index, oils with a low freezing point, oil fractions.*

INTRODUCTION

Along with the scientific and technological development observed in heavy industry, the demand for the quality of lubricants is growing, mineral oils do not meet these requirements, and for this reason the world produces high quality synthetic oils with low viscosity and low temperature. Polyolefin oils (POY) are a major component of motor oils. This is supported by the hypothesis about the role of rheological features of POY. The rheological properties of this POY are found in the high velocity gradients of long-chain isoparaffin molecules, or the compounds of these POY molecules located in adjacent lubricating layers are directed along the displacement vector at high speed sliding conditions. In this case, the layers become stronger due to the increase in the interactions between the particles of the dispersion medium, and the hydrodynamic friction region between the surfaces of the triboses increases.

Ethylene-hexane oils have high viscosity-temperature properties, can be used in industry, compressor, vacuum, etc. In addition, ethylene-hexane oils do not have an aromatic mixture, they are colorless, so they can be used as white oil in medicine and perfume industry. Copoligomerization with ethylene-hexene is carried out in a hexene environment without any inert solvent, as subsequent separation leads to additional energy costs and difficulties. Studies show that in many cases ethylene hexene oils significantly exceed the demand for these oils in a number of ways.

It should be noted that the raw material for this process (ethylene-hexene) is obtained as a result of pyrolysis of the gasoline fraction at the EP-300 plant in Sumgayit Industrial Complex: with ethylene-pyrolysis gases and hexene-liquid pyrolysis products.

EXPERIMENTAL PART

Already during World War II, scientists from leading countries were engaged in the production of synthetic lubricants based on low molecular weight olefins. In his research, Butlerov first noted the possibility of obtaining oil-like products based on low molecular weight olefins. Propylene has been shown to polymerize at room temperature when exposed to triflour boron (BF_3) to form oil-like products. The effect of BF_3 on ethylene polymerization was later studied by other researchers. However, they did not achieve the desired result. In this area, with the participation of the BF_3 catalyst, Japanese scientists have conducted a lot of research and obtained synthetic lubricants as a result of propylene oligomerization. However, most BF_3-based catalysts are not widely used in industry due to toxicity, corrosion, and easy decomposition in humid conditions.

Titanium 4-chloride ($AlCl_3$) was then used for these processes. Advantages: easy to buy, relatively inexpensive and very active in the polymerization process. In the presence of $AlCl_3$, oligomeric products based on α-olefins, which are widely used in various fields, can be obtained, such as lubricants, hydraulic fluids and heat carriers with different properties, etc.

It is possible to obtain oils of different grades and quality from oil using traditional methods such as deasphalting, selective solvent extraction, paraffinization and hydrogenation. However, the viscosity index of these oils is 85-95, depending on the quality of the oil. In contrast to these processes, only the hydrocracking of fat fractions allows the production of oils with a viscosity index greater than 100. At the same time, the production of oils with a viscosity index of more than 100 occurs due to changes in the composition of fat fractions. Hydrocracking occurs during the production of oils with a high viscosity index in the presence of special catalysts at high temperatures and high pressures. This requires special equipment that can work in these conditions. They are also mixed to obtain oils with a viscosity index of 95-100% [1].

It is known from the literature that the use of synthetic oil components is more efficient and affordable, as such oils can increase their performance in extreme conditions. Taking this into account, F.Samadova together with her colleagues developed and proposed a technology that allows the unconventional production of such oils. At the same time, the components of the fat fraction are synthesized by olefins, oligomerization, cyclization of olefins and others. As a result, newly formed hydrocarbons are formed, which produce semi-synthetic oils with a viscosity index of more than 100, mixed with hydrocarbons that do not participate in the reaction of fat fractions. A comparison of the chemical composition of crude and semi-synthetic oils shows that the amount of paraffin fatty hydrocarbons in the process product is 17.4% less and the amount of resinous compounds does not change, which means that they are not involved in the synthesis.

Mass spectrometric studies of refined and synthesized oils show that they differ in structure and molecular weight from the hydrocarbons they contain. In addition, the fat raw material contains significant isoperafin and monocyclic naphthenic hydrocarbons. Thus, the catalytic conversion of fat fractions in the presence of olefins provides oils with high index, low freezing point. This method can be considered one of the most convenient and advanced methods for the synthesis of oils with high viscosity index. Because the proposed method is environmentally friendly and simple, the synthesis and use of highly efficient catalysts in it can provide high quality oils that can be exported to the world market.

It should be noted that recently a mixture of oil and synthetic oils is widely used in the world's leading countries. There are several reasons for this. First, azo-oil bases work in difficult conditions in engines, as a rule, have high volatility and sufficient thermal oxidation stability. For this reason, semi-synthetic oils have found their use. It is mainly a mixture of low-viscosity complex essential oils and medium-viscosity petroleum distillates [3].

Evaporation here and therefore the consumption of such oils is less than that of pure oil bases, they have better washing properties and less coal and varnish are formed in the engines. It has been found that these oils can also be used as additives (ie synthetic oils) used in petroleum oils. Derivatives of hydrocarbons containing phosphoric acid, flour and chlorine, polyphenyl esters, polyolefins were used as components of semi-synthetic oils, but their properties were superior to esters of dicarboxylic acids and polyols.

Synthetic oils have only two disadvantages: some oils cause swelling of the elastomers used as binders, and they are not fully compatible with thickeners and other additives used for petroleum oils. Synthetic oils are 2-3 times more expensive than petroleum oils, but synthetic oils last longer in engine-powered engines, consume relatively little, and are economically viable because they can reduce fuel consumption by 4-5%. The production of synthetic oils is increasing in foreign countries.

With the destruction of ethylene-propylene soligomer, the production of hydrocarbons of a certain structure is of great interest. This is due to the fact that the process of colligerization of ethylene with propylene is very well studied, easily regulated, and in practice it is possible to obtain a coligomer with a certain composition. It should be noted that such hydrocarbon chains have never been in oil and cannot be obtained by direct synthesis. When the thermal destruction process is carried out in a vacuum, double processes are prevented and the yield of the target product is increased.

To obtain engine oil, cracked products are first waxed with urea and then hydrogenated. The obtained oil consists mainly of isoparaffin hydrocarbons and has the following properties.

Table 1

Properties of the obtained oil

Kinematic viscosity at 100 ° C in mm2 / sec	6
At dynamic viscosity -40̊, Pa.s.	1,2
Freezing temperature℃	-52

Essential oils are obtained by the interaction of two basic carboxylic acids (sebasin, azelain, adipine, etc.) and long-chain alcohols (eg, 2-ethylhexyl alcohol):

adenic acid esters are superior to various radical alcohols in terms of viscosity and temperature. Synthetic SAE 5W20 oil obtained from dibasic acid esters with the addition of appropriate additives has the following properties [2].

Table 2

Main indicators of 5W20 oil

Kinematic viscosity at 100 ° C in mm2 / sec	6,5
At dynamic viscosity -40°, Pa.s.	7,6
Freezing temperature ℃	-65
Wear temperature ℃	224

An engine and transmission oil for the synthesis of diacylbenzene-based hydrocarbon oils, as well as a method that can be used as a hydraulic fluid in cold climates, have also been developed. Currently, the oligomerization products of C_2-C_6 olefins (propylene dimers, tri and tetramers, butylene amylene and hexene dimers) are high-tonnage petrochemical products and have a wide range of applications: as alkylating agents, as raw materials for detection, as raw materials for obtaining polymerization regulators, high-performance additives to motor fuels, and so on. These oligomers are often commercially produced by polymerizing C_2-C_6 olefins. Polymerization is carried out in the presence of a catalyst. Phosphoric acid (or liquid) precipitated on supports is used as a catalyst. Therefore, the world's leading countries are looking for new catalytic systems for the oligomerization of olefins.

1. The molecular weight of the reaction product is determined cryoscopically.
2. The refractive index is determined by a refractometer.
3. Separation of the light fraction is carried out in a vacuum device.
4. The iodine number of products is determined by the Marochess method
5. Hydrogenation of the oil fraction is carried out on a catalyst.
6. The viscosity and viscosity index of oils are determined according to DUIST 33-66.
7. The freezing point of oils is determined according to DUIST 20287-74.
8. The ignition temperature of oils is determined according to DUIST 433-78 in an open type device.
9. The density of the products is determined by means of a pycnometer.

Oligomerization of olefins can be carried out in both gas and liquid phases. The catalyst systems used for oligomerization can be either homogeneous or heterogeneous. Catalyst systems used as catalysts include:

1. Compounds of variable valent metals (Ni, Co, Fe, Pt, Mo, Cr, W, Tr), rare-earth elements,
2. alkali metals or their hydrates in various carriers;
3. metal oxides;
4. In the presence of BF_3, $TiCl_4$ acids or various hydrocarbons and chlorine-based solvents.

The oligomerization of olefins was first studied by dimerization of propylene. The presence of organometallic complex catalysts based on dimerized nickel compounds has been identified. These catalysts can also be obtained on the basis of combinations of cobalt, titanium, vanadium, tungsten and individual hexenes of various structures. Later, they developed catalytic systems for the dimerization of propylene to produce linear hexenes. 2-methylpentene, hexene, 2,3-dimethylbutene are formed as a result of propylene dimerization under the influence of nickel oxide precipitated in aluminosilicate in the liquid phase. This process produces small amounts of propylene trimmer, 2,4-dimethylheptene and 4-methylloctene. Of practical interest is the dimerization of propylene at the Olefins Institute, which is carried out at the pilot-industrial level with the participation of alkali metals. This process was carried out in two variants: in both liquid and gas phases [2].

The reaction is carried out at a temperature of 140-170°C and a pressure of 12.0-18.0 MPa. The cooligomerization of various olefins in the presence of metal oxides as a catalyst is of great interest. Because in this way you can get polymers with the desired properties. This allows you to change the properties of the polymers obtained by this method (while maintaining the same properties) in the desired direction. For example, the co-oligomerization of ethylene with high levels of α-olefin (1-butene, 1-hexene, etc.) results in products with a number of valuable qualities. The most important feature in practice is the very high delivery resistance of these oligomers. Suoligomerization of ethylene with 1-butene was carried out at the Olefins Institute with the participation of a chromium oxide catalyst. The use of a chromium-nickel catalyst is even more important here. The process of co-oligomerization of ethylene with 1-hexane in this catalyst was carried out and studied.

With the destruction of ethylene-propylene soligomer, the production of hydrocarbons of a certain structure is of great interest. This is due to the fact that the process of colligerization of ethylene with propylene is very well studied, easily regulated, and in practice it is possible to obtain a coligomer with a certain composition. By breaking down such soligomers, unique hydrocarbon chains with a specific composition and structure can be obtained. It should be noted that such hydrocarbon chains have never been in oil and cannot be obtained by direct synthesis. When the thermal destruction process is carried out in a vacuum, double processes are prevented and the yield of the target product is increased. In addition, the production of synthetic oils based on C_2-C_4 α-olefins has been reported. The difficulty in using petroleum oils here is that their consistency changes dramatically with temperature.

In the Arctic climate, ordinary oil freezes and rots at high temperatures. However, both synthetic lubricants and viscous lubricants can be obtained by cracking small olefins into high molecular weight polymers. It should be noted that viscosity α-olefin detectors are often used today. For example, you can get detergents based on polyethylene polyamines and their interactions, ie succinimide. For this purpose, low molecular weight olefins are used as raw materials. In general, low molecular weight olefins have been found to have different properties. For example, a genesis based on ethylene-propylene elastomer is obtained. Diesel fuel is mainly detected by unsaturated monomers of acrylic or methacrylic acid. The definition of viscosity and depressant is also based on unsaturated carbohydrates. Polymers consist of 45-55% olefins or unsaturated carboxylic acid esters. To date, a number of effective methods for the production of fat components and detectors based on low molecular weight olefins have been scientifically and technologically studied and directed synthesis methods have been developed [5].

It is known that the highest quality synthetic oils are currently used in various fields. The interest in obtaining synthetic oils, especially those with low freezing temperatures, stems from their quality. In this case, the extraction of these oils is carried out by oligomerization of ethylene in a certain ratio with hexane in the presence of a catalyst. Parameters affecting the oligomerization reaction were studied. High-purity ethylene and 1-hexene are used as raw materials in the process. The catalyst used was a product of metallic aluminum reacting with isopropyl chloride and ethylene. Metal-aluminum discs are used in the form of chips, tablets and powder. Isopropyl chloride is used in pure form. The hexane-hexen fraction is brought from Sumgayit in special cylinders in different proportions. In addition, a 3% alkaline solution is used to separate the co-oligomerization product, and calcium chloride is used for drying.

Co-oligomerization of ethylene with 1-hexane was carried out in a 2-liter autoclave with intermittent operation. The lidless autoclave is made of 1X18H9T stainless steel and includes inlet and outlet for the mixer, pressure gauge, temperature pocket, liquid and gas products.

Prior to the experiment, the disc-shaped metal is glued to the aluminum autoclave mixer and the autoclave is carefully cleaned with ethylene to remove traces of moisture, air and oxygen. Cleaning is carried out until the dew points at the inlet and outlet of the conductors are equal. Using an electric oven, the autoclave is heated to 180-2000°C and ethylene is released inside for 60-90 minutes. After cleaning, the sonar is cooled to room temperature with a stream of ethylene. Exhaust ethylene is stored in a certain container. First, the required amount of aluminum metal is fed to the autoclave (1) mixer (2). The aluminum used for the experiment is imported from the Sumgayit aluminum plant in the form of 98.5% purity (or powder). Then, while the mixer is running, ethylene, solvent, chlorine compounds and 15 MPa dispensers are autoclaved from a thermostated cylinder in a water bath. It is stored in an autoclave at the required temperature using an electric oven. Once the temperature in the autoclave has stabilized, the required pressure is created with the help of ethylene and a certain amount of 1-hexane is fed in the autoclave. The onset of the reaction is determined by the decrease in pressure in the autoclave at a constant temperature. The heat generated during the reaction is removed from the walls of the autoclave using a water bath [4].

The process is stopped by adding 3% alkaline solution to the oligomerization reactor. After the reactor has cooled to room temperature, the pressure is released with a holder cooled to 100°C and the reactor is opened. Suoligomerization of ethylene with 1-hexane is also carried out in a continuous apparatus. First, the required amount of sawdust or metal-aluminum powder is placed in an autoclave (4), then autoclaved and sealed with ethylene at 150-200°C for 1-2 hours. The autoclave is heated by an electric oven. The mixture is then transferred from a 1-liter container to an autoclave with a dosing pump at a temperature of 1 point. The mixture of 1-hexene and alkyl chloride is automatically fed in an autoclave, ie according to the pressure regulator. The reaction mixture is collected in a 5 N vessel, emptied, washed with distilled water according to the neutral medium, dried in alugomel or molecular sieves, then lightly boiled and the oil is hydrogenated.

Preliminary studies have shown that the product obtained by coligolating 1-hexene in a catalytic system containing ethylene metal aluminum, isopropyl chloride and ethylene has oil properties, ie the co-oligomer fraction has a low freezing point of 350°C (350-600°C) (-30 -450°C). It also has a high flash point (210-220°C) with a high viscosity index and a viscosity of 12-16.7 mm2 / s.

The effect of various parameters (temperature, ethylene content in the liquid phase, isopropyl chloride content in the reaction zone and contact time) on the process and properties of the obtained products was studied in the process of co-oligomerization of ethylene with 1-hexane in an intermitter and on the properties of the products.

It was found that as the amount of ethylene in the liquid phase increased, the productivity of the fat fraction in the co-oligomeric product (boiling point above 3500 ° C) increased and then decreased. In this case, the amount of butylene in the gas phase increases. In our opinion, the fact that the amount of ethylene in the liquid phase is more than 85% mol leads to deeper side reactions.

The effect of time on the taxonomization process of ethylene with 1-hexane was studied between 15 and 240 minutes. It was found that the time dependence of the reaction also affected the properties of the fat fractions. An increase in the reaction time leads to an increase in the total product and the molecular weight of the co-oligomer product also increases, but the viscosity-temperature properties of the fat fraction decrease.

In our opinion, as the duration of the co-oligomerization reaction increases, the high olefins formed in the process under the influence of the catalyst lead to the formation of co-oligomer chains with higher molecular weights. Poor viscosity and temperature properties of oils occur as a result of external reactions (cyclic and isomerization).

When studying the effect of ethylene on the process of co-oligomerization with 1-hexane at a temperature in the range of 80-150°C, it was found that the induction period for the formation of the active catalytic complex is sharply reduced: from 120 minutes to 3 minutes. However, the total productivity of oligomeric products and their fat fractions increases. The kinematic curves of the taxation rate of ethylene with 1-hexane, which characterizes the change in the activity of the catalytic complex, can be conventionally divided into 3 cycles. Initial period: here the degree of co-oligomerization reaches a maximum. Second period: the speed remains constant. Third stage: here the speed of the co-oligomerization reaction is minimized. In addition, the figure shows that at a relatively low temperature (100°C) the kinematic curve of the taxomerization rate is very stable, which is not observed at high temperatures (150-200°C) [6].

The velocity curve of high-temperature taxonomy decreases immediately when it reaches its maximum and approaches the abscissa axis. This is due to the increase in the acquisition and deactivation of active centers. In the initial period, the increase in the reaction rate is associated with an increase in the concentration of active centers. After a while, the rate of deactivation of active centers coincides with the rate of their formation. During this period, the number of newly created and liquidated deactivation centers is the same, ie the process is stationary. After a while, the rate of formation of new active centers is less than the rate of deactivation of the centers, which means a decrease in the overall reaction rate. Temperature changes during co-oligomerization also affect the properties of fat fractions.

It has been determined that different degrees of fats can be obtained by coliglating ethylene with 1-hexane. They can be used as industrial, compressor and vacuum oils. In addition, it can be used to produce azo bases and white oils for all seasonal transport oils. Various parameters affecting the properties of oils obtained in the process of joint oligomerization were studied: temperature, contact time, concentration of isopropyl chloride and the ratio of ethylene to 1-hexene, the effect of heat on the process of co-oligomerization. The effect of temperature was studied in the range of 90-180°C. It was found that increasing the temperature of the co-oligomerization process increased the reaction rate (ie, the absorption of ethylene), but decreased the productivity of the fat fraction.

Since the catalytic complex is obtained by the interaction of metallic aluminum isopropyl chloride and ethylene in the final reaction zone, the amount of isopropyl chloride applied to the reaction zone has a significant effect on both the colligolization process and the properties of the resulting oils. Studies were performed with isopropyl chloride 1-hexene in the range of 0.3-5%. It was found that with increasing the amount of isopropyl chloride applied to the reaction zone in 1 hexane, the productivity of the fat fractions of the co-oligomerized product increased rapidly, and the increase in the amount of isopropyl chloride in 1 hexane up to 2% did not affect the properties of the obtained oils. However, when the IPX content is more than 2% per 1 hexane, it affects the properties of the resulting oils and weakens the properties of the oils. This is due to the parallel reactions that lead to the diversification of co-oligomerization chains.

The effect of contact time on the process of co-oligomerization. The contact time (ie the time the product remains in the autoclave) is determined by the dosing pump between 10 and 45 minutes. It has been studied that the productivity of the fat fractions of the total product and the soligomer product increases with the increasing contact time. However, over time, the viscosity of the resulting fats deteriorates, which is associated with parallel reactions (isomerization and cyclization). Chromatographic analysis of the obtained co-oligomers shows the presence of isopropyl chloride in the reaction products, ie part of the isopropyl chloride applied to the reaction zone is not used. Based on this, we can say that the increase in the contact time leads to an increase in the amount of catalyst, provided that the amount of isopropyl chloride applied to the reaction zone is the same, ie most of the isopropyl chloride is converted into a catalytic complex.

RESULTS AND DISCUSSION

Co-oligomerization of ethylene with 1-hexane in the presence of a catalytic system in an intermittent apparatus (Al + İPX + C_2H_4) was studied. In this catalyst, the co-oligomerization of ethylene with 1-hexane is rapid and an oil-type oligomer is obtained.

The effect of various parameters (temperature, reaction time, amount of IPX in the reaction zone and the amount of ethylene in the liquid phase) on the process and the characteristics of the fat fraction was studied, optimal conditions for the synthesis of a good oil base were determined.

Oils obtained by co-oligomerization of ethylene with hexene on the studied catalysts can be used as bases for synthetic oils. The process of taxation of ethylene on a catalyst with 1-hexane was studied in a continuous device. The catalyst was obtained by the reaction of metallic aluminum with isopropyl chloride and ethylene in the reaction zone.

The reactivity ratios, monomer bulk concentration ratio, and homopolymerization kinetic constants ratio all impact the co-polymerization equation derived from this complexation model (KX). This is in contrast to the traditional copolymerization equation, which is only based on reactivity ratios and monomer concentration ratios and is obtained by a first order Markov mechanism.

An experimental setup for ethylene homo- and copolymerizations at high temperatures has been presented. At isothermal and isobaric conditions with highly active and fast deactivating catalysts in solution homo- and co-polymerizations of ethylene with 1-octene, polymerization rate profiles could be calculated only a few seconds after catalyst injection. For both homo and co-polymerization, the experimental findings are reliable and repeatable. Although the obtained polymerization rates are exceptionally high, mass transfer limitations cannot be ruled out. The behavior of co-polymerizations was found to be lower. For defining the reaction rate, a 2nd order deactivation model was suggested, which only includes two parameters, a lumped deactivation model. With the optimized kinetic constants, the obtained copolymerization equation will explain the integrated co-monomer weight fractions. With almost identical kinetic constants, this model also explains ethylene homo-polymerizations. The optimized kinetic constants tend to be a good match for the experimental results.

The influence of various factors on the process (temperature, reaction time, amount of IPX in the reaction zone, contact time and comonomer ratio) was studied, optimal conditions for obtaining oils of different viscosities were determined. Rational conditions for the use of these oils have been established. The resulting oils have been shown to be used as medicinal and aromatic oils. The resulting white oils meet the requirements of WHO due to their properties and sometimes even exceed them.

CONCLUSION

In conclusion, In this case, the layers become stronger due to the increase in the interactions between the particles of the dispersion medium, and the hydrodynamic friction region between the surfaces of the triboses increases.

Preliminary studies have shown that the product obtained by coligolating 1-hexene in a catalytic system containing ethylene metal aluminum, isopropyl chloride and ethylene has oil properties, ie the co-oligomer fraction has a low freezing point of 350°C (350-600°C) (-30 -450°C). It also has a high flash point (210-220°C) with a high viscosity index and a viscosity of 12-16.7 mm2 / s

The effect of various parameters (temperature, reaction time, amount of IPX (isopropyl chloride) in the reaction zone and ethylene in the liquid phase) on the process and the characteristics of the fat fraction was studied, optimal conditions for the synthesis of a good oil base were determined. When studying the effect of temperature on the process of so oligomerization of ethylene with 1-hexane in the range of 80-150^{0}C, it was found that the induction period for the formation of the active catalytic complex decreases sharply: from 120 minutes to 3 minutes. However, there is an increase in the total yield of oligomeric products and their fat fractions. It was determined that the optimal temperature for the production of oils with viscosity-temperature properties is 100-120^{0}C. Above this temperature, the properties and quality of the oil deteriorate. At temperatures of 80^{0}C and below, so oligomerization reactions proceed very slowly

REFERENCES

1. Andreva L.N, Chiro L.V, Unger F.D. Depressive suppressions and mechanisms of action Izv. Universities. Oil and Gas. 2006, №1, pp. 102-108
2. Ilyasov K.L, Tsvetkov O.N, Kestaksovskaya Y.V, Shkolnikov T.V, Shkolnikova V.M. New transmissible semi-synthetic oil World of Petroleum Products. 2005, №1, pp.10-11

3. Samadova F.I, Theoretical bases of oil production processes, Baku, Science. 1992, 180 p
4. Samedova F.I, Hasanova R.Z. Azerbaijan Oil Economy. 1991, № 3, pp.17-21
5. Samedova F.I, Hasanova R.Z. Chemistry and technology of fuel and oil. 1991, № 10, pp.12-14
6. Zakidullin R.N, Kurgaeva S.N, Idrisova V.A, Multi-base amines of Bagkirsky. Chemistry Libre Texts. 2006, № 3, pp.73-77

ПОЛУЧЕНИЕ МАСЕЛ С НИЗКОЙ ТЕМПЕРАТУРОЙ ЗАМЕРЗАНИЯ И ГЕКСЕНА-1

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В статье рассмотрены способы приготовления масел с низкой температурой замерзания. Этилен-гексеновые масла широко применяются в промышленности в качестве компрессорных , вакуумных и др масел, так как обладают высокими вязкостно-температурными свойствами. Изучалась соолигомеризация этилена с гексеном-1 в присутствии каталитической системы в аппарате периодического действия (Al+ИПХ+C_2H_4*). Этот катализатор ускоряет процесс соолигомеризации этилена с гексеном-1 и получается олигомер жирново типа. Изучено влияние различных параметров (температуры, времени реакции, количества ИПХ (изопропилхлорида) в зоне реакции и количество этилена в жидкой фазе) на процесс и фракционные свойства масел, определены оптимальные условия синтеза хорошей масляной базы. При изучении влияния температуры на процесс соолигомеризации этилена с гексеном-1 в интервале 80-150°*C *установлено ,что индукционный период образования активного каталитического комплекса сокращается с резкой скоростью: от 120 до 3 минут. Но, несмотря на это, наблюдается общий выход олигомерных продуктов и увеличение жирных фракций в их составе. Установлено, что оптимальная температура для получения масел, обладающих вязкостно-температурными свойствами, составляет 100-1200°*C*. Выше этой температуры свойства и качество масел ослабевают. При температуре 800°*C *и ниже реакции соолигомеризации протекают с очень небольшой скоростью. По мере увеличения содержания ИПХ, время образования каталитического комплекса резко уменьшается, скорость реакции и общий выход со-олигомера увеличиваются,,только выход ИПХ при расчете на 1 г в минуту уменьшается.Увеличение количества ИПХ в зоне реакции до 10 г/л практически не влияет на свойства фракций масел.Но при содержании в зоне реакции ИПХ более 10 г/л отрицательно сказывается на свойствах фракций масел. Таким образом, были определены рациональные условия применения масел.Установлено, что полученные масла могут применяться в качестве медицинских и парфюмерных масел.Полученные белые масла по своим свойствам удовлетворяют требованиям ГОСТ, а иногда и превосходят его.*

Ключевые слова: *этилен и гексен-1, смазочные материалы, традиционные методы, индекс вязкости, масла с низкой температурой замерзания, масляные фракции.*

ETELEN VƏ HEKSEN-1 ƏSASINDA AŞAĞI DONMA TEMPERATURLU YAĞLARIN ALINMASI

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Məqalədə aşağı donma temperaturlu yağların hazırlanması üsulları araşdırılmışdır. Etilen-heksen yağları yüksək özlülük-temperatur xüsusiyyətlərinə malik olduqları üçün , sənayedə kompressor, vakuum və s. yağlar kimi istifadə edilə bilər. Fasiləli işləyən aparatda (Al + IPX + C_2H_4*) bir katalitik sistem iştirakı ilə etilenin 1-heksenlə sooligomerizasiyası öyrənilmişdir. Bu katalizator etilenin 1-heksenlə ko-oliqomerləşməsi prosesini sürətləndirir və yağ tipli bir oliqomer alınır. Müxtəlif parametrlərin (temperatur, reaksiya müddəti, reaksiya zonasındakı IPX(izopropil xlorid) miqdarı və maye fazada etilenum miqdarı) prosesə və yağ fraksiya xüsusiyyətlərinə təsiri öyrənilmiş, yaxşı yağ bazasının sintezi üçün optimal şərtlər müəyyən edilmişdir. Etilenin 1-heksenlə sooliqomerləşmə prosesinə temperaturun 80-150*^{0}*C intervalında təsiri öyrənildiyi zaman müəyyən edilmişdir ki, aktiv katalitik kompleksin əmələ gəlməsinin induksiya dövrü kəskin sürətdə azalır: 120 dəqiqədən 3 dəqiqəyə qədər. Amma ona baxmayaraq oliqomer məhsullarının ümumi çıxımı və onların tərkibində yağ fraksiyaların artması müşahidə edilir. Müəyyən olunmuşdur ki, özlülük-temperatur xassələrinə malik olan yağların alınması üçün optimal temperatur 100-120*^{0}*C-dir. Bu temperaturdan yuxarı yağın xassələri və keyfiyyəti zəifləşir. 80*^{0}*C temperaturda və ondan aşağı temperaturlarda sooliqomerləşmə reaksiyaları çox az sürətlə gedir. İPX-nin tərkibi artdıqca katalitik kompleksin əmələ gəlmə müddəti kəskin sürətdə azalır, reaksiyanın sürəti və sooliqomerin ümumi çıxımı artır,yalniz dəqiqədə 1q İPX-ə görə çıxım azalır.Reaksiya zonasında İPX-nin miqdarının 10q/l qədər artması praktiki olaraq yağ fraksiyalarının xassələrinə təsir göstərmir.Lakin İPX-in reaksiya zonasında 10 q/l-dən çox olduqda yağ fraksiyalarının xassələrinə mənfi təsir göstərir. Beləliklə yağların tətbiqi üçün rasional şəraitlər müəyyən edilmişdir.Müəyyən edilmişdir ki, alınan yağlar tibbi və parfümer yağlar kimi tətbiq oluna bilərlər.Alınan ağ yağlar öz xassələrinə görə QOST-un tələbatlarını ödəyir və bəzən üstün olurlar.*

Açar sözlər: *Etilen və heksen-1, sürtkü yağları, ənənəvi metodlar, özlülük indeksi, aşağı donma temperaturlu yağlar, yağ fraksiyaları.*

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CHANGE DYNAMICS OF KINEMATIC VISCOSITY AND DENSITY OF TRANSMISSION OILS IN KAMAZ VEHICLES UNDER OPERATION CONDITION

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The article presents a comparative study of the dynamics of changes in the density and kinematic viscosity of TCn-15K of regenerated transmission oil in the transmission units of KAMAZ vehicles under operation condition in commodity and production. The results of the research show that the dynamics of changes in the density of transmission oil during operation is characterized by an increase in density from 0 km to 21000 km as a result of the accumulation of edible products and insoluble impurities in the oil. The dynamics of change of kinematic viscosity is characterized during the initial operation period. The decrease in viscosity begins at 6,000 km, and the increase in viscosity begins at 45,000 km.

Keywords: *transmission oil, transmission units, a KAMAZ car, density, kinematic viscosity.*

INTRODUCTION

When transmission oils are used in transmission units, they must be replaced with new ones when the maximum value is reached. The longevity of transmission details depends on the timely change of oils. Delayed replacement of oil after loss of its properties leads to a decrease in “coefficient of performance” and high erosion of components of transmission mechanisms. To do this, it is necessary to know the dynamics of changes in the basic physicochemical and operational parameters of transmission oils. One of the important properties influencing the quality of oils is density and kinematic viscosity [4-8].

The quality of transmission oils is controlled by various methods performed on simple laboratory devices and the most advanced equipment. Today, all test methods for transmission oils are divided into two groups: physicochemical and operational. Physicochemical characteristics determine the physical and chemical condition of oils, and the ability of oils to control the reliable operation of mechanisms under continuously changing complex conditions refers to their operational properties. Determination of kinematic viscosity, which is one of the most important performance properties of oil quality, is traditionally related to physicochemical methods [1].

The kinematic viscosity of transmission oils characterizes the energy losses in the operating transmission unit, determines the bearing capacity of the oil wedge under sliding friction conditions. Viscosity has a significant effect on the cost of power loss. It has been found [9-10] that energy losses in automotive transmission units can reach up to 80% of the power generated by the engine. In this regard, the study of the dynamics of changes in the kinematic viscosity of transmission oils which are used in the transmission units of cars in real operating conditions is an important issue for the economy of different companies [2] .

EXPERIMENTAL PART

In order to determine the change in the kinematic viscosity of medium-span ТСп-15К transmission oils, studies are being conducted in the real operation of KAMAZ vehicles.

The transmission oils were tested in accordance with the developed operational research program. A sample of the transmission oil was taken from the transmission units, namely from the middle bridges of KAMAZ cars, for analysis, using the transmission oil at certain times and intervals, and then the same amount of fresh oil was added.

Preparation and sampling of test transmission oil should be carried out directly at the workplace. Samples are taken at the end of the work shift, when the oil temperature is in the range of 40–60ºC. Transmission oils have a minimum kinematic viscosity at the time of sampling at high temperatures. This situation allows us to claim that all the rain is in a mixed state of density and proportion. Sampling should be used for bridge crankcase holes where filter plugs are located.

All samples were analyzed according to the available indicators and the results were averaged [3].

Determination of kinematic viscosity is carried out at a temperature of 100ºC in viscometers type “ВПЖ-2” and “ВПЖ-4” with internal circular and cutter 0.99 and 1.47, respectively “DUIST” 33-2000. The flow time of transmission oils from the viscometer was measured as the interval between the moments of oil passage marked on the upper and lower ends of the mechanical stopwatch connected viscometers.

The density of transmission oils was determined using a hydrometer AHT-2 at a temperature of 20ºC, with a measuring range of 830-910 kg/m^3 and 910-990 kg/m^3, respectively. The flask has a thermometer at the bottom to control the oil temperature and a density scale in the glass tube at the top. To perform the analysis, the test transmission oil is poured into a tall glass cylinder, after which a dry clean hydrometer is immersed in it so that it does not touch the walls of the cylinder. After the hydrometer is moved, the temperature of the oil is measured and the density scale on the lower edge of the meniscus is measured.

RESULTS AND DISCUSSION

The tests were evaluated and determined: during the study, the kinematic viscosity of ТСп-15К transmission oil on the middle bridge of KAMAZ decreased from 14.4 mm^2/sec to 13.3 mm^2/sec at 15000 km, increased from 14.4 mm^2/sec to 14.6 mm^2/sec at 51000 km (fig 1). A decrease in the development of kinematic viscosity is observed at 6,000 km, and an increase at 21,000 km.

In order to detect the dynamics of changes in the density of transmission oils during operation, as well as to conduct comparative tests of the initial ТСп-15К and regenerated oil, research was conducted on two groups of KAMAZ vehicles of different modifications. The first group includes cars running on primary ТСп-15К oil. The second group of vehicles used regenerated transmission oils due to their performance characteristics. Based on the results of studies on the determination of the density of samples of transmission oils in the gearbox, middle and rear axles, graphs of the dependence of the change in density on the transmission units on the mileage of vehicles were constructed (fig. 2-4).

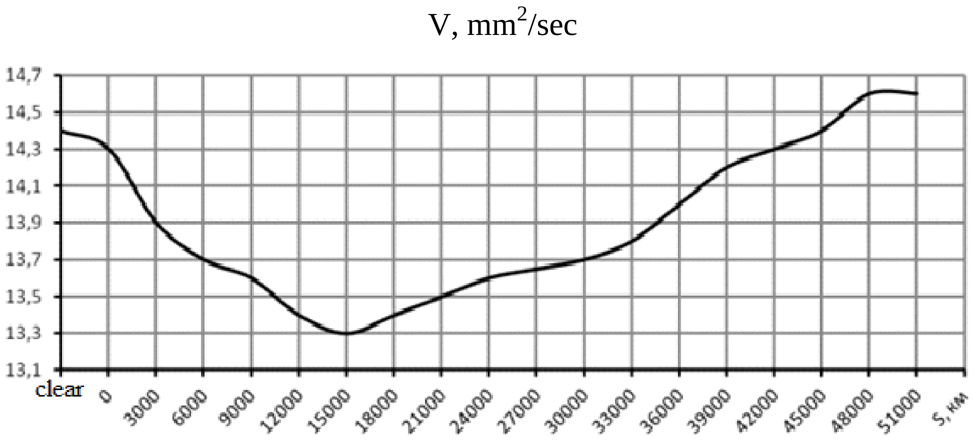

Fig. 1. Change of kinematic viscosity of transmission oil in the middle bridge of KAMAZ car.

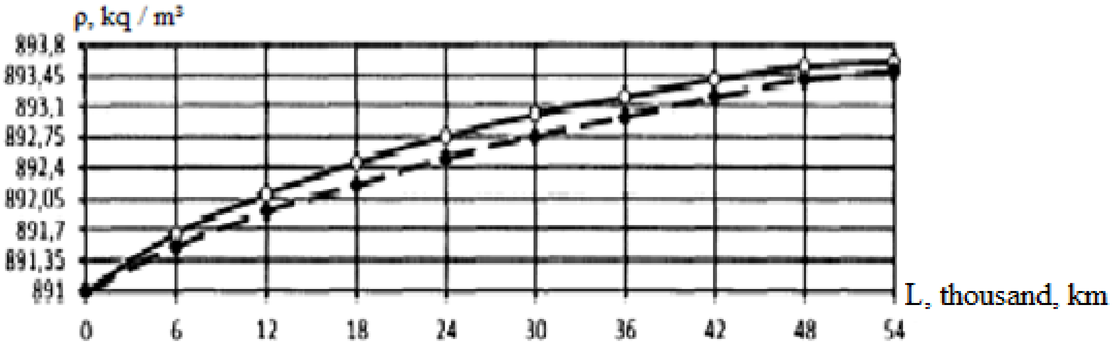

Fig. 2. Change of kinematic viscosity of transmission oil in the middle bridge of KAMAZ car.

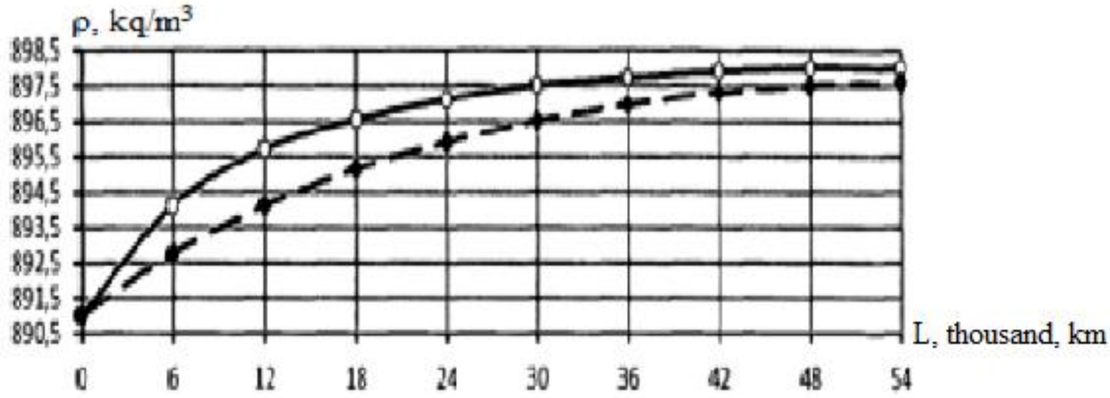

Fig. 3. Dependence of the change of density of transmission oils on the middle bridge of KamAZ cars on the mileage S: staff, regenerated oil 891 891.35 891.7 892.05 892.4 892.75 893.1 893.45 893.8 0 3 6 9 12 15 18 21 24 27 30 33 36 39 42 45 48 51 S, ext. km. 890.5 891.5 892.5 893.5 894.5 895.5 896.5 897.5 898.5 0 3 6 9 12 15 18 21 24 27 30 33 36 39 42 45 48 51 S, thousand km. ρ, 84 kg/m³.

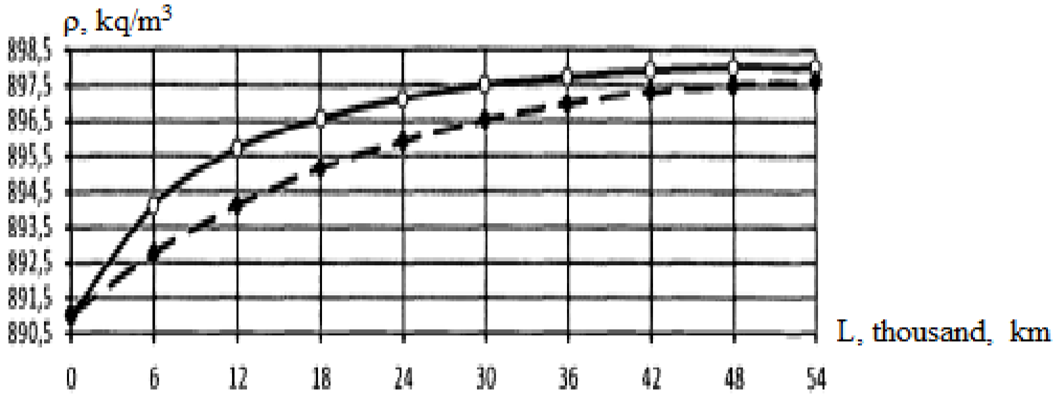

Fig. 4. Dependence of the change of density of transmission oils ρ on the rear axle of KAMAZ cars on the mileage S, staff, regenerated oil.

The results obtained are averaged. As a result of the research, it was determined that the average density of the state TCп-15K transmission oil increased from 891 kg/m³ to 893.6 kg/m³ during the 51000 km mileage during the research in the gearbox. The average value of the regenerated oil density in the gearbox increased from 891 kg/m³ to 893.5 kg/m³ during the 51,000 km. The average density of TCп-15K oil in the middle bridge increased from 891 kg/m³ to 898 kg/m³ at the end of the study. The average density of regenerated transmission oil increased from 891 kg/m³ to 897.6 kg/m³ on a 51000 km run on the middle bridge. The average density of TCп-15K oil in the rear axle increased from 891 kg/m³ to 895.5 kg/m³ during the study with a mileage of 51,000 km. At the end of the study, the average density value in the regenerated transmission oil increased from 891 kg/m³ to 895.2 kg/m³.

CONCLUSION

1. The dynamics of changes in the kinematic viscosity of TCп-15K transmission oil is characterized by a subsequent increase and a decrease during the initial operation. A significant decrease in viscosity is observed during the 6000 km run. The increase in viscosity to the level of fresh oil corresponds to a mileage of 45,000 km.
2. The dynamics of change of density of transmission oils in all transmission units of KAMAZ cars is practically the same. Intensive increases in mileage from 0 km to 21000 km occur as a result of the accumulation of corrosive products (iron, chromium, nickel) and insoluble impurities in the transmission oils during the current operating period. Comparative studies of transmission oils have shown that the state corresponds to TCп-15K oil in terms of the quality of the regenerated oil.

REFERENCES

1. Vilenkin A. V. Oils for gear drives .M.: Chemistry. 1982,248 p
2. Klimov K.I, Kichkin G.I "Transmission oils", M.: Chemistry. 1970, 232 p
3. Seleznev M. V., Holmanov V. M., Glushchenko A. A. "Change in the kinematic viscosity of transmission oil in transmission units during the operation of KAMAZ vehicles" // Collection of articles of the All-Russian scientific-practical conference "Operation of automotive equipment: experience, problems , innovations, prospects Penza: RIO PGSKhA.2013, 139 p

4. Gnatchenko II Automobile oils, lubricants, additives: Handbook. /I.I. Gnatchenko, Borodin V.A., Repnikov V.R - M: LLC Publishing House "AST"; SPb . Publishing house "Polygon".2000, 360 p
5. Kirichenko N.B. Automotive maintenance materials: Textbook. manual for stud. institutions of environments. prof. education / N.B Kirichenko - 2nd ed., erased. - M.: Publishing Center "Academy". 2005, 208 p
6. Reeves C.J, Menezes P.L Advancements in eco-friendly lubricants for tribological applications: past, present, and future: ecotribology research developments—materials forming, machining and tribology,Vol.2, №2 Springer, Switzerland. 2016, pp. 41–61
7. Zwierzycki W., Operating fluids for means of road transport, Publishing house of the Poznań University of Technology. 2016, pp. 300–302
8. Tora B., Kurzac M., Czerwiński J: Utilization of used oils. Clean Energy, Clean Environment.2016, pp. 457-464
9. Boniecki R., Szala G. Economic and environmental aspects of used oil treatment. Operation problems . 2016, pp. 165—177
10. Jacob A. Sonibare, James A.Omoleye. Data on the treatment of used lubricating oil from two different sources using solvent extraction and adsorption, Data in Brief. Vol.19,№1, August 2018, pp. 2240-2252

ДИНАМИКА ИЗМЕНЕНИЯ КИНЕМАТИЧЕСКОЙ ВЯЗКОСТИ И ПЛОТНОСТИ ТРАНСМИССИОННЫХ МАСЕЛ В УСЛОВИЯХ ЭКСПЛУАТАЦИИ АВТОМОБИЛЕЙ КАМАЗ

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В статье представлены сравнительные исследования и рассмотрена динамика изменения плотности и кинематической вязкости товарного трансмиссионного масла ТСп-15К и восстановленного, по эксплуатационным свойствам, в агрегатах трансмиссии автомобилей КАМАЗ в условиях производственной эксплуатации. Результаты исседований показали, что динамика изменения плотности трансмиссионного масла в период эксплуатации характеризуется увеличением плотности от 0 кмдо 21000 км пробега в результате накоплении в масле продуктов износа и нерастворимых примесей. А динамика изменения кинематической вязкости характеризуется в начальный период эксплуатации. Снижение вязкости наступает при пробеге в 6000 км, а увеличение вязкости при пробеге 45000 км.

Ключевые слова: *трансмиссионное масло, агрегаты трансмиссии, автомобили КАМАЗ, плотность, кинематическая вязкость.*

KAMAZ AVTOMOBİLLƏRİNDƏ İSTİSMAR ŞƏRAİTİNDƏ TRANSMİSSİYA YAĞLARININ KİNEMATİK ÖZLÜLÜYÜNÜN VƏ SIXLIĞININ DƏYİŞMƏ DİNAMİKASI

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Məqalədə əmtəə və istehsalatda istismar şəraitində KAMAZ avtomobillərinin transmissiya aqreqatlarında istismar xassələrinə görə bərpa edilmiş transmissiya yağının TCn-15K sıxlığının və kinematik özlülüyünün dəyişmə dinamikasının müqayisəli tədqiqi göstərilmiş və nəzərdən keçirilmişdir. Tədqiqatların nəticələri göstərir ki, istismar dövründə transmissiya yağının sıxlığının dəyişmə dinamikası yağda yeyilmə məhsulları və həll olmayan qarışıqların toplanması nəticəsində 0 km-dən 21000 km-ə qədər yürüşdə sıxlığın yüksəlməsi ilə xarakterizə olunur. Kinematik özlülüyün dəyişmə dinamikası isə başlanğıc istismar dövründə xarakterizə olunur. Özlülüyün azalması 6000 km yürüşdə, özlülüyün yüksəlməsi isə 45000 km yürüş zamanı başlayır.

Açar sözlər: *transmissiya yağı, transmissiya aqreqatları, KAMAZ avtomobili, sıxlıq, kinematik özlülük.*

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SYNTHESIS, PROPERTIES AND USING OF RHENIUM COMPLEXES WITH NICOTINIC ACID AMIDE

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Methods for the synthesis of coordination compounds Re (V) with one of the well-known bioligands, nicotinic acid amide have been developed. The composition and structure of the complexes isolated in the crystalline state were established on the basis of a set of data from elemental analysis, IR and electronic spectroscopic methods, thermography, and molar electrical conductivity. According to the results of the studies, the monodentate coordination of nicotinic acid amide through the nitrogen atom of the heterocycle was established. The binuclear structure of the rhenium complex has been proved. EAS data and measurements of molar electrical conductivity indicate that the interaction of rhenium complexes with nicotinamide in polar solvents is accompanied by the exchange of acidoligands for donor solvent molecules.The synthesized rhenium complexes were investigated in the experiment along with known antioxidants and immunocorrectors in order to prevent the effects of nitrogen oxides and silicon dioxide on the respiratory organs. It has been found that they largely prevent these organs from the damaging effects of toxic gases and dust.It is suggested that the mechanism of action of rhenium complexes on a living cell differs from the action of known antioxidants and immunocorrectors, which occupy the first rank places. Experimental data have confirmed that rhenium complex compounds are not antioxidants and, moreover, are not toxic to living organisms.

Keywords: *rhenium complexes, nicotinic acid amide, IR spectra, electronic absorption spectra, molar electrical conductivity, binuclear complex, medical aspect of use.*

INTRODUCTION

Studies of rhenium compounds make it possible, in addition to the already known fields of application of complexes of this metal - metallurgy, electronics, catalysis, to find new ones. For example, as substances with biological activity [1-3].

The coordination chemistry of rhenium has undergone significant development in recent years, driven largely by interest in the creation of radiopharmaceuticals. In this case, the radiotherapy drug can be delivered directly to a large organ of the patient using specific molecular carriers, i.e. in the form of coordination compounds with a certain type of ligands [3-5].

Another main area of consumption of rhenium is the production of catalysts for the petrochemical industry [6], as well as the production of filters-neutralizers for exhaust gases of cars. Rhenium-promoted catalysts are widely used in various technological processes [5-9].

Despite the increased interest in the chemistry of rhenium, much in the chemistry of rhenium remains unexplored; the regularities in the change in the physicochemical properties of their compounds, depending on the nature of the ligands, have not yet been established.

Against the background of research in the field of complex compounds of rhenium with S- and P-containing ligands, there is a certain gap in the study of their compounds in high oxidation states with N-containing ligands. This circumstance played a significant role in the formulation of this study.

All this necessitates the search for new, convenient and targeted methods for the synthesis of Re (5) complexes with a nitrogen-containing ligand - nicotinic acid amide. The interest in this ligand is due to its broad practical research in medicine and interesting donor potential.

The aim of this work is to develop an effective method and optimal synthesis conditions, to study the process of complexation between rhenium halides and nicotinamide, to study the structure and composition of the complexes, to establish the nature of the chemical bond and the type of coordination of the ligand.

EXPERIMENTAL PART

Synthesis of complex compound Re (V) with nicotinamide.

In a two-necked flask was placed 0.83 g ($1{\cdot}10^{-3}$mol) trans- [$ReO(Ph_3P)CI_3$], then 0.294 g ($2.5{\cdot}10^{-3}$ mol) NAA (ratio 1: 2.5) and added 80 ml of a mixture of IPA: benzene = 3: 1. The synthesis was carried out in an inert atmosphere (Ar) at the boiling point of the solvent (about 720 C) for 1.5 h. After 4-5 hours, shiny crimson crystals precipitated from the cooled dark brown solution. They were filtered off and washed several times with IPA and ether. The resulting substance is soluble in acetone, acetonitrile, DMSO, DMF, chloroform, but practically insoluble in water.

Found,%: Re 27.24; C 43.78; H 3.31; N 3.70.
For $Re_2C_{48}H_{42}O_5N_4CI_4P_2$
Calculated,%: Re 27.99; C 43.23; H 3.16; N 4.21.

Chemical analysis was carried out on a Carlo Erba - 11 - 08 device. The determination of the mass fraction of rhenium in the obtained compounds was carried out by the gravimetric method in the form of nitrone perrhenate. IR spectra in the range 4000-400 cm^{-1} were recorded in potassium bromide tablets on a BRUKER IFS-85 Fourier spectrometer. Electronic absorption spectra of solutions of the complexes in various solvents were obtained on Specor d UV VIS spectrophotometers, Germany. The thermogravimetric analysis of the obtained complexes was studied on a 9900 analyzer (DuPont). The weighed portions of the complexes were 5.0-15.0 mg.

The molar conductivity of the complex solutions was measured in a closed cell and an EC-08 AC bridge was used at a frequency of 1x104 Hz. The accuracy of maintaining the temperature was ~ 0.10 C. The electrical conductivity of the solutions of the complexes was determined by the conductometric method on a device consisting of a G3-111 generator, a zero indicator F 582 of an AC bridge R 5021.

RESULTS AND DISCUSSION

Nicotinic acid amide is certainly a very interesting ligand. It is interesting in that it contains three donor atoms and is able to participate in complexation reactions with various metals. Moreover, nicotinamide and its derivatives are widely used in medicine. The complexation of rhenium (V) with NAA has not been previously studied.

Analysis of the IR spectra data for the synthesized Re (V) complex with NAA, as well as the starting materials, suggests the monodentate coordination of NAA and the dimeric structure of the complex (table 1)

The amide of nicotinic acid has three competing donor atoms: oxygen of the carbonyl group, nitrogen of the amide group, and nitrogen of the heterocycle.

It is known from the literature that amides of pyridinecarboxylic acids (with the exception of picolinic acid amide) do not exhibit a tendency to coordinate through the nitrogen atom of the amide group [2]. The presence of two other donor atoms in the NAA molecule suggests the possibility of both monodentate and bidentate coordination [3]. The absorption band "amide I" corresponds to a complex vibration, the main contribution to which is made by bending vibrations of the amino group and vibrations of the pyridine ring. In the complex, this band is split into two components: one remained practically unchanged at a frequency of 1680 cm^{-1} (as in the spectrum of a free ligand), while the other shifted to a longer wavelength region up to 1650 cm^{-1}. According to [4], such a splitting may be due to the non-equal value of the carbonyl groups of the two ligands due to the mutual influence of cis-located nicotinamide molecules and the possible formation of intramolecular hydrogen bonds. The absorption band related to the deformation vibrations of the NH_2 - group at 1620 cm^{-1} does not undergo changes in the spectrum of the complex, which allows us to assume the absence of coordination of nicotinamide with respect to the carbonyl oxygen or nitrogen of the amino group. The splitting of the absorption band at 1030 cm^{-1}, which is responsible for the vibrations of the heterocyclic ring of the free ligand, into two components, 1050 $cm^{-1}$and 1020 cm^{-1} in the spectrum of the complex, indicates the coordination of NAA to the central rhenium atom through the nitrogen atom of the heterocycle [5].

In the range of 680-750 cm^{-1}in the spectrum of the complex compound, absorption bands corresponding to vibrations of the Re-O-Re bond appear. However, oscillations of the Re-P bond occur in the same region, therefore, it is not possible to make clear assignments of the spectrum in this region. The absorption band at 969 cm^{-1}in the IR spectrum related to ν (Re = O), in a complex with nicotinamide, shifts to a longer wavelength region (925 cm^{-1}). Such a low value of ν (Re = O) was observed in dimers containing linear groups O = Re - O - Re = O.

Table 1.

Characteristic IR frequencies of NAA and complex

Compound	ν(C=O)(см$^{-1}$) «amide I»	σ (NH_2)(см$^{-1}$) «amide II»	ν(rings) (см$^{-1}$)	ν(Re=O) (см$^{-1}$)
NAA	1680	1620	1030	969
$[Re_2O_5(NAA)_2(Ph_3P)_2Cl_4]$	1680, 1650	1620	1050,1020	925

The study of the EAS of the complex compound in various solvents showed that the spectral picture in the visible region changes with time. For the study, we used solutions of the complex in such solvents as dimethylformamide, acetonitrile, and chloroform. The concentration of solutions is C = 2.07-3.21 mol / l. It was found that the spectral picture in the visible region changes with time. Moreover, the rate of change depends on the nature of the solvent: the more donor the solvent is, the greater the rate of change. Thus, in DMF, the spectrum recorded immediately after the dissolution of the complex gives three distinct maxima (13500, 17880, and 29160 cm^{-1}), a shoulder (23000 cm^{-1}) in the visible region and a maximum at 38260 cm^{-1} in the UV region (acetonitrile). The position of the last two maxima does not change with time, and the band at 17880 cm^{-1} in the visible region completely disappears within 6 hours. In acetonitrile, this phenomenon was observed after two days, and in chloroform, no changes in the spectral picture occurred. According to the literature data, the absorption bands at 13500 cm^{-1} and 17880 cm^{-1} can be attributed to oxychloride complexes of rhenium (V). The presence of a band at 23000 cm^{-1} may also testify in favor of the dimeric structure of the obtained complex. The disappearance of the band at 17880 cm^{-1} with time can be explained by the replacement of the acidoligand with donor solvent molecules, the interaction with which does not appear in this spectral region. The retention of the unchanged bands characterizing the chromophore system of nicotinamide (29160 and 38260 cm^{-1}) indicates that nicotinamide is more strongly bound in the complex than chloride ion (fig.1). The interaction of the [$Re_2O_3(NAA)_2(Ph_3P)_2Cl_4$] complex with polar solvents is confirmed by the data on the measurement of electrical conductivity in various solvents.

In DMF, when the concentration of the complex solution is $C = 1{\cdot}10^{-3}$mol, the molar conductivity changes with time. After dissolution of the sample of the complex, the molar conductivity values corresponded to the non-electrolytic type of compounds (25,000 m^{-1}· cm^{2} · mol^{-1}), and then gradually increases and after 1 hour reaches a value corresponding to the electrolyte 1: 1 (65,10 0m^{-1} · см^{2} · mol^{-1}). In the future, the growth of the values of molar electrical conductivity slows down. After 4 hours, it reached a value of 80.05 0m^{-1} · cm^{2} · mol^{-1}. Measurements a day after the beginning of the experiment showed that stabilization occurred and the values of molar electrical conductivity did not go beyond (65-90 0m^{-1} · cm^{2} · mol^{-1}) values corresponding to a 1: 1 type electrolyte (83.76 0m^{-1} · cm^{2} · mol^{-1}).

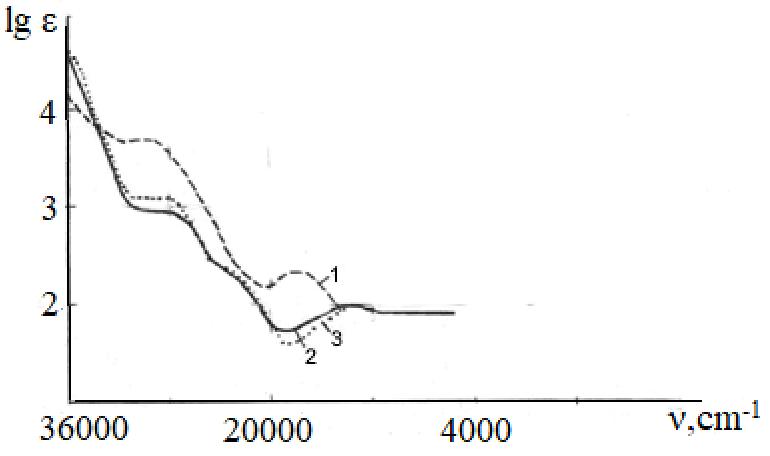

Fig. 1. EAS of [$Re_2O_3(NAA)_2(Ph_3P)_2Cl_4$] solution in DMF: immediately after preparation - (1), after 6 (2) and 18 hours (3) at $C = 6 \cdot 10^{-4}$mol / l.

In acetone, the value corresponding to the indicated type of electrolyte (103.00 0m^{-1} · cm^{2} · mol^{-1}) was reached after two days, and in chloroform the molar conductivity practically did not change over time and remained at the level of values for non-electrolyte (2.83 0m^{-1} · cm^{2} · mol^{-1}).

When the concentration of the complex compound C = $1 \cdot 10^{-4}$mol / l in DMF, 0.5 hours after dissolution, the molar conductivity has values of 220.67-255.56 0m^{-1} · cm^{2} · mol^{-1}, which corresponds to the values electrolyte type 4: 1. Dilution of the solution by a factor of 10 probably accelerates the exchange of acidoligands of the $[Re_2O_3(NAA)_2(Ph_3P)_2Cl_4]$complex with donor solvent molecules (table 2).

The above data make it possible to assume the binuclear structure of the resulting compound-rhenium (V) complex with nicotinic acid amine.

Table 2

The values of the molar conductivity of the complex
$[Re_2O_3(NAA)_2(Ph_3P)_2Cl_4]$ in DMF

Indicators	Time, τ , min									
Molar electrical conductivity, μ, Om^{-1} · cm^{2} · mol^{-1} at concentration of complex compound C, mol /l:	2	5	10	20	30	45	60	120	180	240
$1 \cdot 10^{-3}$ $1 \cdot 10^{-4}$	25,00 220,67	29,10 240,05	33,70 248,63	44,50 255,56	52,20 311,26	61,70 316,43	66,60 –	75,80 –	79,00 –	80,05 –

An increase in the electrical conductivity and a change in the EAS of acetonitrile, acetone, and dimethylformamide solutions of the complex are likely due to the displacement of acidoligands (in our case, Cl^{-}) by polar solvent molecules from the inner sphere of the neutral complex compound.

Thermal analysis of the complex showed the stability of the sample in an inert atmosphere of dry argon up to 186 ^{o}C. After that, the decomposition of the organic part of the complex begins with the formation (at a temperature of about 600 ^{o}C) of X-ray amorphous rhenium nitride, which is a black shiny crystalline powder. It should be noted the chemical inertness of this compound, namely resistance to the action of organic substances, water and mineral acids.

CONCLUSION

Methods for synthesis of rhenium (V) complex compounds with nicotinic acid amide were developed. The composition and structure of the synthesized compounds were established on the basis of a set of elemental analysis data and various physicochemical methods: IR spectroscopy, EAS, thermogravimetric, molar electrical conductivity.

The monodentant coordination of nicotinic acid amide through the nitrogen atom of the heterocycle was established. The binuclear structure of the rhenium (V) complex with nicotinic acid amide was proved. EAS data and measurements of molar electrical conductivity show that the interaction of rhenium (V) complexes with nicotinic acid amide in polar solvents leads to the exchange of acidoligands for donor solvent molecules.

The use of the synthesized complex compounds of rhenium in medical practice revealed the absence of toxicity for living organisms and a positive effect to prevent the action of toxic gases and dust.

REFERENCES

1. Amindzhanov A.A, Karimova M. Kh., Vezen A.E Study of the biological activity of complex compounds of rhenium (V) with benzoxazole and benzothiazole derivatives. Coordination connections and aspects of their application. Dushanbe 1991, part 2, pp.46
2. Justin J. Wilson and Stephen J. Lippard. Synthetic methods for the preparation of Platinum Anticancer complexes. Chemical Review. 2014,114(8), pp. 4470-4495
3. Zhao Y. Woods J.A., Farrer N. J., Robinson K. S., Pracharova Y. Diarido mixed-amine platinum (4) anticancer complexes activatable by visible-light form novel DNA adducts. Chemistry. 2013, №19 (29), pp. 9578-91
4. Bauer E. B., Haase A. A., Reich R. M., Crans D. C., Kühn F. E. Organometallic and coordination rhenium compounds and their potential in cancer therapy. Coord. Chem. Rev. 2019 ,part 393, pp.7-11
5. Vishkaee T. S., Fazaeli R., Youseti M. Teoretical Analysis at Soluent Effect on the NMR. A Platinum-Based Anticancer Drug. Russ J. Inorg. chem. 2019, part. 64, pp.237-241
6. Ryashentseva M. A. Rhenium containing catalysts in petrochemistry // Bulletin of MITHT. 2007 ,Vol. 2, №2, pp. 12-26
7. Khadzhiev S.N, Maksimov A.L New perspective catalytic systems for processing hydrocarbon raw materials // Catalysis in solving problems of petrochemistry and oil refining. II Ros. Azerb. International Symposium. 2019,pp.43
8. Goto A., Fukuda T. // Prog. Polym Sci .2004, 29, pp.329
9. Tfoumi E // Coord Chem. Rev. 2000, Vol.196,№1, pp.281

СИНТЕЗ, СВОЙСТВА И ИСПОЛЬЗОВАНИЕ КОМПЛЕКСОВ РЕНИЯ С АМИДОМ НИКОТИНОВОЙ КИСЛОТЫ

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Разработаны методы синтеза координационных соединений Re (V) с одним из широко известных биолигандов – амидом никотиновой кислоты. Состав и структура выделенных в кристаллическом состоянии комплексов установлены на основании совокупности данных элементного анализа, ИК и электронных спектроскопических методов, термографии и молярной электропроводности. По результатам проведенных *исследований установлена монодентатная координация амида никотиновой кислоты через атом азота гетероцикла. Доказана биядерная структура комплекса рения. Данные ЭСП и измерения молярной электропроводности свидетельствуют, что при взаимодействии комплексов рения с никотинамидом в полярных растворителях происходит процесс обмена ацидолигандов на донорные молекулы растворителя. Синтезированные рениевые комплексы исследовались в эксперименте наряду с известными антиоксидантами и иммунокорректорами с целью профилактики воздействия на органы дыхания оксидов азота и диоксида кремния. Установлено, что они в большей степени предотвращают эти органы от повреждающего действия токсичных газов и пыли. Сделано предположение, что механизм действия комплексов рения на живую клетку отличается от действия известных антиоксидантов и иммунокорректоров, занимающих первые ранговые места. Экспериментальные данные подтвердили, что комплексные соединения рения не являются антиоксидантами и кроме того не токсичны для живых организмов.*

Ключевые слова: *комплексы рения, амид никотиновой кислоты, ИК- спектры, электронные спектры поглощения, молярная электропроводность, биядерный комплекс, медицинский аспект использования.*

RENİUM (V) NİKOTİN TURŞUSUNUN AMİDİ İLƏ KOMPLEKSLƏRİNİN SİNTEZİ, XÜSUSİYYƏTLƏRİ VƏ TƏTBİQİ

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Geniş yayılmış bioligandlardan biri olan nikotin turşusunun amid ilə Re (V) koordinasiya birləşmələrinin sintez metodları işlənib hazırlanmışdır. Kristal vəziyyətdə təcrid olunmuş komplekslərin tərkibi və quruluşu element analizi, İQ və elektron spektroskopik metodları, termoqrafimetrik və molar elektrik keçiriciliyindən alınan məlumatlar əsasında təyin olunmuşdur. Tədqiqatların nəticələrinə görə, heterosiklin azot atomu vasitəsilə nikotin turşusunun amidinin monodentat koordinasiyası təsdiq olunmuşdur. Renium (V) kompleksinin binüvəli quruluşu sübut edilmişdir. EUS məlumatları və molar elektrik keçiriciliyi ölçüləri, reniumun komplekslərinin polyarhəlledicilərində nikotinamid ilə qarşılıqlı təsirinin, asidoliqandların donor həlledici molekulları ilə mübadiləsi ilə müşayiət olunduğunu göstərir. Sintez olunmuş reniumun kompleksləri, azot oksidləri və silikon dioksidin tənəffüs orqanlarına təsirinin qarşısını almaq üçün məlum antioksidantlar və immunokorektorlarla birlikdə təcrübədə tədqiq edilmişdir. Bu orqanların zəhərli qazların və tozun zərərli təsirlərindən daha çox dərəcədə qarşısını aldıqları aşkar edilmişdir. Renium komplekslərinin canlı bir hüceyrəyə təsir mexanizminin, birinci dərəcə yerlərini tutan bilinən antioksidan və immunokorektorların təsirindən fərqli olduğu irəli sürülmüşdür. Təcrübə məlumatları renium kompleks birləşmələrinin antioksidant olmadığını və üstəlik canlı orqanizmlər üçün zəhərli olmadığını təsdiqlədi.

Açar sözlər: *renium kompleksləri, nikotin turşusunun amidi, İQ spektrləri, elektron udma spektrləri, molar elektrik keçiriciliyi, binüvəli kompleks tətbiqinin tibbi aspekti.*

UDC 678.01:532.135

RHEOLOGICAL CHARACTERISTICS OF THE FLOW OF NANOCOMPOSITES BASED ON BENTONITE AND POLYMER MIXTURES RANDOM POLYPROPYLENE WITH NITRILE BUTADIENE RUBBER

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The paper presents the results of a study of the influence of the nitrile butadiene rubber concentration in a composition based on random polypropylene and nanosized bentonite on the rheological features of the dynamically vulcanized nanocomposites flow. The effect of temperature and shear stress on the flow curves and the dependence of the effective viscosity from the shear rate and inverse temperature are investigated. The activation energy of viscous flow of nanocomposites of polymer mixtures is determined. A universal temperature-invariant characteristic of nanocomposites is constructed.

Keywords: *nitrile butadiene rubber, compatibility, melt viscosity, rheology, activation energy, compatibilizer.*

INTRODUCTION

With the improvement of techniques and technology of industrial production in the field of mechanical engineering, shipbuilding, aviation, military and space technology, special attention is paid to the development of fundamentally new types of polymer materials, differing in manufacturability, high physicomechanical and thermophysical properties [1-3]. However, the development of a polymeric material should not be aimed only at improving their basic physicomechanical characteristics, but should also take into account their technological capabilities and ability to be processed on standard equipment by injection molding and extrusion [4-6]. In order to competently carry out the processing of new types of polymeric materials, it is necessary first of all to investigate their rheological properties. The problem is aggravated by the fact that the production uses the only rheological property of polymers, as a melt flow index (MFI). However, this method cannot reveal in-depth processes occurring in the polymer melt during their processing under the influence of temperature and shear forces [7].

Studies on the study of the rheological properties of nanocomposites, where a mixture of incompatible polymers of different nature is used as a polymer matrix, are completely limited. The simultaneous solution of the problem of polymer compatibility and the use of nanosized fillers is a rather complex scientific and technical problem [7, 8].

In this regard, in this work, we focused on studying the complex of rheological characteristics of nanocomposites based on polymer mixtures.

EXPERIMENTAL PART

Random polypropylene (RPP), or a thermoplastic random copolymer of ethylene with propylene brand RP2400 characterized by the following properties: ultimate tensile stress – 28.5 MPa, elongation at break – 600%, MFI = 1.78 g/10min., density 0.904g/cm^3, melting point 146°C, heat resistance 131°C.

SKN - nitrile butadiene rubber with 40% acrylic acid nitrile content (SKN -40).

Bentonite is a mixture of natural aluminosilicate minerals based on montmorillonite $Al_2O_3·4SiO_2n·H_2O$ (60-70%). As a result of natural substitution of silicon atoms in the crystal lattice of bentonites with magnesium, iron or other metal ions, they contain saponite - $Al_2O_3[MgO]\ 4SiO_2n·H_2O$, nontronite - $Al_2O_3[Fe_2O_3]4SiO_2n·H_2O$, beidelite - $Al_2O_3·3SiO_2n·H_2O$ and pyrophyllite - $Al_2[Si_4O_{10}](OH)_2$. Bentonite contains kaolinite and other minerals.

Bentonite nanoparticles with a size of 85-120 nm were obtained on a special laboratory mill A-11 with a rotor speed of up to 30000 rpm.

Exxelor PO1200 compatibilizer is intended for use as a binding agent in order to improve the compatibility of polymeric materials and to improve the reactivity when interacting with inorganic fillers. This is achieved in a reactive extrusion process by the graft copolymerization of polypropylene with maleic anhydride (MA). The MA concentration in the compatibilizer is 3.0 wt%.

Polymer composite materials based on nanosized bentonite and a mixture of RPP + SKN were obtained in the process of mixing on rollers at a temperature of 170°C. After the RPP was melted, 2.0 wt %of PPMA was loaded, and then, in the process of intensive mixing, SKN crumbs were loaded on the rollers for 8 minutes. To obtain vulcanizates, 2.0 wt% sulfur was additionally loaded during mixing.

Rheological studies were carried out on a rheometer (INSTRON, Italy) on a MELT FLOW TESTER, CEAST MF50 device in a temperature range of 170-230°C and a load of 2.16 - 21.6 kg.

RESULTS AND DISCUSSION

Before start off on the study of the problem under consideration, it seemed interesting to dwell on the discussion of some points that would allow a more in-depth approach to the assessment of the rheological features of polymers and polymer mixtures. First, when studying polymer mixtures, in addition to solving the problem of compatibility of the mixed components of the mixture, it is necessary to understand that each of the polymer components has its own rheological features of the flow. And how these individual characteristics of the polymer components will collectively affect the overall rheology of the polymer mixture. Secondly, will additivity remain in the change in the rheological characteristics of the mixture with a change in the concentration of one of the components of the mixture and with what it may be connected. In order to improve the technological compatibility of mixtures of RPP with SKN-40, a graft copolymer of polypropylene with maleic anhydride (PPMA) was used as a compatibilizer. The concentration of maleic anhydride in the PPMA composition was 3.0 wt %. Earlier, in work [9], we showed that to increase the technological compatibility of RPP with SKN, it is sufficient to use 2.0 wt % PPMA. In the process of mixing RPP with SKN-40, a two-phase system is formed, where the elastomer forms a dispersed phase in the dispersed RPP medium. In this case, the loading of PPMA contributes to the fact that it is distributed in the boundary region of the dispersed phase. Based on the principle "like dissolves like", we assume that the polar groups of maleic anhydride will be located in the dispersed phase, and the hydrocarbon segments not occupied by the grafted units will be located in the dispersed medium. This theory suggests that the PPMA macrochains enhance the van der Waals forces of intermolecular interaction due to adhesive forces [9, 10].

Figure 1 shows the flow curves of nanocomposites based on RPP + 5.0 wt% bentonite (fig.1.1), SKN-40 + 5.0 wt% bentonite (fig.1.5), as well as, based on nanocomposites of polymer mixtures RPP + SKN-40 + 5.0 wt% of bentonite fig.2-4) with various concentrations of SKN-40. The concentration of SKN-40 in the RPP composition varied within the range of 20-40 wt%. From a comparative analysis of the flow curves, it can be established that with an increase in the concentration of SKN-40 in the composition of the RPP, a decrease in the shear rate of the melt is observed. The latter circumstance is due to the fact that SKN-40, in comparison with RPP, is characterized by high melt viscosity. That is why the flow curves of nanocomposites of polymer mixtures are located between the flow curves of RPP and SKN-40 according to an additive regularity. As shown in [9, 10], nanocomposites of polymer mixtures at 40 wt% SKN-40 and in the presence of PPMA are thermoplastic elastomers and exhibit good miscibility and technological compatibility.

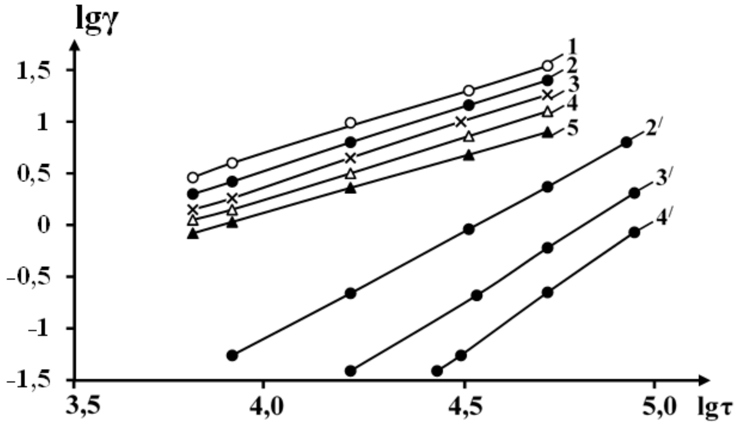

Fig.1. Effect of SKN-40 concentration on the flow curves of mixtures based on RPP + 5.0 wt% bentonite in the presence of 2.0 wt% PPMA (1-5) and sulfur vulcanizates of these mixtures (2'; 3'; 4'): 1-RPP+5.0wt%bentonite; 2-RPP+20wt% SKN-40 + 5.0wt%bentonite; 3- RPP+30wt% SKN-40 + 5.0wt%bentonite; 4- RPP+40wt% SKN-40+5.0wt%bentonite; 5-SKN-40+5.0wt%; 2'- RPP+20wt% SKN-40+5.0wt% bentonite+2.0wt% sulfur; 3'- RPP + 30 wt% SKN-40 + 5.0wt% bentonite + 2.0 wt% sulfur; 4'- RPP + 40wt% SKN-40 + 5.0wt%bentonite + 2.0wt% of the sulfur.

Figure 1 (2', 3', 4') shows the rheological features of the flow of sulfur vulcanizates of nanocomposites based on RPP + SKN-40 polymer mixtures (at a sulfur concentration of 2.0 wt%). From the comparative analysis of the flow curves in this figure, it can be seen that in this case, with an increase in the concentration of SKN-40 in the composition of the RPP, an increase in the viscosity of the melt of polymer mixtures is observed. In contrast to unvulcanized polymer mixtures, the flow curves of vulcanized ones are more sensitive to changes in the shear stress and concentration of

SKN-40. The sensitivity is manifested in the fact that with an increase in the concentration of SKN-40 in the vulcanized composition based on RPP from 20 to 40 wt %, the shear rate decreases 5 times more. Such a sharp change in the shear rate may be associated with the special nature of the flow of the macrochain associates in the melt. It is quite obvious that as a result of using bentonite nanoparticles in the melt, in addition to homogeneous centers, heterogeneous nucleation centers are also formed, which are responsible for the formation of macrochain associates. In accordance with the Frenkel-Eyring theory, in the process of thermal fluctuation action, the destruction and regeneration of the macrochain associates occurs before the establishment of thermodynamic equilibrium [9, 11]. The experimental data obtained allow us to assert that in the case of vulcanized polymer mixtures, larger macroassociates are formed, which contribute to a significant increase in the viscosity of the nanocomposite melt. And, the higher the SKN concentration, the higher the melt viscosity. There is reason to believe that with an increase in the shear stress, the decomposition of macroassociates into smaller ones is accompanied by a sharp increase in the shear rate. The larger the macroassociates formed in the melt, the less resistant they are to temperature and shear stresses.

Figure 2 shows the flow curves of polymer mixtures based on RPP + 40 wt% SKN-40 + 2.0 wt% PPMA + 5.0 wt% bentonite in the temperature range 170-230°C. The choice of this composition was determined by the results of the study of the physicomechanical properties of nanocomposites of polymer mixtures given in [9]. Analyzing the flow curves in fig.2, it can be established that with an increase in temperature and shear stress, a regular increase in the shear rate is observed. At the same time, in the range of shear stresses taken, we have not established the regions of the Newtonian flow.

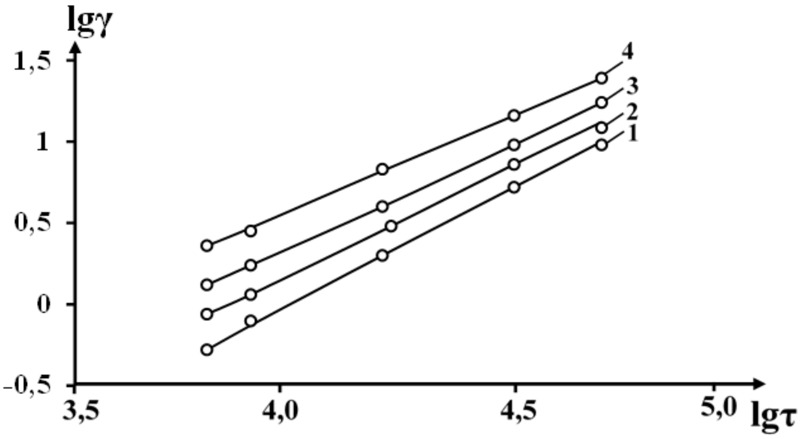

Fig.2. Flow curves of nanocomposites based on RPP + 40 wt% SKN-40 + 5.0 wt% bentonite + 2.0 wt% PPMA at different temperatures: 1-170; 2 - 190; 3 - 210; 4-230°C.

The task of the study was to find out how the regularity of polymer flow changes in complex 4-component polymer mixtures RPP + SKN + PPMA + bentonite. It becomes obvious that, despite the lack of compatibility of RPP with SKN, the use of a compatibilizer can significantly improve the miscibility and technological compatibility of the mixture under consideration. Otherwise, we would observe an abnormal pattern in the variation of the rheological flow curves.

One of the important features in the rheology of polymers is the determination of the dependence of the effective viscosity on the shear rate at different temperatures, the results of which are illustrated in fig.3. Comparative analysis of the curves in this figure gives grounds to assert that in 4-component filled polymer mixtures, the regularity of changes in rheological curves proceeds, as in homopolymers. The components make adjustments mainly in the numerical values of the rheological indicators, provided that the general pattern of polymer flow is preserved. Attention should also be paid to the fact that at low values of shear rates, the effective viscosity changes to a lesser extent. This can be seen especially clearly at a temperature of 190-230°C. The regularity of changes in the curves of effective melt viscosity at low shear rates approaches the highest Newtonian viscosity. From the flow curves in fig.2, this state corresponds to low values of the shear stress lgτ=3.8 and 3.9 and, accordingly, the shear rate.

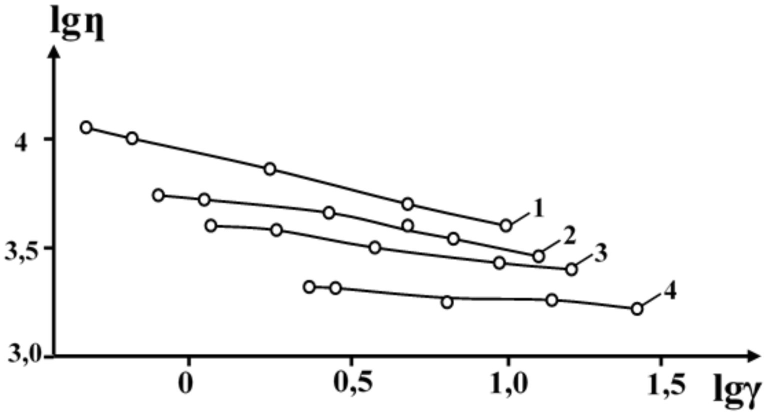

Fig.3. Influence of temperature on the dependence of effective viscosity on shear rate in logarithmic coordinates: 1-170; 2 - 190; 3 - 210; 4-230°C.

One of the informative methods for assessing the rheological characteristics is the dependence of the effective viscosity of the melt on the inverse temperature in semilogarithmic coordinates (fig. 4). This dependence makes it possible to determine the activation energy of a viscous flow, which, for example, in the temperature range of 170-210°C varies in the range of 27-39 kJ / mol. In this case, it is characteristic that with an increase in the shear stress (lgτ) from 3.8 to 4.7, the value of the activation energy for viscous flow decreases.

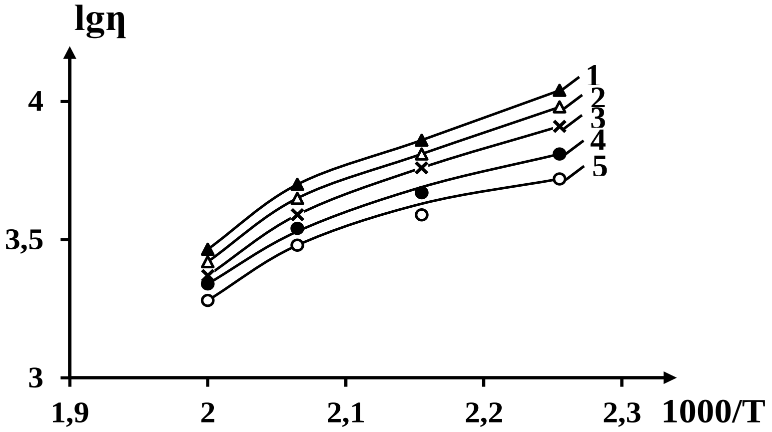

Fig.4. Influence of the inverse temperature on the effective melt viscosity of mixtures based on RPP + 40 wt% SKN-40 + 5.0 wt% bentonite + 2.0 wt% PPMA in Arrhenius coordinates at various values of shear stress (lgτ, Pa): 1- 3.8; 2- 3.9; 3- 4.2; 4 - 4.5; 5- 4.7.

To obtain a sufficiently complete picture of the state of polymers in the steady-state flow regime, it is very useful to use the universal temperature-invariant viscosity characteristic shown in fig.5. Extrapolation of this dependence to the region of high shear rates, close to the region of polymer processing, allows in a simplified form to measure the viscosity of the melt in a relatively wide range of temperatures and shear stresses. As can be seen from fig.5, with an increase in the reduced shear rate ($\gamma\eta_o$), the reduced viscosity (η_e/η_o) decreases, where η_o is the highest Newtonian viscosity, and η_e is the effective viscosity of the melt. Moreover, the horizontal section on this curve, located parallel to the abscissa axis, i.e. where $\eta_e = \eta_o$, unambiguously indicates the existence of a Newtonian flow region, which could not be fixed in the considered range of shear stresses.

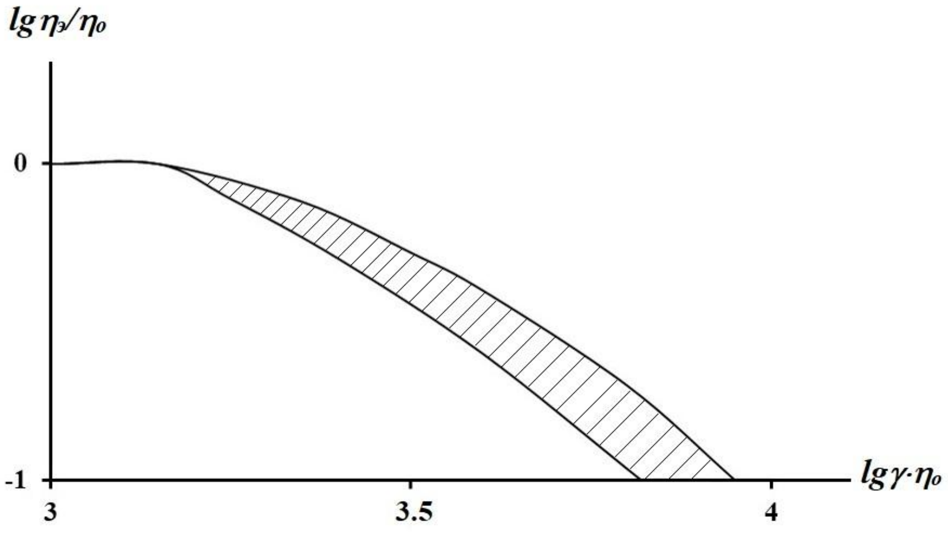

Fig.5. Temperature-invariant characteristic of the dependence of the reduced viscosity **(**lgηe/η**o)** on the reduced shear rate (lgγ × ηo) of the DVEP based on RPP + 40 wt% SKN-40 + 5.0 wt% bentonite + 2.0 wt% PPMA.

From the dependence of the reduced viscosity on the reduced shear rate, it can be seen that for the considered nanocomposites of the DVEP, the temperature-invariant characteristic changes according to the same regularity (shaded area). The universal characteristic of the viscosity properties of polymeric materials shows that, as a result of the applied shear stress and temperature, the deformation process in the melt flow has a cooperative character. It should be borne in mind that the effect of the rate of deformation on molecular interaction, the creation and destruction of asoocyates and macroassociates in the melt mode is independent of their nature and is qualitatively the same [10].

It should also be taken into account that the very process of processing polymers and their composites during extrusion and injection molding proceeds at relatively high shear rates, which is difficult to calculate using only flow curves. Taking this into account, extrapolating to the region of high shear rates, using the universal characteristic of the viscosity properties of polymers, it is possible to make approximate calculations of their effective viscosity, which is close to the processing conditions.

CONCLUSION

1. The flow curves of nanocomposites based on polymer mixtures of RPP, SKN-40 and bentonite in the temperature range 170-230°C have been studied. For comparison, the flow curves of sulfur vulcanizates of DVEP nanocomposites based on bentonite, RPP, and SKN are presented. It is shown that these curves differ significantly from the regularity of the flow of unvulcanized nanocomposites.
2. The use of the compatibilizer - PPMA made it possible to significantly improve the miscibility and technological compatibility of polymer mixtures of nanocomposites based on bentonite, RPP, and SKN-40.
3. The regularity of the effective viscosity on the shear rate and on the inverse temperature is considered. It has been established that the activation energy of viscous flow of DVEP nanocomposites varies in the range of 27-39 kJ / mol.

REFERENCES

1. Berlin A.A., Volfson S.A., Oshman V.G. The principles of creating composite materials. M.: Himiya. 1990, 240 p
2. Simonov-Emelyanov I.D., Kuleznev V.N., Trofimicheva L.Z. Generalized parameters of the dispersed structure of filled polymers. // Plasticheskie massy — Plastic masses. 1989, №1, pp. 19-22
3. Kakhramanov N.T., Ismailzade A.D., Arzumanova N.B., Mammadli U.M., Martinova Q.S. Filled composites based on polyolefins and clinoptilolite. // American Scientific Journal. №4 (4), 2016, pp.60-65
4. Bessonova N.P., Krashennikov S.V., Korobko A.P. and etc. Structure and properties of low-crystalline polyolefins modified with nanodiamonds. // Vyisokomolekulyarnyie soedineniya - High molecular weight compounds. 2015, Vol. 57, №6, pp. 544-554
5. Osama Al Helo, Osipchik V.S., Petuhova A.V., Kravchenko T.P., Kovalenko V.A. Modification of filled polypropylene. // Plastmassyi - Plastics. 2009, №1, pp.43-46

6. Osipchik V.S., Nesterenkova A.I. Talc-filled compositions based on polypropylene. // Plastmassyi - Plastics. 2007, №6. pp.44-46
7. Ermakov S.N., Kerber M.L., Kravchenko T.P. Chemical modification and blending of polymers in reactive extrusion // Plasticheskie massy — Plastic masses. 2007, №10, pp.32-41
8. Pesetskiy S.S., Bogdanovich S.P. Nanocomposites obtained by dispersing clays in polymer melts. / Abstracts of the International Scientific and Technical Conference "Polymer composites and tribology", Gomel city. 2015, pp.5
9. Kakhramanov N.T., Guliev A.D., Pesetskiy S.S. Dynamically vulcanized nanocomposites based on random modified polypropylene, nitrile butadiene rubber and kaolin. // Kompozity i nanostruktury — Composites and nanostructures. 2019, Vol.11,Iissue 4(44), pp.131-136
10. Kakhramanov N.T., Mustafayeva F.A., Arzumanova N.B., Hamedova L.H., Lyalyaeva R.N. Rheological properties of polymer blends based on low and high density polyethylene. // Kompozity i nanostruktury — Composites and nanostructures. 2018,Vol. 10, Issue 4(40), pp.166-170
11. Cherdyintseva S.V., Belousov S.I., Krasheninnikov S.V. and etc. Influence of the type of organic modifier montmorillonite on the physicochemical properties of nanocomposites based on polyamide-6, obtained by mixing in the melt. // Plasticheskie massy — Plastic masses. 2013, №5, pp.39-43

РЕОЛОГИЧЕСКИЕ ОСОБЕННОСТИ ТЕЧЕНИЯ НАНОКОМПОЗИТОВ НА ОСНОВЕ БЕНТОНИТА И ПОЛИМЕРНЫХ СМЕСЕЙ РАНДОМ ПОЛИПРОПИЛЕНА С БУТАДИЕН-НИТРИЛЬНЫМ КАУЧУКОМ

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В работе приводятся результаты исследования влияния концентрации бутадиен-нитрильного каучука в композиции на основе рандом полипропилена и наноразмерного бентонита на реологические особенности течения динамически вулканизованных нанокомпозитов. Исследовано влияние температуры и напряжения сдвига на кривые течения, зависимость эффективной вязкости от скорости сдвига и обратной температуры. Определена энергия активации вязкого течения нанокомпозитов полимерных смесей. Построена универсальная температурно-инвариантная характеристика нанокомпозитов.

Ключевые слова: *бутадиен-нитрильный каучук, совместимость, вязкость расплава, реология, энергия активации, компатибилизатор.*

BENTONİT VƏ RANDOM POLİPROPİLEN İLƏ BUTADİEN NİTRİL KAUÇUKU POLİMER QARIŞIĞI ƏSASINDA OLAN NANOKOMPOZİTLƏRİN AXICILIĞININ REOLOJİ XÜUSİYYƏTLƏRİ

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Məqalədə random polipropilen və nanoölçülü bentonit əsasında olan kompozisiyada butadien nitril kauçukunun miqdarının dinamiki vulkanlaşmış nanokompozitlərin axıcılığının reoloji xüsusiyyətlərinə təsiri tədqiqatlarının nəticələri verilmişdir. Temperatur və yerdəyişmə gərginliyinin axma əyrilərinə, effektiv özlülüyün yerdəyişmə sürəti və əks temperaturdan asılılığına təsiri tədqiq olunmuşdur. Polimer qarışıqların nanokompozitlərinin özlü axıcılığının aktivləşmə enerjisi müəyyən olunmuşdur. Nanokompozitlərin universal temperatur-invariant xarakteristikası qurulmuşdur.

Açar sözlər: *butadien nitril kauçuku, uyğunluq, ərintinin özlülüyü, reologiya, aktivləşmə enerjisi, kompatibilizator.*

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THE ROLE OF DYE PLANTS IN THE DEVELOPMENT OF AZERBAIJAN CARPET WEVING

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The article discusses the role of dye plants in the development of Azerbaijani carpet weaving. It is noted that dye plants have long played an important role in the artistic design of Azerbaijani carpets, which are now the decoration of many world museums. The article explores the history and area of cultivation of plants such as dye plant and saffron, which are widely used in dyeing carpets in red and yellow, and their role in Azerbaijan's foreign trade. Also, the methods of dyeing grass, shrubs and trees used in dyeing yarns intended for carpet weaving and their application in carpet weaving were studied.

Keywords: *carpet weaving, yarn, dye plant, color, dyeing, saffron, indigo, additive.*

INTRODUCTİON

Carpet weaving is one of the most widespread and ancient field of arts in Azerbaijan. According to researchers, this art first appeared in Egypt and Mesopotamia, and later spread from these countries to Asia Minor, Iran and India. It can be assumed that the emergence of carpet weaving in Azerbaijan coincided with Iran, which has long had close economic, political and cultural ties. During archeological excavations, a jar found in the ancient settlement of Kultapa in Nakhchivan proves that the people living here were engaged in weaving in the Neolithic and Eneolithic periods [1]. The ancients were able to make a variety of household items from linen and sheep's wool in simple ways, including outerwear and simple carpets. At that time, the artistic design of the product was carried out through the natural color of wool. The Greek historian Herodotus, who lived in the 5th century BC, reports that the peoples of the Caucasus dyed their clothes with colors derived from the leaves of trees growing in the surrounding forests [2].

EXPERIMENTAL PART

Empirical, qualitative, quantitative, multi-method, longitudinal, cross-sectional study, case study methods used in the study. Using methods determined the role of dye plants in the development of Azerbaijani carpet weaving that was the important part of the Azerbaijan's foreign trade. Red color and its various shades were obtained by boiling of roots of the marena plant in water, the yellow color was obtained from the saffron us plant, respectively. The blue color which widely used in Azerbaijani carpet weaving was derived from a plant Indigo. İn this case, the method of fermentation was used extensively

RESULTS AND DISCUSSION

Although carpet weaving has a very ancient history in Azerbaijan, its transformation into an independent field of art took place in the early Middle Ages. It is from this period that carpet weaving became widespread in Azerbaijan and became an independent field of art, as evidenced by archeological excavations in Mingachevir. These archeological finds consisted of mill parts and the remains of carpet-palaz product concerning to the III-VIII centuries [3]. The settlement of Hun, Oghuz, Kanger, Sabir, Khazar and other Turkic tribes in Azerbaijan, whose main occupation was sheep-breeding, played a decisive role in the transformation of carpet-weaving into an independent field of art from this period. Both in the early Middle Ages and later, various types of carpets became the most important element of the life of these tribes. A sack woven of sheep's wool, a sack, sackcloth, and so on played an invaluable role in the transportation of goods for the tribes, who were always in search of new pastures. Carpets and other carpet products were used to cover huts and trucks. Pile carpets were used to lay the huts [4].

In the late Middle Ages, the development of urban life and trade in Azerbaijan led to a sharp increase in demand for carpet products. Until now, carpet weavers, who only produced carpets for their families, began to market some of their products. The growing demand for carpet products has led to the widespread use of this art not only in rural areas, but also in cities. According to a source compiled in the 10th century, during this period Mugan became famous for its sacks and pieces, and the cities of Nakhchivan, Khoy and Salmas for their carpet products. The city of Nakhchivan became the main center of production and sale of 'zili' and 'khali' type carpet products [5].

The fact that carpet products are becoming more and more a commodity has brought to the fore the issue of its artistic design. Carpets woven from yarn dyed in cheerful and fresh colors were highly valued in the market. Azerbaijani nature was rich in various types of grass, shrubs and trees to obtain all the colors and shades necessary for the artistic design of carpet products. According to experts, 1,500 species of wild, cultivated trees, shrubs and grass grow in Azerbaijan [6]. Despite the richness of the dye-bearing plants, the dyers used only part of them to obtain color, depending on the nature and vegetation of each region [4].

Until the end of the 19th century, when artificial chemical dyes were invented, the dye plant (Rubia L.), which was an excellent raw material for obtaining red and its various shades, played an important role in the artistic design of Azerbaijani carpets. If we take into account the widespread use of red and its various shades in the artistic design of carpet products, it becomes clear why this plant was in great demand not only in Azerbaijan but also far beyond its borders during the whole Middle Ages. Commenting on the importance of this plant, better known in Russian sources as 'marena', one of the authors wrote that "in addition to dyeing wool, silk and even cotton red, it also helps to dye various products in other colors"[7]. The roots of this plant, which contain alizarin and purpur, were especially valuable. It was possible to get brown from the first layer of its shell, red from the second layer, and dark red from its core. Depending on the time of delivery, the degree to which the root is peeled, as well as the method of preparation of the dye solution, it was possible to obtain several more shades of color from the root of the dye [4]. According to available ethnographic data, the root of the dye plant was also used to dye wool yarns red with the help of animal origin dyes. In addition to wine stone or cherry lavashana, powdered coconut root powder was added to the solution made from the insect called cochineal, which was widespread in the territory of Nakhchivan, Yerevan and Karabakh khanates [8]. The red color obtained by this method was very bright and did not lose its freshness for a long time.

Medieval data show that Azerbaijan was one of the main cultural centers of the dye plant in the world. Ibn Hovgal, an Arab geographer-traveler who lived in the 10th century, gives information about the cultivation of a large number of dye plants in Varsan, Barda, Bab al-Abwab (now Derbent) provinces of Azerbaijan, the islands in the Caspian Sea, the basin and estuary of the Kura and Araz rivers. There is information that in the XVII century the dye plant was mostly grown in Nakhchivan, in the Azadabadadli circle on the left bank of the Araz River, as well as in Shirvan and exported to neighboring countries [5].

The cultivation of the dye plant in Azerbaijan became more widespread in the 18th and 19th centuries, and became increasingly important for industry. During this period, the main centers of dye production were considered to be Guba and Derbent khanates. The city of Derbent also played an important role in trade in the roots of the dye. The large-scale production of dyes in these regions was given a serious impetus by the sharp increase in demand for natural dyes due to the development of the textile industry in Russia. It should also be noted that the interest in the dye plant grown in Azerbaijan in Russia in Russia dates back to the first half of the XVIII century. Russian Tsar Peter I, who occupied the Caspian littoral regions of Azerbaijan in 1722-1723, demanded that the Russian commandant in Derbent send 10 or 20 pounds of dye roots and study its market price [9].

In the late 18th and early 19th centuries, the dye root produced in Azerbaijan was exported to Russia both by land and by sea. Official reports from the customs offices in the cities of Astrakhan and Gyzlar show that in 1778-1781, 39,382 pounds of dye roots were shipped from Azerbaijan to Russia by land through the city of Gyzlar, and in 1789-1793 by sea via Astrakhan [10]. The German traveler P. Pallas informs that in 1794, 5 ships, each loaded with 5,000 pounds of dye roots, were docked in the port of Astrakhan at the same time [11, p.193]. The rapid growth of demand for dye root in the Russian market has led to a sharp rise in its selling price in this country. Thus, while each pound of this product was sold for 2-4 rubles in 1781-1782, it rose by 11-14 rubles in the 90s [8, p. 98], and by 18 rubles in the middle of the 19th century [11].

The Russian Empire, which occupied the lands of Azerbaijan at the beginning of the 19th century, along with its other riches, adapted the production of dye to its economic interests and began to pay great attention to the development of this field. The Russian business community, which flows into the Guba and Derbent regions, has managed to significantly expand the area of dye plantations and get more crops. Suffice it to say that in 1850, 72,632 pounds of dye were sent to Russia from Derbent alone [11]. In the following years, the production of dye in Guba and Derbent regions became more widespread, and its exports to Russia increased even more. According to the available statistics, in 1863-1872, 2.5 mln. rubles worth of dye root was sent [4].

The dye plant was also successfully cultivated in Ganja, Shirvan and Karabakh regions of Azerbaijan. The dye grown in these regions not only met local demand, but was also exported to neighboring provinces and states. At the beginning of the 19th century, there are reports that the Karabakh khanate sent 10,000 pounds of dye roots to Iran every year [13]. However, the discovery of alizarin, an artificial dye, in 1869 dealt a severe blow to the cultivation of the dye plant and soon led to its complete extinction. Azerbaijani carpet weavers also widely used the flowers of a plant called saffron (Crocus Sativus L.) in the artistic design of their products. There is information about the cultivation of 4 types of saffron in Azerbaijan, of which there are 1,800 species in the world. The flowers of saffron, a perennial herb that blooms in the fall, have been used as a spice in many confectionery, traditional dishes, and soft drinks. This plant also played an invaluable role in the textile industry, as well as in the dyeing of yarns for weaving various types of carpets.

The available data show that saffron has historically been grown mainly in the Absheron Peninsula and Derbent region of Azerbaijan. The sandy soil and warm climatic conditions of the Absheron Peninsula were especially favorable for the cultivation of this plant and had a very positive effect on its productivity. Although the cultivation of saffron required a great deal of labor from the farmer, the large income earned led to the constant expansion of the sown areas of this plant. The traveler SG Gmelin, who visited Azerbaijan in the 70 s of the XVIII century, gives information about the sale of saffron for each pound of saffron for a very large amount for the period - 100 rubles [15]. According to the information of the 1930 s, the residents of Absheron earned an average of 360,000 rubles a year from the sale of saffron. The annual income of traders engaged in the export of this product to Iran and Russia was 200,000 rubles [4]. Despite its high price, the high demand for Absheron saffron in the Shamakhi, Guba, Sheki and Lankaran khanates of Azerbaijan, as well as in neighboring countries such as Russia and Iran, led to a steady increase in its area under cultivation. Our calculations based on archival documents compiled at the beginning of the 19th century show that at that time there were 943 saffron gardens in 26 villages of Absheron. The fact that saffron production is a very lucrative field encouraged the people of Baku to do the same. Again, it is clear from the information given in that document that the number of saffron gardens belonging to Baku residents reached 277 [16]. In the 1930s of the 19th century a total of 1,000 pounds of saffron was harvested from Absheron's saffron orchards. The main centers of saffron production in Absheron were the villages of Shuvalan, Bilgah and Mashtaga. According to the information of 1885-1886, more than half of the 1643 farms engaged in saffron production in the whole Absheron peninsula fell to the share of Mashtaga village [17].

Dyers also used a plant called “naz”, a branch called “orange tree”, wild apple root, autumn leaves of mulberry tree, onion peel and core to dye carpets yellow. In general, dyes preferred plants that were more accessible to them, depending on the region in which they worked. Walnut, pomegranate, peach, apricot, quince, mulberry, apple, cornel and other fruit trees' leaves, shoots, fruits and even bark were used for this purpose in the regions where horticulture is widespread, including the foothills and plains of Guba, Karabakh, Ganja and Gazakh. Carpet weavers working near the forests give oak (Gvercus sessitlora), wild plum (Prunus insititia), elm (Ulmus campestris), sumac (Rhus cotinus), maple (Acer platanoinos), maple (Acer platanoides) to give their products the color they want. , as well as walnut, Rhamnus L., rabbit apple, bird pear (Sorbus L.), sagebrush (Cotinus Hill) and other trees, which are unique to the forests of certain regions [4].

During the dyeing of wool yarn, Azerbaijani carpet weavers used alfalfa and subalpine meadows near the carpet-weaving regions to weed alfalfa, sarikol, geranium, varlik, khinagulu, gulkhatmi, daziotu, sabahgul, gulumbahar and others. They were also able to benefit from annual and perennial grasses and flowers. The painters knew exactly what color it was possible to get from each of these plants, when they were harvested, and passed this knowledge on to those who came after them. Collected plants, flowers, roots, etc. after careful drying, it was crushed and some were even pulverized. All this work was carried out in spring, summer and autumn.

The best raw material for dyeing carpets blue was considered to be a dye plant called indigo. This plant, native to India, was in great demand in all countries where the art of weaving was developed, including Azerbaijan. The widespread use of blue in the artistic design of Azerbaijani carpets played an important role in the constant growth of this demand. It should also be noted that after the occupation of Azerbaijan by Russia, the demand for this plant increased even more. This is confirmed by the import of 51,000 pounds of indigo to Russia in 1850 alone, worth 2.5 million rubles. Rusiya hökuməti bu vəziyyətdən qurtarmaq üçün Yelizavetpol və Lənkəran qəzalarında indiqo yetişdirmək üçün cəhd göstərsə də uğur qazana bilməmişdi [19].

Carpet weavers dyed wool yarns with dyes obtained from dyed plants, after the main field work was completed, or rather in the autumn. Until the autumn, they also spun wool into various yarns and made it ready for dyeing and then weaving.

Dyeing of wool yarns with dyed plants was carried out in the same way in almost all regions of Azerbaijan, except for indigo. It should also be noted that more women were involved in both the supply of dye plants and the dyeing process. The women carpet weavers used to add wool yarn before dyeing it to the desired color. Studies show that 22 types of additives were used to add wool to different parts of the South Caucasus. Additives such as zay, iron sulphate, wine stone, potash, cornel and cherry lavash, which dyers call “kalagar”, were considered to be the best helper in absorbing plant dyes into wool yarns firmly and evenly [20].

After the addition, the wool was dyed. Large copper pots or earthenware vessels were used for this purpose. Depending on the nature of the dye plant, dyers carried out the dyeing process in different ways. To dye the wool yarn red, they peeled the washed and dried root of the dye and kept it in water for 3 days. The wool was then placed in a pot and boiled over a low heat until the desired color was obtained. To get a darker color, had to continue boiling for a day, sometimes two days. 4 kg of yarn, 3 kg of cherry acid and 12 kg of dye were used to dye 16.4 kg of yarn red. Immature walnut shells and walnut and oak bark were used to obtain black. The wool was taken out of the pot after being boiled with walnuts all day long. Iron sulphate was added to the solution in the pot after filtering. The yarn was then re-immersed in the solution and kept there for another 12 hours. In order to get the yellow color, white clover was placed in a pot with a thread and boiled. In the mountainous part of Karabakh and Zangazur, white clover was first boiled in water until a thick solution was obtained, and only then was the yarn put into it. Various methods and combinations of dye plants were used to obtain the brown color. In Guba, for this purpose, a solution made of crab cherry bark was added to the cleaned dye, or the dye dyed with the dye was put into a jar containing indigo solution for a few minutes. In Shusha, yellow dye was obtained by boiling it with quince leaves and shoots. [4].

As mentioned above, indigo was used as the main raw material to get the blue color. The method of obtaining blue was also significantly different from the method of obtaining other colors. While the dye was boiled in water in various combinations to obtain most of the colors, the fermentation method was used to obtain the blue color. For this purpose, 2 pounds of lime and 4 pounds of potash were dissolved in water, and after the addition of 1 pound of honey or raisins, the solution was heated to 50-60 degrees. The solution, prepared in a pottery jar, began to ferment after a few days and was ready for painting. The yarn, intended for dyeing blue, was removed from the jar and squeezed after 20-30 minutes. When removed from the cube, the yellow thread turned green first and then blue under the influence of air. When it was necessary to get a darker color, the placement of the yarn in the jar was repeated several times [21]. Dyeing was also called "cube dyeing" because the dyeing of textiles into blue was done in pottery jars.

Dyeing the product green was also done by dyeing the jars. Since it was not possible to obtain a ready-made dye for this color, the dyers first dyed the product yellow and then put it in a jar prepared to obtain a blue color. It should also be noted that the dyeing of textiles in blue and green gangs required perfect skill and hard work from those engaged in this work. As a result, professional artisans called “dyers” dyed wool and silk blue and green in Azerbaijani cities. One of the two painting workshops operating in Ganja at the beginning of the XIX century [13], and one of the three painting workshops in Shusha [7] specialized in dyeing wool and silk products blue. The so-called “weavers” were engaged in dyeing textiles in other colors.

CONCLUSION

As can be seen, dyed plants grown in the territory of Azerbaijan, and in some cases imported from abroad, played an important role in the development of the art of carpet weaving. Carpets woven from yarns dyed with dyes derived from dyed plants have sometimes retained their cheerfulness and freshness for centuries, and were highly regarded by carpet experts as a work of art. It is no coincidence that various types of carpets woven by Azerbaijani carpet weavers with great skill are now displayed as valuable exhibits in many famous museums around the world. However, the use of plant colors in carpet weaving required a great deal of effort and time from the craftsmen. In addition to the supply of dye plants, these plants were required to spend 2 days to obtain yellow and brown colors, 3 days to obtain black colors, and 4 days to obtain red and blue colors. If we take into account that 7-12 colors and shades of colors are used in the artistic design of Azerbaijani carpets, we will see that more time is spent on this work. All this necessitated the discovery of cheaper and easier-to-use artificial chemical dyes.

REFERENCES

1. Habibullayev O.H. Archaeological excavations in Kultapa. Baku. 1959, 128 p
2. Latyshev V.V News of the ancient writers about the Scythians and the Caucasus. Volume I, Saint Petersburg, 1890, 289 p
3. Vahidov R.M. Mingachevir in III-VIII centuries. Baku, Publishing House of the Academy of Sciences of Azerbaijan. 1961, 179 p
4. Isaev M.D. Carpet production of Transcaucasia. Published by the Scientific Research Institute of Caucasian Studies of the USSR Academy of Sciences. Tiflis.1932, 224 p
5. Heydarov M.Kh. Cities and urban craft of Azerbaijan in the 13th - 17th centuries Baku, "Elm". 1982, 280 p
6. Kasumov M. Dyeing plants of Azerbaijan and their use in carpet production. // Art of Oriental Carpets. September 5-11, 1983 Baku, "Elm". 1988, pp. 141-149

7. Survey of Russian possessions beyond the Caucasus. Part III-IV, St. Petersburg. 1836,476 p
8. Alieva A. Pile carpets of Azerbaijan in the 19th and early 20th centuries. Baku, "Elm". 1987, 144 p
9. Lystsov V.P., Persian campaign of Peter I. 1722-1723 M., 1951, 344 p
10. Mustafayev J. Craftsmanship in Azerbaijan during the khanates. Baku, “Science”. 2002, 272 p
11. Pallas P.S. Remarks on a trip to the southern state holder of the Russian Empire in the years 1793 and 1794. Bd. İ, Leipzig. 1797, 76 p
12. Niftaliev R.Yu., Alieva E.K. Mare-breeding in Derbent in the first half of the 19th century. // 250 years of the unity of Ingushetia with Russia: time, events, people - Collection of scientific articles based on the materials of the international scientific-practical conference. Magas, June 3-6, 2020 Nazran, Ken LLC. 2020, 324 p
13. Acts of the Caucasian Archaeographic Commission. Vol.II IV, Tiflis, 1870, Vol.II, 1238 p, Vol.IV, 1016 p
14. Gasimov M., Muradov V. Painting. Baku, “Science”, 2017, 292 p
15. Gmelin S.G. Travels across Russia to explore all three kingdoms of nature. Volume III, Part I, St. Petersburg, 1785, 336 p
16. Azerbaijan State Historical Archive. f.24, siy.1, work 51, 407 p
17. Ethnography of Azerbaijan. In 3 Vol. I Vol.II, Baku, “East-West”, 2007, 344 p
18. Newspaper "Caucasus". 1851,№ 3, pp. 46
19. Caucasian calendar for 1855, Tiflis. 1854, pp. 86-115
20. Voronkov N.V. Dyeing wool carpet yarn with durable dyes. // Carpet production. KOIZ. 1931, pp. 71-96
21. Piralov A.S. A short sketch of the handicrafts of the Caucasus. SPb., Typo-Lithograph "Anchor". 1913, 127 p

РОЛЬ КРАСИЛЬНЫХ РАСТЕНИЙ В РАЗВИТИИ АЗЕРБАЙДЖАНСКОГО КОВРОТКАЧЕСТВА

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В развитии азербайджанского ковроткачества, имевшее глубокие исторические корни, важную роль сыграли красильные растения, которые росли как в диком, так и в культурном виде в различных регионах Азербайджана. На азербайджанские ковры, в художественном оформлении которых использовались растительные краски,был большой спрос как на внутреннем, так и на внешнем рынках. Азербайджанские ковроткачихи после протравления шерстяных ниток окрашивали их в нужные цвета, получаемые из различных растений. Ковры, окрашенные растительными красками, не линяли и долгое время сохраняли свою свежесть и блеск. В художественном оформлении каждого экземпляра ковровых изделий Азербайджана использовались 7-12 цветов и оттенков растительного характера.

Ключевые слова: *ковроткачество пряжа, красильные растение, цвет, красильное дело, марена, шафран, индиго, протрава.*

AZƏRBAYCAN XALÇAÇILIQ SƏNƏTİNİN İNKİŞAFINDA BOYAQ BİTKİLƏRİNİN ROLU

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Qədim tarixə malik olan Azərbaycan xalçaçılığının inkişafında ölkəmizdə yetişən, bəzi hallarda isə xarici ölkələrdən gətirilən boyaqxassəli bitkilər mühüm rol oynamışdır. Bu bitkilərin köməyi ilə yüksək bədii keyfiyyətlə tərtib edilən Azərbaycan xalçalarına istər daxili, istərsə də xarici bazarlarda böyük tələbat var idi. Boyaqxassəli bitkilərin xüsusiyyətlərini dərindən mənimsəyən xalçaçı qadınlar yun iplikləri əvvəlcə aşqarlama prosesindən keçirir, sonra isə bitki mənşəli boyalarla rəngləyirdilər. Araşdırmalar göstərir ki, Azərbaycanın müxtəlif bölgələrində toxunan xalça məmulatlarınınhər birinin tərtibatında bitki mənşəli 7-12 rəng və rəng çalarından istifadə olunurdu.

Açar sözlər: *xalçaçılıq, iplik, boyaqxassəli bitki, rəng, boyaqçılıq, boyaqotu, zəfəran, indiqo, aşqar.*

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INVESTIGATION OF PYROCONDENSATE OBTAINED DURING PYROLYSIS OF VACUUM GAS OIL

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It is known that in the current petrochemical industry, the use of liquid products from thermal pyrolysis rich in aromatic hydrocarbons as a raw material is of great importance. The widespread use of these products in the chemical synthesis, paint and varnish industry and in the manufacture of medicines makes it urgent to increase the yield of these products and create a new raw material base for their purchase. For this purpose, our research was carried out not with direct expulsion gasoline, which is the traditional raw material for thermal pyrolysis, but with a vacuum gas oil rich in naphthenic and aromatic hydrocarbons. We analyzed our experiments by comparing the yield of products obtained without subjecting the vacuum gas oil to hydrotreating and then without subjecting to hydrotreating. In this case, although a decrease in the yield of propane and an increase in the yield of butane was observed, a 10% (mass) increase(from33.31% to 43.31% of the mass) in the yield of pyrocondensate was observed in the thermal pyrolysis of vacuum gas oil compared to thermal pyrolysis of direct-fired gasoline. As a result, it is convenient to use vacuum gas oil as a raw material to increase the yield of pyrocondensate in the process of thermal pyrolysis.

***Keywords**: thermal pyrolysis, vacuum gas oil, gasoline, pyrocondensate, propane, ethane, butane, benzene, toluene, xylene, water vapor, zeolite, mordemite, coke.*

INTRODUCTION

Developing countries in the petrochemical industry differ in the scale of production of low-molecular olefins - ethylene and propylene. About 90% of organic matter is produced using oil and natural gas as raw materials. This raw material is widely used in the production of large quantities of petrochemical products: ethylene, propylene, butadiene, benzene, toluene, xylene and methanol, which is a basic part of the organic chemical industry [1].

Thus, the main unsaturated hydrocarbons - ethylene, propylene and butadiene fractions are obtained by thermal pyrolysis at different temperature ranges (750-850^{0}C) using raw materials from ethane to gas oil fraction in the presence of water vapor [2,3]. Along with these products, piocondensates are also obtained at various costs.

In European countries, 90% (mass) production of ethylene is obtained directly from expulsion gasoline. When using a lower molecular weight gasoline fraction, a decrease in ethylene yield is observed, thus increasing the consumption of raw materials for the production of 1 ton of ethylene. However, there is a significant change in the composition of the liquid products- pyrocondensate obtained from the process. In this case, the concentration of aromatic hydrocarbons in the pyrocondensate and the yield of heavy pyrolysis resin above 200° C also increase. In the process of medium-temperature pyrolysis (770-780° C) of gasoline, the concentration of the fraction with a high boiling point is 14-16%, but when the process is switched to a high temperature mode, this concentration increases to 18-20% (mass). The concentration of the fraction with a high boiling point in the liquid products obtained during the pyrolysis of atmospheric gas oil is 50% (mass) [4].

Table 1.

Products obtained during thermal pyrolysis of various raw materials

№	Raw material	Product yield, %(mass)				
		ethylene	propylene	butadiene	BTX	other
1	Ethane	84.0	1.4	1.4	0.4	13.8
2	Propane	44.0	15.6	3.4	2.8	34.2
3	Gasoline (light)	40.3	15.8	4.9	4.8	34.2
4	Gasoline (heavy)	31.7	13.0	4.7	13.7	36.8
5	Gas oil (light)	25.0	12.4	4.8	11.2	46.7

- BTX -benzene, toluene, xylene

In the present study, we aimed to investigate the yield of pyrocondensate, mainly by replacing disposal expulsion gasoline, which is the traditional raw material of the pyrolysis process, with vacuum gas oil. The selected raw materials were analyzed.
By “FİSHER” reactive method, moisture content of vacuum gas oil, density of GOST3900-85, kinematic viscosity of GOST33-2016, conventional viscosity of GOST6258-85, coking of GOST5987-51, freezing temperature of GOST20287-91, sulfur content of GOST19121-73, ash content of GOST7885-86 were determined by methods. The composition of the obtained pyrogas was determined on a gas-liquid chromatograph "ЦВЕТ -500".

EXPERIMENTAL PART

To carry out these experiments, we took a vacuum gas oil from a vacuum device at the Baku Oil Refinery. The vacuum we choose as a raw material is obtained by processing fuel oil in a gas oil-fired vacuum device. The resulting vacuum is subjected to a gas-oil hydrocracking process and fed to the catalytic cracking process to obtain high-octane gasoline. Vacuum gas oil is also used as a raw material in the production of solid paraffins and ceresins using selective solvents.

The research was carried out in a flow-type thermal pyrolysis unit built in a laboratory. Vacuum gas oil, which is a heavy crude oil, contains some nitrogen and sulfur compounds, as well as aromatic hydrocarbons and asphaltenes. If the content of sulfur in gasoline, which we take as a raw material, is 0.01-0.07%, in vacuum gas oil (VG) it is 0.3%, where sulfur is mainly in the form of thiophenes, and nitrogen compounds in the form of pyridine and quinoline. [5]. From this point of view, we must subject the vacuum gas oil to the process of thermal pyrolysis by subjecting it to the process of hydrotreating. We first analyzed the vacuum gas oil we took for the process and gave the indicators in table 2.

Table 2

Vacuum gas oil indicators

№	Name of the indicators	Quantity, % (mass.)
1	Fractional composition: - boiling point, ^{0}C , not too much -20% is distilled at a certain temperature, not too much; - 902% is distilled at a certain temperature, not too much - end of boiling, ^{0}C	240 350 535
2	Conditional viscosity, at 50^{0}C	1.76
3	Kinematic viscosity, at 50^{0}C, mm^{2}/sec	8.96
4	Coking, not more than %	0.4
5	Mass fraction of sulfur, not more than %	2.5
6	Mass fraction of mechanical mixtures, %	-
7	Ignition temperature in a closed bowl, not lower than ^{0}C	148
8	Density at 20^{0}C, kg/m^{3}	860-950
9	Freezing temperature, ^{0}C, not lower	+8

We began our research by conducting thermal pyrolysis of the first vacuum gas oil and then the vacuum gas oil, which underwent a disposable and double hydrotreating process. The results are given in table 3.

Table 3

The main products from the pyrolysis of vacuum gas oil

№	Products	Raw materials % (mass.)		
		1	2	3
1	H_2+CH_4	8.2	7.8	9.8
2	C_2H_4	17.6	19.1	20.1
3	C_3H_6	10.9	11.5	12.0
4	C_4H_8	4.4	3.8	4.0
5	C_4H_6	4.5	3.3	4.0
6	Fraction C_5-200^{0}C Benzene Toluene	17.0	19.0 4.3 2.7	20.0 4.9 2.1
7	Fraction >200^{0}C	36.0	32.0	26.0

Note: 1-initial vacuum gas oil; 2-Disposable hydrotreating vacuum gas oil: 3 -Double hydrotreating vacuum gas boiler.

Table 4 shows the results of thermal pyrolysis of vacuum gas oil with disposable expulsion gasoline at different temperatures. Zeolite catalyst was used as a catalyst here.

It can be seen from table 4 that the amount of basic products obtained during the thermal pyrolysis of vacuum gas oil differs from the amount of products obtained from the catalytic pyrolysis of disposable gasoline. As can be seen, the amount of ethylene and propylene decreases, and the difference in output decreases with increasing temperature. During thermal pyrolysis of vacuum gas oil, the amount of butylene increases, and here, this difference begins to decrease with increasing temperature. The amount of olefins in C_2-C_4 gases differs by 1-1.5% (mass) from the amount of gases obtained from the pyrolysis of light fractions. During pyrolysis of vacuum gas oil at a temperature of 600^0C , the amount of gaseous fractions is higher than in disposable expulsion gasoline. However, we see that at a temperature of 650-700^0C, a decrease in excess gaseous fractions is observed.

Table 4

Thermal pyrolysis of various oil fractions

Products	Concentration of gaseous reaction products , %.(mass.) T^0C					
	600	650	700	600	650	700
	Disposal expulsion gasoline			Vacuum gas oil		
Hydrogen	1.52	1.79	1.99	1.05	1.69	2.31
Methane	6.31	8.74	15.15	8.9	13.73	16.73
Ethan	2.22	3.29	4.78	5.60	5.56	8.53
Propane	6.59	7.99	2.16	5.31	5.23	2.95
Butane	9.61	8.69	3.26	3.29	3.05	1.51
i-butane	10.59	6.74	3.18	5.80	4.42	2.59
Ethylene	7.94	11.44	20.01	7.39	8.62	19.54
Propylene	36.64	22.25	32.75	28.81	27.65	2548
∑butylene	18.59	22.07	14.56	33.29	28.68	17.53
divinyl	0.00	0.00	2.15	0.56	1.38	2.78
Amount of olefins in the gas, % (mass)	63.17	65.76	67.32	69.50	64.95	62.54
Yield of olefins, % (mass)	11.19	18.87	37.94	22.37	23.97	30.13
Yield of ethylene and propylene,% (mass)	7.90	12.54	29.74	11.65	13.38	21.68
Gaseous C_1-C_4	17.72	28.70	56.36	32.19	36.90	48.17

RESULTS AND DISCUSSION

Table 5 shows the physicochemical parameters of pyrocondensate obtained during thermal pyrolysis of vacuum gas oil. During thermal pyrolysis of vacuum gas oil, its decomposition into products depends on its hydrocarbon content and, of course, the conditions of the process. According to our research, paraffin-naphthenic hydrocarbons make up 50-55% of the hydrocarbon content of vacuum gas oil.

Here, parfins have a normal structure, while naphthenes have a mono and hexacyclic structure. Vacuum gas oil differs from disposable expulsion gasoline by its high content of aromatic hydrocarbons and relatively b-i and tricyclic aromatic hydrocarbons and small content of mono and polycyclic hydrocarbons. The high thermal stability of aromatic hydrocarbons in vacuum gas oil slows down the formation of gaseous olefins. It is known that this is due to the fact that bi- and polycyclic hydrocarbons slow down the formation of olefins from the corresponding paraffins.

It can be said that the retardation effect of polycyclic hydrocarbons is higher than that of bicyclic hydrocarbons.

Table 5

Yield of pyrocondensate obtained from thermal pyrolysis of vacuum gas oil at 700^{0}C subjected to hydrotreating process with disposable expulsion gasoline.

Products	Yield, % (küt.)	
	BQB	VQ
pyrocondensate	33.31	43.31
coke	2.08	14.90
The amount of olefin in the gas ,%(mass.)	56.36	62.25

The reason why polycyclic hydrocarbons slow down the formation of olefins is explained by the fact that strong bi- and polyphenyl radicals combine with weak free radicals formed during the decomposition of aliphatic hydrocarbons, breaking the chain of targeted reaction. However, our results show that the yield of olefins during the pyrolysis of vacuum gas oil is not lower than that of disposable gasoline. As the temperature rises to 700^{0}C, a significant amount of resin is formed, which leads to the formation of coke [6].

As a result, the ratio of carbon to hydrogen increases during the pyrolysis of vacuum gas oil at a temperature of 700^{0}C. In this case, the amount of saturated hydrocarbons in the released gas increases. The amount of olefin hydrocarbons decreases. As a result, coke is formed due to the participation of some unsaturated hydrocarbons in the condensation reaction.

The main point in the evaluation of vacuum distillate as a raw material is the yield of pyrocondensate (liquid products) obtained in the process of thermal pyrolysis with a boiling point above 200^0 C.

The yield of this pyrocondensate also directly depends on the rate of coking formation in the device. According to the literature and our research, this coking should not exceed 15% [7].

CONCLUSION

As a result of the research, based on the results obtained during the thermal pyrolysis of the vacuum gas oil, we can say that its application to this process had a positive effect on increasing the yield of liquid fractions of vacuum gas oil. Under certain conditions obtained during the application of vacuum gas oil as a raw material, an increase in the yield of low-molecular olefins is observed, and at the same time, the yield of pyrocondensate obtained directly from the pyrolysis of gasoline, which is the main product of our research goal, was 31.3% (mass), while in vacuum gas oil this yield was 43.3% (mass). This means an increase of about 10% (ass). In this regard, we can note that by expanding the research, it is possible to intensify the process of thermal pyrolysis using heavy fractions of oil as a raw material and increase the raw material reserves of the pyrolysis process to obtain procondensate with high flow at the expense of vacuum gas oil. In this regard, it can be noted that by expanding the research, it is possible to intensify the process of thermal pyrolysis using heavy fractions of oil as a raw material and increase the raw material reserves of the pyrolysis process to obtain procondensate with high yield at the expense of vacuum gas oil.

REFERENCES

1. Mukhina T.N., Barabanov N.L., Babash S.E. and other Pyrolysis of hydrocarbon raw materials. // M .: Chemistry. 1987, 239 p
2. Berenc A.D., Vol-Epshtein A.B., Mukhina T.N., Avrekh ETC. Processing of liquid pyrolysis products. // M .: Chemistr. 1985, 216 p
3. Rubiner I.A., Belyaikin V.M., Elistratov S.T., Starkovskaya M.N., Zelenkova A.F. High-temperature pyrolysis of hydrocarbon raw materials. Review inf. Ser. petrochemistry and oil shale refinery. // TsNII inf. and technical-econom. issled. oil refinery and petrochem. prom-sti. 1989,No.6,pp.1-50
4. Sheit V.P., Murtazin F.R., Akhmetov S.A., Bashirov R.F. Pulse and flow-through method for studying thematic and catalytic pyrolysis. Chemistry and chemical technology. Issue 2, UFA, 2001, pp.35-40
5. Lukianov P.I.,Batistov A.G. Pirolysys of oil raw materials.-Gostoptekhizdat.2002.-247 p
6. Yusif-zade A.A., Dadaeva G.Ch. “Study of catalytic pyrolysis of a fraction at a temperature of 130-2300C. "Bulatov Readings. Materials of the IV International Scientific and Technical Conference (March 31, 2020) Technical and technological developments. Volume-6 İSSN 2587-8913 Krasnodar. 2020,pp.44-47
7. Yusif-zade A.A., Dadaeva G.Ch. Abbaslı N.A. "Coking of liquid products of catalytic pyrolysis" Colloquium-journal.№10 (34), 2019, ISSN 2520-6990, pp.197-202

ИССЛЕДОВАНИЕ ПИРОКОНДЕНСАТА ПОЛУЧЕННОГО В ПРОЦЕССЕ ПИРОЛИЗА ВАКУУМ ГАЗОЙЛЯ

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Известно, что в современной нефтехимической промышленности использование в качестве сырья жидких продуктов термического пиролиза, богатых ароматическими углеводородами, имеет большое значение. Широкое использование этих продуктов в химическом синтезе, лакокрасочной промышленности и производстве фармацевтических препаратов создание новой сырьевой базы и увеличение выхода этих продуктов является актуальным. С этой целью наши исследования проводились не с бензином прямого сгорания, который является традиционным сырьем для термического пиролиза, а с вакуумным газойлем, богатым нафтеновыми и ароматическими углеводородами. Мы проанализировали наши эксперименты, сравнив выход продуктов, полученных без гидроочистки вакуумного газойля и выход продукта с гидроочисткой *вакуумного газойля. Несмотря на то, что в течении процесса наблюдалось снижение выхода пропана и увеличение выхода бутана, в процессе термического пиролиза вакуумного газойля по сравнению с термическим пиролизом бензина прямого сгорания наблюдалось увеличение выхода пироконденсата от 33.31% до 43.31%масс, на 10% (масс.). По результатам исследований нужно отметить, что для увеличения выхода пироконденсата в процессе термического пиролиза в качестве сырья выгодно использовать вакуумный газойль.*

Ключевые слова: *термический пиролиз, вакуумный газойль, бензин, пироконденсат, пропан, этан, бутан, бензол, толуол, ксилол, водяной пар, цеолит, мордепит, кокс.*

VAKUUM QAZOYLUNUN PİROLİZİ ZAMANI ALINAN PİROKONDENSATIN TƏDQİQİ

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Hal hazırki dövrdə inkişaf etmiş neftkimya sənayesində aromatik karbohidrogenlərlə zəngin termiki piroliz prosesindən alınan maye məhsulların xammal kimi istifadəsi böyük əhəmiyyət kəsb edir.Bu məhsulların kimya sintezində, lak-boya sənayesində və dərman peraparatlarının hazırlanmasında geniş tətbiq olunması bu məhsulların çıxımının artırılmasını və onların alınması üçün yeni xammal bazasının yaradılmasını aktual edir. Bu məqsədlə tədqiqat işimizi termiki piroliz prosesinin ənənəvi xammalı sayılan birbaşa qovulma benzini deyil, tərkibi naften və aromatik karbohidrogenlərlə zəngin olan vakuum qazoylu götürülmüşdür. Təcrübələrimizi vakuum qazoylunu hidrotəmizləməyə məruz etmədən və daha sonra hidrotəmizləmə məruz edərək alınan məhsulların çıxımını müqaisə edərək təhlil etdik. Bu zaman propanın çıxımında azalma, butanın çıxımında artma müşahidə edilsədə birbaşa qovulma benzininin termiki pirolizinə nisbətən vakkum qazoylunun termiki pirolizində pirokondensatın çıxımının 33.31% dən 43.31% kütləyə qədər,10% (küt.) artması müşahidə edildi. Nəticə etibarı ilə qeyd etmək olar ki, termiki piroliz prosesində pirokondensatın çıxımının artırılması istiqamətində xammal kimi vakuum qazoylundan istifadə etmək əlverişlidir.

Acar sözlər: *termiki piroliz, vakuum qazoyl, benzin, pirokondensat, propan, etan, butan, benzol, toluol, ksilol, su buxarı, seolit, mordemit, koks.*

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ADSORPTION TREATMENT OF WASTE WATER FROM OIL AND PETROLEUM PRODUCTS

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Sorption treatment of waste water from oil and oil products was carried out. Methods for determining the oil capacity of sorbents are selected. For wastewater purification, 3 samples of sorbents were examined: coal from apricot kernels, from walnut shells, and coal from hazelnut shells. The most effective sorbent used was selected, namely, hazelnut shell charcoal. A cleaning scheme is proposed. The optimal parameters of the process have been determined. At optimal process parameters (temperature 20^0C, pressure 760 mm mercury table), the degree of purification is 99.5%.

Keywords: *adsorption, adsorbent, cleaning, analysis, oil, petroleum products.*

INTRODUCTION

The problem of wastewater treatment (WT) is urgent due to the alarming rate of depletion of drinking water supplies on Earth.

Wastewater treatment is a targeted change in the characteristics of wastewater discharged into open water bodies or sewers using various technical methods and means.

The problem of clean water is very acute in Azerbaijan [1]. This is mainly due to the high level of contamination of water bodies with dumped waste, which are contaminated with oil hydrocarbons (HC).

At present, none of the existing methods of wastewater treatment from oil and oil products, separately, allows water to be purified to the level of maximum permissible concentration (MPC), from an environmental - economic position. Wastewater treatment to the MPC level is carried out by various treatment methods: mechanical, physicochemical or chemical, biological method [2,3].

Mechanical methods of wastewater treatment from oil and oil products are based on mechanical settling, separation of solid and liquid phases of pollutants from water.

The biological method is based on the ability of microorganisms to use the hydrocarbons contained in wastewater as a food source. Due to the structural features, the processes of biological oxidation of hydrocarbons are slow.

Physicochemical methods of purification consists in the introduction of chemical reagents into the purified water - surfactants, which contribute to the enlargement of emulsified particles as a result of their interaction and combining into aggregates [4-6].

The use of physicochemical methods for wastewater treatment has a number of advantages in comparison with others: the ability to remove toxic, biochemically non-oxidizable organic contaminants from wastewater; achieving a deeper and more stable degree of cleaning; smaller structures; less sensitivity to load changes; the possibility of full automation; no need to monitor the activity of living organisms; the possibility of recovering various substances [7].

In recent years, sorption methods have been mainly used to purify wastewater from oil and oil products. Sorption wastewater treatment allows achieving the required hygienic standards, but this method requires a lot of money for the purchase and replacement of spent sorbents. This method is mainly used at the post-treatment stage.

The purpose of this article is to study various adsorbents for the purification of dry matter from oil and oil products and the choice of an effective sorbent [8].

Adsorption methods are widely used for deep purification of wastewater from dissolved organic substances after biochemical treatment, as well as in local installations, if the concentration of these substances in water is low and they are not biodegradable or are highly toxic. The use of local installations is advisable if the substance is well adsorbed at a low specific consumption of the adsorbent.

Adsorption is used to neutralize wastewater from phenols, herbicides, pesticides, aromatic nitro compounds, surfactants, dyes, etc. The advantage of the method is high efficiency, the ability to purify wastewater containing several substances, as well as the recovery of these substances. Adsorption treatment can be regenerative, that is, with the extraction of a substance from the adsorbent and its utilization, and destructive, in which the substances extracted from the wastewater are destroyed together with the adsorbent. The efficiency of adsorption cleaning reaches 80 - 95% and depends on the chemical nature of the adsorbent, the size of the adsorption surface and its availability, on the chemical structure of the substance and its state in solution.

Active carbons, synthetic sorbents and some production wastes (ash, slags, flasks, sawdust, etc.) are used as sorbents. Mineral sorbents are used relatively rarely, since the energy of their interaction with water molecules is high and sometimes exceeds the energy of adsorption.

EXPERIMENTAL PART

To determine the content of oil products in water, the following methods were used:

IR spectroscopy and fluorimetric. The method of IR spectroscopy is intended for measuring the mass concentration of oil products in samples of natural, drinking and waste water using an infrared Fourier - spectrometer "Infralum FT - 02". The fluometric method is designed to determine the mass concentration of petroleum products with a measured concentration range of 0.005 - 50 mg / dm^3. Measurements are carried out using the Fluorat-02 device.

To identify the activity of the sorbents used, it is necessary to determine the oil capacity of the adsorbents [9,10]. For this purpose, the necessary equipment and materials are used:

- technical laboratory scales of the 4th accuracy class;
- stopwatch of the 3rd accuracy class;
- medical plastic syringe with a volume of 150 sm^3;
- laboratory stand;
- sieves with a diameter of 80 mm, a height of 30 mm, a mesh size of 0.2 mm;
- graduated cylinder according to GOST 1770 - 74, with a volume of 100 sm^3;
- measuring ruler;
- chemical glasses according to GOST 25336-82, volume 50-100 sm^3;
- steel spatula.

To determine the oil capacity of the sorbent, the syringe with the piston is first weighed with an error of not more than 0.01 g. A portion of the bulk sorbent with a volume of 50 sm^3 is weighed. The sorbent is placed in a container filled with water with an oil layer floating on its surface and kept until the sorbent is completely saturated with oil. The sieve is removed, the oil is allowed to drain for 30 seconds, and the sorbent is transferred with a spatula into the syringe. The syringe with the saturated sorbent is weighed. The difference in the mass of the syringe before and after the absorption of the oil sorbent is used to calculate the total oil absorbed by the used sorbent.

Then the oil is squeezed out of the syringe into a pre-weighed glass. The spin is stopped 10 minutes after the oil stops flowing. The amount of free (squeezed out) oil is determined by the difference in the mass of the glass before and after pressing oil into it.

The syringe is removed from the device and weighed with the squeezed out sorbent, determining the amount of bound oil.

The absorption cycle is repeated 5 times.

After that, we process the result as follows:

The mass of total oil (M_{HO}) is determined by the formula:

$$M_{HO} = M_O - M_S - M_C$$

M_O – weight of the syringe with the oil-saturated sorbent, g;
M_S – weight of the syringe with sorbent, g;
M_C – weight of a sample of sorbent, g.

The mass of squeezed oil (M_{Hsq}) is determined by the formula

$$M_{Hsq}(g) = M_2 - M_1,$$

M_2 – weight of a glass with oil, g;
M_1 – glass weight without oil, g.

The mass of absorbed oil (M_{Hsq}) is determined by the formula:

$$M_{Hsq}(g) = M_{HO} - M_{Hsq},$$

M_2 – weight of a glass with oil, g;
M_1 – glass weight without oil, g.

The ratio of squeezed out and absorbed oil (%), determined by the formula:

$$M_H(\%) = 100xM_{HO}/M_{Hsq}$$

M_{Hsq} - mass of absorbed oil, g.

If necessary, consider the oil-carrying capacity of the structured sorbent for 5 cycles.

Determination of the sorption capacity of adsorbents is carried out as follows. 250 ml of water is poured into a beaker and a certain amount of oil or petroleum product is added and a blurred spot of an emulsion with water is obtained. Next, this emulsion is passed through a layer of adsorbent with a particle size of 0.5-3.0 mm, and then the mass of the sorbent is calculated. Thus, the oil absorption capacity of the sorbent for the purification of waste water from oil and oil products is determined, which is 98 - 99.5% (fig.1).

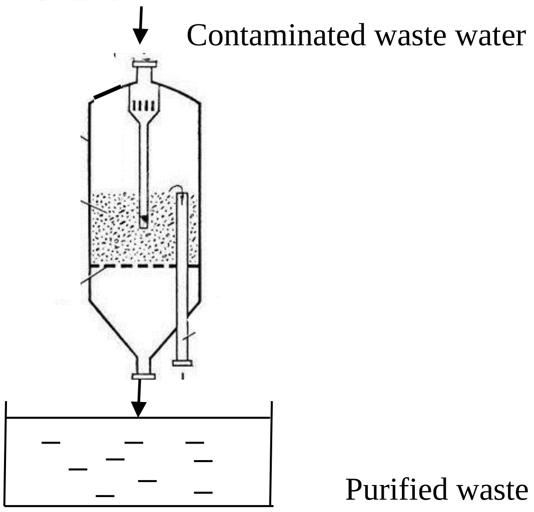

Fig.1. Adsorber.

The study of sorbents, namely coal from apricot kernels and coal from walnut shells, showed low oil capacity at dynamic transmission mode: 0.13-0.14 g / g and 0.15-0.17 g / g, respectively [11].

Table 1

The physical properties of the studied sorbents are shown

№	Sorbent	Physical properties	
		Density, kg / m^3	Average humidity,%
1	Apricot kernel charcoal	690	50
2	Walnut shell charcoal	750	82
3	Hazelnut shell charcoal	800	91

RESULTS AND DISCUSSION

The research results are presented in fig. 2.

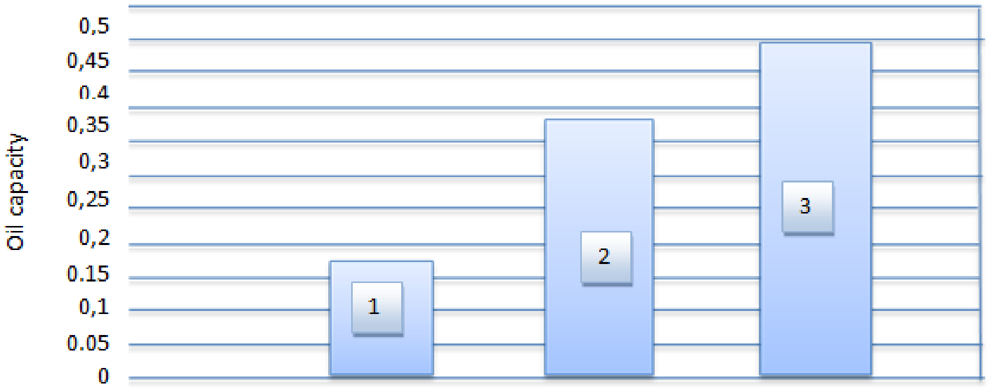

Fig.2. Histogram of the oil capacity of sorbents with a fraction diameter of 0.5 - 3.0 mm at an initial concentration of oil (oil products) of 1 g / l. 1-charcoal from apricot kernels, 2-charcoal from walnut shells, 3- charcoal from hazelnut shells.

To obtain a complete picture of the effectiveness of sorbents, the dependence of the oil capacity of the sorbents on their density and moisture was studied [12]. The research results are shown in table 2.

Table 2

Oil Capacity of used adsorbents depending on their density and moisture content

№	Сорбент	Density, kg / m^3	Moisture,%	Oil capacity, g / g
1	Apricot kernel charcoal	690	50	2,0
2	Walnut shell charcoal	750	82	2,4
3	Hazelnut shell charcoal	800	91	3,5

The lower figure graphically shows the oil absorption capacity of sorbents over time.

Figure 3 shows the dependence of oil absorption on sorbents.

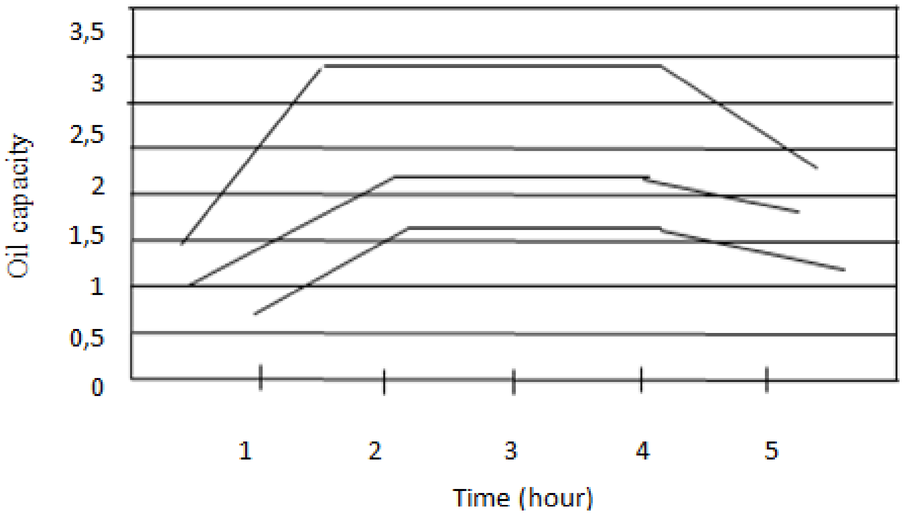

Fig.3. Graph of the dependence of the oil absorption capacity of sorbents on time.

Summarizing the data obtained, we can conclude that the sorbent from hazelnuts with a density of 800 kg / m^3 and a fraction diameter of 0.5-3.0 mm has the best oil-absorbing properties.

Experiments have shown that walnut shells treated at 300^{0}C is an effective and cheap sorbent that cleans wastewater from oil and oil products.

Methods for purification of waste water from oil and oil products have been developed. Samples of sorbents from apricot kernels, walnuts and hazelnuts were selected. Methods for the analysis of oil and oil products in wastewater have been carried out. A method for determining the oil capacity of sorbents has been developed. The studies of the absorbed capacity of the sorbents were carried out on the selected samples.

CONCLUSION

Sorption treatment of waste water from oil and oil products was carried out. Methods for determining the oil capacity of sorbents are selected.

For wastewater purification, 3 samples of sorbents were examined: coal from apricot kernels, from walnut shells, and coal from hazelnut shells.

The most effective sorbent used was selected, namely, hazelnut shell charcoal.

A cleaning scheme is proposed.

The optimal p`arameters of the process have been determined.

At optimal process parameters (temperature 200^0C, pressure 760 mm Hg), the degree of purification is 99.5%.

REFERENCES

1. Kelbaliev G.I., Suleimanov G.Z., Phariborz A. Zoroufi, Gasanov A.A. Rustamova A.I. Extraction separation and cleaning of sewage waters by organic solvents with recirculation / Russian journal of applied chemistry, Moskva. 2011, Vol. 83 № 6, pp. 1114-1119
2. El-Naas M., Alhaija M., Sulaiman A.Z. Evaluation of an activated carbon packed bed for the adsorption of phenols from petroleum refinery wastewater. Environ. Sci. Pollut. Res. 2017, pp. 24-31
3. Jung K., Oh S., Bak H., Song G.H., Kim H.T. Adsorption of Arsenic and Lead onto Stone Powder and Chitosan-Coated Stone Powder. Processes 2019,№ 7, pp.593-599
4. Yuan M., Tong S., Zhao S., Jia C.Q. Adsorption of polycyclic aromatic hydrocarbons from water using petroleum coke-derived porous carbon. J. Hazard. Mater. 2010, 181, pp.1115–1120
5. Cortés F., Water Remediation Based on Oil Adsorption Using Nanosilicate Functionalized with a Petroleum Vacuum Residue. Adsorpt. Sci. Technol. 2014, 32, pp. 197–207
6. Kunjirama M, Saman N, Johari K., Song S.T., Kong H., Cheu S.C., Lye J, Mat H. Adsorption affinity and selectivity of 3-ureidopropyltriethoxysilane grafted oil palm empty fruit bunches towards mercury ions. Environ. Sci. Pollut. Res. Int. 2017 , pp.19-24
7. Behnood R., Anvaripour B., Fard N.,Farasati M. Petroleum hydrocarbons adsorption from aqueous solution by raw sugarcane bagasse. Int. J. Emerg. Sci. Eng. 2013, 1, pp.96–99
8. Nethaji S., Sivasamy A., Mandal A.B. Adsorption isotherms, kinetics and mechanism for the adsorption of cationic and anionic dyes onto carbonaceous particles prepared from Juglans regia shell biomass. Int. J. Environ. Sci. Technol. 2013, 10, pp.231–242
9. Yagodovsky V. D. Adsorption / Porous adsorbents, 2015, pp.87-93
10. Zubareva G.I. Deep purification of waste waters of petrochemical production / G.I. Zubareva, E.V. Kopytova, A.V. Gurinovich //Ecology and Industry - March 2007, pp.15-21
11. Xenicus. T.V. New sorbent for cleaning waste water from organic pollutants / T.V. Ksenik, A.A. Yudakov, A.V. Perfiliev // Ecology and Industry - April 2009, pp.19-21

12. Lebedev I.A. Development of technology for filtering and sorption water purification from oil products / I.A. Lebedev, L.F. Komarova // Ecology and Industry - June 2008, pp. 43-45

АДСОРБЦИОННАЯ ОЧИСТКА СТОЧНЫХ ВОД ОТ НЕФТИ И НЕФТЕПРОДУКТОВ

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Проведена сорбционная очистка сточных вод от нефти и нефтепродуктов. Выбраны методы для определения нефтеемкости сорбентов. Для очистки сточных вод исследовали 3 образца сорбентов: уголь из абрикосовых косточек, из скорлупы грецких орехов и уголь из скорлупы фундука. Выбран самый эффективный из использованных сорбентов, а именно уголь из скорлупы фундука. Предложена схема очистки. Определены оптимальные параметры процесса. При оптимальных параметрах процесса (температура 20^0*C, давление 760 мм рт. ст.) степень очистки составляет 99,5%.*

Ключевые слова: *адсорбция, адсорбент, очистка, анализ, нефть, нефтепродукты.*

TULLANTI SULARININ NEFT VƏ NEFT MƏHSULLARINDAN ADSORBSIYA ÜSULU ILƏ TƏMIZLƏNMƏSI

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Neft və neft məhsullarının tullantı sularının sorbsiya təmizlənməsi həyata keçirilmişdir. Sorbentlərin yağ tutumunu təyin etmək üsulları seçilmişdir. Tullantı sularının təmizlənməsi üçün 3 sorbent nümunəsi araşdırıldı: ərik ləpələrindən kömür, qoz qabığından kömür və fındıq qabığından kömür. İstifadə olunan ən təsirli sorbent, yəni fındıq qabığı kömürü seçildi. Təmizləmə sxemi təklif olunur. Optimal proses parametrləri təyin olundu. Optimal proses parametrlərində (temperatur 20^0*C, təzyiq 760 mm civə sütunu) təmizlənmə dərəcəsi 99,5% -dir.*

Açar sözlər: *adsorbsiya, adsorbent, təmizləmə, analiz, neft, neft məhsulları.*

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THE USE OF UREA TO OBTAİN A COMPOSİTİON FOR CLEANİNQ SURFACES FROM DEPOSİT OF SALTS OXİDES AND METAL HYDROXİDES

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The demand for new inhibitors and their compositions, which are easily obtained from existing petrochemical raw materials also have economical advantages in terms of application is growing significantly. This article presents the content and results of research conducted to produce of corrosion inhibitor. For that reason , compounds based on urea and phosphoric acid were synthesized firstly. Optimal reaction conditions of the synthesis process were invistigated~~:~~ temperature 95 - 100 °C, the duration of the mixture residence in the reactor is 8 hours. The kinetic regularities of the reaction were investigated. Based on the obtained products, a corrosion inhibitor with protective effect of up to 90% at a flow rate of 100 mg / l in hydrocarbon deposits in mineral water was developed. Higher carbonic acids are obtained by oxidation of cobalt (CORK) and 2-ethylhexenal. Optimum conditions for the process have been invistigated. Oxidation period 24 hours, temperature 120°C, oxygen consumption 20 l / h. On the based of synthesized products, a corrosion inhibitors with a protective effect of 91 + 92% at a flow rate of 25 mg / l was obtained for oilfield equipment of hydrocarbon deposits.

Keywords: *higher carboxylic acids,bottoms, cobalt regeneration (KORK), 2-ethylhexenal, corrosion inhibitor, oxidation products, diamines.*

INTRODUCTION

A large number of compounds and their mixtures are known to possess the properties of corrosion inhibitors. However, the ever-growing requirements for their quality, availability and low cost determine the need for targeted improvement of existing inhibitors and the search for new inhibitors and their compositions that are highly effective, easily obtained from available petrochemical raw materials and economical both from the point of view of their synthesis and use. Therefore, the synthesis of compounds, on the basis of which effective corrosion inhibitors can be obtained, is an urgent problem. The aim of this work is to synthesize multifunctional compounds based on urea and by-products of butyl alcohol production and development of corrosion inhibitors based on them.

To achieve this goal, the following tasks were solved:

1.Synthesis of compounds based on carbamide and phosphoric acid. Development of a method for producing a corrosion inhibitor based on the synthesized compound, sodium nitrite and methanol fraction for the production of butyl alcohols.

2. Development of a technology for obtaining higher carboxylic acids by oxidation of the bottom residue of cobalt regeneration (KORK) and 2-ethylhexenal, development of a method for producing a corrosion inhibitor based on oxidation products and diamines.

For the first time, the synthesis of urea with phosphoric acid was carried out. The kinetics of the reaction has been studied. On the basis of the synthesis products, a new effective corrosion inhibitor with a protective effect of 90% at a flow rate of 100 mg / l has been developed.

A technology has been developed for the oxidation of the distillation residue of the regeneration of cobalt and 2-ethylhexeneal with air oxygen. It is shown that the use of Panchenkov's packing in an oxidizing column increases the rate of oxidation processes by 3 times. A new effective corrosion inhibitor has been obtained on the basis of higher carboxylic acids.

EXPERIMENTAL PART

For the first time developed an effective solvent for imidazolines in the formulation inhibitors based on the methanol fraction of the bottoms of cobalt regeneration and the production of butyl alcohols.

$$(NH_2)_2CO + (HO)_3\,PO > NH_2C(O)\,NH\,P(O)(0H)_2 + H_2O$$

Based on laboratory experiments, the most optimal dilution ratio was selected. It was found that the molar ratio (MS) water: carbamide: phosphoric acid 5: 2.2: 1 at a temperature of 95°C, and atmospheric pressure allows you to obtain a homogeneous reaction mass.

The synthesis product is characterized by the following indicators: the degree of corrosion protection of steel is St. 3 87%, pour point - 38°C.

The kinetics of the reaction has been studied; it is characterized by a low rate. We have investigated the possibility of accelerating the reaction. The rate of reaction of carbamide with phosphoric acid was judged by the time it took to reach the pH of the medium equal to 4. At this value of the acidity of the medium, approximately 50% of the conversion of the starting reagents achieved; therefore, this parameter is chosen for the convenience of measurements. It was found that the intensity of stirring does not affect the reaction rate; the reaction is not complicated by diffusion inhibition and proceeds in the kinetic region. As the temperature rises from 60 to 95°C, the reaction rate increases. An increase in the concentration of urea increases the rate of polycondensation. However, an excess of urea creates conditions for its precipitation at low temperatures [1-3]. Therefore, studies were carried out on the effect of dilution of urea with water on the condensation rate.

To increase the degree of protection, we included sodium nitrite in the product composition, the addition of which does not affect the reaction rate; as a result, the protective effect of the corrosion inhibitor is increased by 5%.

It should be noted that the methanol fraction is a by-product of butyl alcohol production, which determines the feasibility of its use from the standpoint of increasing the economic efficiency of production.

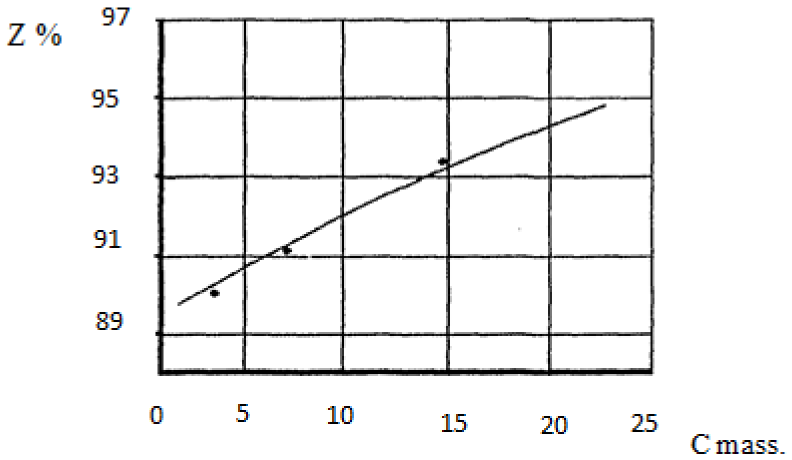

Fig.1. Influence of sodium nitrite concentration (C) on the protective action of the inhibitor (Z). n = 60 rpm "1, T = 95°C, the amount of water is 5 mol, *MS* carbamide / phosphoric acid = 2.0.

Pour point reduction can be achieved by dilution.Indeed, the dilution of the reaction mixture with methanol helps to reduce the pour point of the inhibitor from -38 to -46,°C, without exerting a significant effect on the protective effect (fig. 3). However, methanol is an expensive product, and therefore we tested water-soluble alcohols and methanol fraction of butyl alcohol production It was found that their use equally effectively allows to reduce the pour point of the inhibitor (fig. 4). Based on the results of laboratory studies, a scheme for obtaining the IK-10 inhibitor has been developed (fig. 2).

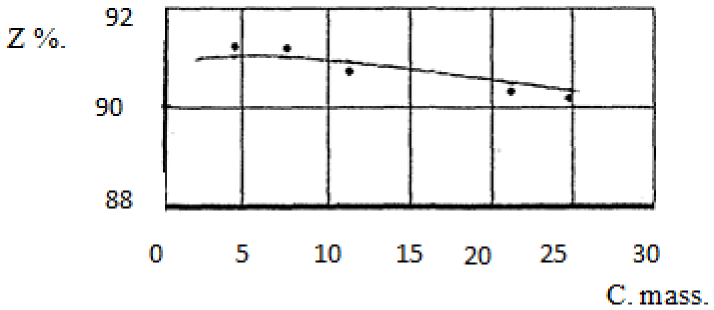

Fig.2. Dependence of the protective action of the inhibitor (Z) on the concentration of methanol (C), n = 60 rpm "', T = 95°C, concentration of $NaN0_2$ = 15 wt%, U «r carbamide = about p phosphorus to –ta.

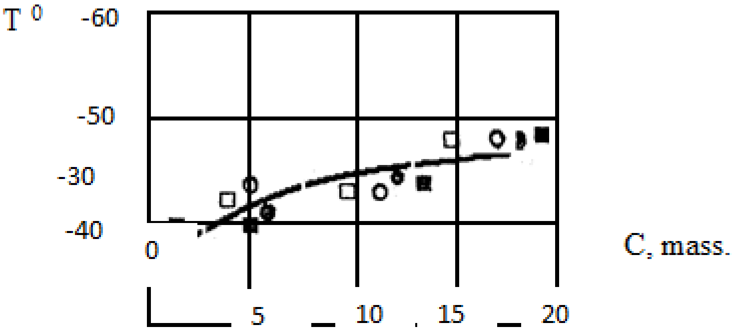

Fig.3. Influence of the concentration of solvents(C) on the pour point of the inhibitor (t). "- ethanol; ° - methanol; • - methanol fraction producedbutanol; * - isopropanol.

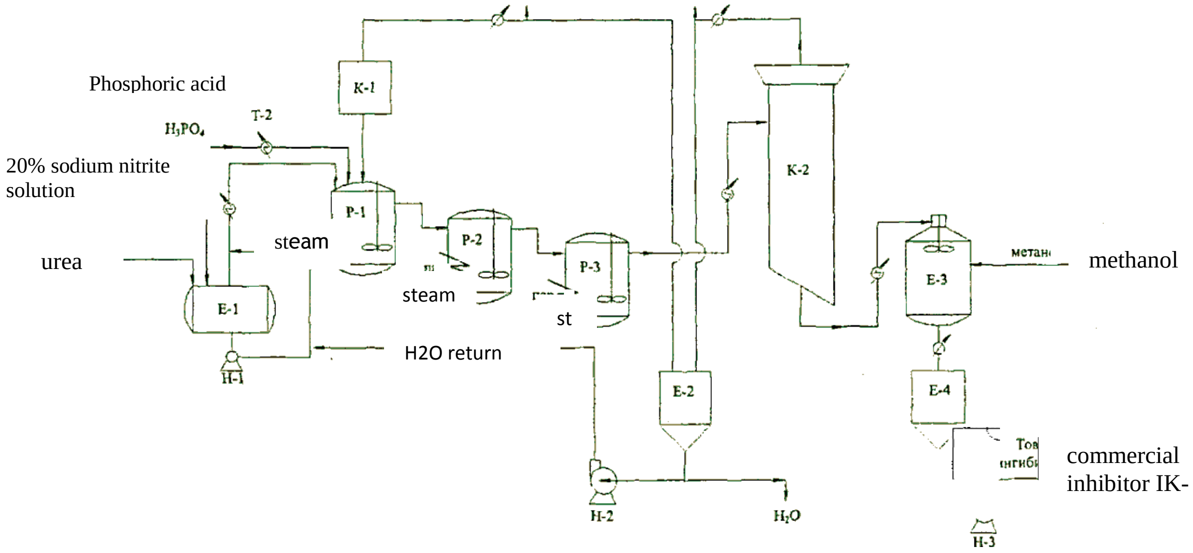

Fig.4. Basic technological scheme for the production of corrosion inhibitor IK-10.

RESULTS AND DISCUSSION

The process takes place in a cascade of reactors (R-1, R-2, R-3) at a temperature of 95 -100°C, conditional residence time 6 hours, molar ratio of carbamide: phosphoric acid 2.0: 1, sodium nitrite concentration 10% by weight, methanol in a commercial corrosion inhibitor 15%. Protective action of a corrosion inhibitor is 90% at a flow rate of 100 mg / l.

The optimal performance of a batch reactor of a calon type with a volume of 5 m3 filled with a packing (F max) of Panchenkov was determined using the graph and formula

$$F_{max} = G_p \cdot x / \tau_{op} + \tau_a$$

Where, G_p - weight of reaction mass, x- conversion degree, fraction, $\tau_{op} + \tau_{a.op}$ - optimal timing and timing of auxiliary operations.

It should be noted that the methanol fraction is a by-product of butyl alcohol production, which determines the feasibility of its use from the standpoint of increasing the economic efficiency of production.

Pour point reduction can be achieved by dilution.Indeed, dilution of the reaction mass with methanol helps to reduce the pour point of the inhibitor from -38 to -46 "C, while not exerting a significant effect on the protective effect. However, methanol is an expensive product, and therefore we have tested water-soluble alcohols and methanol fraction of butyl alcohols production It was found that their use equally effectively reduces the pour point of the inhibitor. Based on the results of laboratory studies, a scheme for obtaining the IK-10 inhibitor has been developed [4-5].

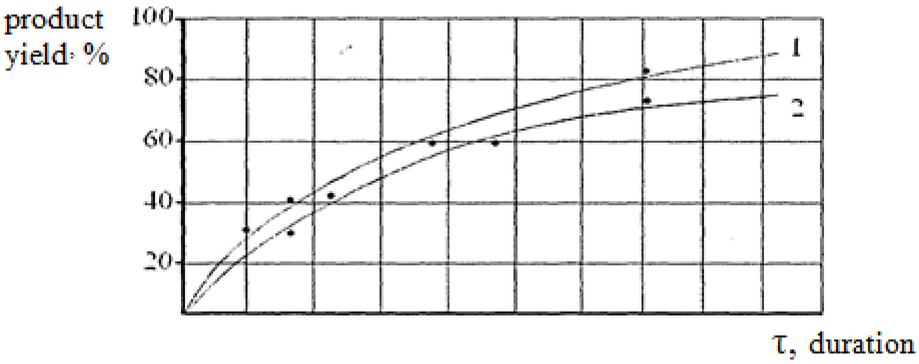

Fig.5. Dependence of the yield of reaction water on the duration of the experiment. Temperature 180-200 °C, oxidized mass: (OM-1: PEPA 1: 1) (1) and (OM-2: NEPA 5: 1) (2).

Table 1

Comparative characteristics of industrial inhibitors of the IKB-2-2, Tal-25-13R and IK-12 brands in the field waters of the Arlanskoye field.

№	Names	İKB-2-2	Tal-25-13P	İK-12
1.	Colour	Dark brown homogeneous liquid without mechanical impurities		
2.	Viscosity, Ct no more	40	100	30
3.	Pour point, °C, no more	-20	-25	-50
4.	Water content,%, no more	5	5	1,0
5.	Offset with oil	complete	complete	complete
6.	Protective action at an inhibitor consumption of 30 mg / l, not less	85	90	92

The results of the experiments indicate that the synthesis of imidazolines is completed within 8-9 hours. The products of synthesis were used to obtain a commercial inhibitor İK-12; distillate from distillation of KORK, metal fraction of butyl alcohols, as emulsifying agent - neonol. It has been established that an increase in the concentration of neonol NS affects the degree of protection in the gas phase. The protective effect is slightly increased in the oil and water phases and significantly depends on the concentration inhibitor [6-9].

The inhibitor of the following composition has the maximum protective action, wt%: active base - 20, neonol -4, solvent mixture - 76. At an inhibitor consumption of 25 mg / l, the protective action in the field water of the Arlanskoye field is 75% in gas, 92% in oil and 80% in aqueous phases.

Comparative characteristics of industrial corrosion inhibitors grade IKB-2-2, Tal-25-13R and the prototype IK-12 inhibitor are shown in table 1. The developed inhibitor of the IK-12 brand has a pour point of -46° C and a protective effect of 92% of the mass.

Carried out the synthesis of carbamide with phosphoric acid. The reaction of synthesis was studied, the optimal reaction conditions were found: temperature 95 - 100 ^{0}C, the residence time of the reaction mixture in the reactor 8 hours. The kinetic regularities of the reaction were investigated. On the basis of the synthesis products obtained, a corrosion inhibitor was developed, the protective effect of which in the field water Urengoyskoye field reaches 90% at a flow rate of 100 mg / l.

Fraction 140 - 260° C with a yield of 70% was isolated by rectification of the still residue from the regeneration of cobalt, which is recommended as a solvent for the imidazoline base in the production of corrosion inhibitors.

Higher carboxylic acids were obtained by oxidation of KORK and 2-ethylhexenal.

The duration of the oxidation is 24 hours, the temperature is 120° C, the oxygen consumption is 20 l / h. The use of the Panchenkov nozzle increases the rate of oxidation of the distillation residue from the regeneration of cobalt and 2 ethylhexenal by 3 times.

On the basis of higher carboxylic acids, a corrosion inhibitor was obtained, the protective effect of which for oilfield equipment of the Arlanskoye and Ishimbayskoye fields is 91 + 92% at a flow rate of 25 mg / l.

CONCLUSION

Compounds based on carbamide and phosphoric acid have been synthesized. A method for producing a corrosion inhibitor based on a synthesized compound, sodium nitrite and a methanol fraction of butyl alcohol production has been developed. A technology has been developed for obtaining higher carboxylic acids by oxidation of the cobalt regeneration bottom residue (KORK) and 2-ethylhexenal, and a method for producing a corrosion inhibitor based on oxidation products and diamines has been developed.

REFERENCES

1. Rakhmatullina Zh. F. Technology of oxidation of aldehyde to carboxylic acids and synthesis of corrosion inhibitors: materials of the XIII International conference of young scientists, students and graduate students / Rakhimkulov R.A. // Synthesis, study of properties, modification and processing of high-molecular compounds. Kazan, KSTU. 2009,pp.79-80.
2. Rakhimkulov A.G. Influence of the thermal effect of the reaction and process parameters on the corrosion rate of metals / Rakhimkulov R.A., Rakhmatullina J.F. conf. – Ufa. 2010, pp. 256-260

3. Rakhmatullina Zh.F. Technology of production of corrosion inhibitors for the oil industry / Rakhimkulov A.G., Evdokimova A.S., Muratov MM.// Bashkir Chemical Journal. - 2006.- T. 13, № 3, pp. 57-59
4. Nafikova R.F. The use of vat residues of butyl alcohols / Rakhmatullina Zh.F., Rakhimkulova A.A., Rakhimkulov A.G. // Bashkir Chemical Journal.2006,T. 13, № 3, pp. 60-62
5. Evdokimova A.S. Inhibitors of hydrogen embrittlement and hydrogen sulfide corrosion of metals / Rakhmatullina Zh.F. II Oil and gas processing and petrochemistry - 2007: materials of the VII Congress of oil and gas producers of Russia- Ufa, 2007, pp. 275 - 277
6. Rakhmatullina Zh.F ..Hydrogen embrittlement of main pipelines / Rakhimkulov RA, // VIII Congress of oil and gas producers of Russia: materials of the scientific-practical conference "Problems and methods of ensuring the reliability and safety of oil, oil pipelines and gas transportation systems." - Ufa . 2009, pp. 60 - 61
7. Rakhimkulov A.G. Production technology of corrosion inhibitor brand IK-10 for the oil industry / Rakhimkulov R.A., Rakhmatullina Zh.F. // VIII Congress of Russian Oil and Gas Industrialists: Materials of the International Scientific and Practical Conference "Oil and Gas Processing - 2009", Ufa, 2009, pp. 246-248
8. Rakhmatullina Zh.F. Development of recommendations for the protection of technological oilfield equipment from corrosion under the influence of water, hydrogen sulfide, carbon dioxide, acids, alkalis / Rakhimkulov R.A., Rakhmatullina J.F. // Problems and methods of ensuring the reliability and safety of oil, oil products and gas transportation systems: materials scientific-practical conf.,Ufa.2010,pp. 288-290
9. Rakhimkulov A.G. The mechanism of evaporation of metals and the influence of the thermal effect of chemical corrosion on the rate of dissolution of metals in water-salt solutions / Rakhimkulov R.A., Rakhmatullina J.F. Problems and methods of ensuring the reliability and safety of oil, oil products and gas transport systems: scientific and practical materials conf. – Ufa.2010, pp.283-287

ИСПОЛЬЗОВАНИЕ МОЧЕВИНЫ ДЛЯ ПОЛУЧЕНИЯ КОМПОЗИЦИИ ДЛЯ ОЧИСТКИ ПОВЕРХНОСТЕЙ ИЗ ОТЛОЖЕНИЙ ОКСИДОВ СОЛЕЙ И МЕТАЛЛИЧЕСКИХ ГИДРОКСИДОВ

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Спрос на новые ингибиторы и их композиции, легко синтезируемые из существующего нефтехимического сырья и экономичные с точки зрения синтеза и применения, растет с каждым днем. В статье представлены результаты исследований, проведенных для получения ингибитора коррозии. Для этого впервые были синтезированы соединения на основе мочевины и фосфорной кислоты. Найдены оптимальные реакционные условия процесса синтеза: температура 95-100^{0}С, время нахождения реакционной смеси в реакторе 8 часов. Исследованы кинетические закономерности реакции. На основе синтезированных продуктов, разработан ингибитор коррозии с защитным действием углеводородных отложений в минеральных водах до 90% при расходе 100 мг / л.

Высшие карбоновые кислоты получают окислением кобальта (CORK) и 2-этилгексеналя. Найдены оптимальные условия для процесса. Время окисления 24 часа, температура 120^0 *С, расход кислорода 20 л/час. На основе синтезированных высших карбоновых кислот получен ингибитор коррозии с защитным действием 91+92% при расходе 25 мг / л для нефтепромыслового оборудования углеводородных месторождений.*

Ключевые слова: *высшые карбоновые кислоты,, кубовой остаток, регенерация кобальта (КОРК),этилгексеналь, ингибитор коррозии, продукты окисления.*

METAL SƏTHLƏRİN DUZ OKSİDLƏRDƏN VƏ HƏRDƏN TƏMİZLƏNMƏSİ ÜÇÜN KARBAMİDDƏN İSTİFADƏ

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Mövcud neft-kimya xammalından asanlıqla əldə edilən və istifadəsi nöqteyi nəzərindən qənaətcil olan yeni inhibitorlara və onların kompozisiyalarına tələbat günü gündən artır. Məqalədə korroziya inhibitorları istehsal etmək üçün aparılmış tədqiqat işlərinin məzmunu və nəticələri verilmişdir. Belə ki bu məqsədlə əvvəlcə karbamid və fosfor turşusu əsasında birləşmələr sintez edilmişdir. Sintez prosesinin optimal reaksiya şərtləri tapılmışdır: temperatur 95-100^0 *C, reaktor qarışığının reaktorda qalma müddəti 8 saat. Reaksiyanın kinetik qanunauyğunluqları araşdırılmışdır. Alınan sintez məhsulları əsasında karbohidrogen yataqlarının mədən sularında qoruyucu təsiri 100 mq / l axın sürətində 90% -ə çatan korroziya inhibitorları hazırlanmışdır.*

Kobaltın (KORK) və 2- etilheksenalın oksidləşməsi yolu ilə ali karbon turşuları alınmışdır. Prosesin optimal şəraiti tapılmışdır. Oksidləşmə müddəti 24 saat, temperatur 120^0 *C, oksigen sərfi 20 l / saat. Sintez edilmiş ali karbon turşuları əsasında, karbohidrogen yataqlarının neft mədən avadanlığı üçün qoruyucu təsiri 25 mq/l axın sürətində 91+92% olan korroziya inhibitorları əldə edilmişdir.*

Açar sözlər: *Ali karbon turşuları,kub qalığı, kobaltın regenerasiyası, (KORK), 2-etilheksenal, korroziya inhibitorları, oksidləşmə məhsulları.*

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THE SYNTHESIS OF THE NANOENSEMBLE ON THE BASIS OF CROWN ETHER

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We synthesized the compound of azacrown class with macrocyclic structure. On the basis of synthesized macrocyclic compund, supramolecular ensembles with nanoparticles were structured. Structured azacrown macrocycles were studied by methods of the NMR and mass spectroscopy. Obtained nanoparticles were analyzed and their structures were studied by the methods of scanning electron microscopy, FTIR and also x-ray diffraction analysis. The Lambert-Buger-Bere UV spectroscopy method was used to determine the quantitative composition of nanoparticles. Also the mechanism of reaction with oxygen containing diamine were investigated.

Keywords: *azacrown ether, macrocycle, supramolecular ensemble, composite material.*

INTRODUCTION

Nowadays the magnetic nanoparticles found wide range of applications in various fields of science, technology and also in everyday life, for instance, in structure of composite materials in biotechnology and in up-to-date technologies. Directed transportation of medications[1], hypothermia[2], and also immune diagnosis[3] were considered as the best fields for application of magnetic nanoparticles. Using the magnetite nanoparticles[4], first of all, is related to ease of obtaining magnetite of required dispersion and its relative inertia. Today magnetite nanoparticles used in immune analysis and clinic diagnosis have superparamagnetic properties[5]. By linking azacrown ether and Fe_3O_4 nanoparticles we get ensembles of new generation and as a result, combining supramolecular chemistry and nanotechnology for designing new compunds based on supramolecular ensembles.

EXPERIMENTAL PART

The chemicals we used in the synthesis were of analytical grade sodium salicylate, thionyl chloride, solution of NaOH, n-butanol, $FeCl_3•6H_2O$, $FeSO_4•7H_2O$, chloroform, .2,2-(ethane-1,2-diylbis(oxy))bis(ethan-1-amine) , 1,3-dichloro-2-propanol, , NH_4OH (25 %), were purchased from Sigma-Aldrich ; Nutrient Broth was purchased from Biolife (Milano, Italia).

We put a number of cascading reactions. At first, we synthesized salicyloyl chloride and in the second step N,N'- ((ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl)bis(2-hydroxybenzamide) was synthesized (fig.1.). In third step of synthesis we obtained 2,3-hydroxy-7,8,10,11,14,15,23,24-octahydro-22H-dibenzo[i,p][1,4,11,15]-tetraoxa [7,19]diazacyclohenicosine-5,16(6H,13H)-dione (fig.2.). The NMR spectrum of intermediate sintone N,N'- ((ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl)bis(2-hydroxybenzamide) is given below.

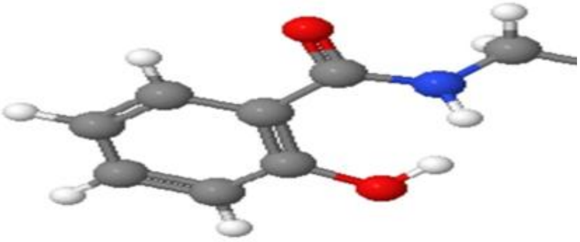

Fig.1. Fragment of the peptide bond in the synthon obtained.

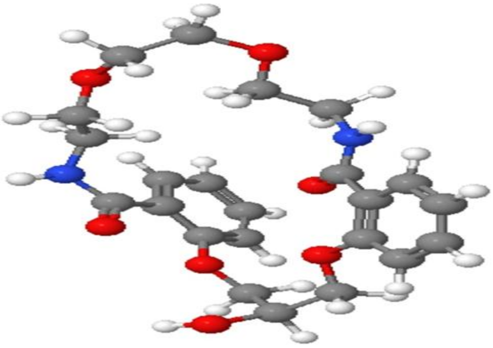

Fig.2. Molecule model: 2,3-hydroxy-7,8,10,11,14,15,23,24-octahydro-22H-dibenzo[i,p] [1,4,11,15]-tetraoxa[7,19]diazacyclohenicosine-5,16(6H,13H)-dione.

Synthesis

Salicyloyl chloride.

To the 500 ml flask containing 24 gr sodium salicylate while stirring accompanied by cooling 20 ml of thiony chloride were added by dripping. Flask used for reaction was equipped with calcium chloride tube. After reaction obtained mixture was cooled during 48 hours.

N,N'-((ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl))bis(2- hydroxybenzamide).

To the 200 ml flask with 3.0234 g of salicyloyl chloride in presence of pyridine catalyst and ortho xylene solvent diamine(2,2'-(ethylenedioxy)-bis(ethyleneamine)) was added by dripping. Reaction was accompanied by cooling.Found: ^{13}C NMR spectra: (DMSO-d6, δ, ppm.),69.09(2CH2), 69.81 (2CH2), 69.92 (2CH2), 117.98(2CH), 119.9 (2CH), 126.1 (2CH), 126.7 (2CH), 148.01 (2C), 160.3 (2C), 169.2 (2CO). ^{1}H NMR spectra: (DMSO-d6, ppm.),3.34t (4H, 2CH2), 3.47 t (4H, 2CH2), 4.3 s (4H, 2CH2), 6.91-8.18m (8H, Ar), 8.87s (2H, NH), 10.19s (2H, OH).

2,3-hydroxu-7,8,10,11,14,15,23,24-octahydro-22H-dibenzo[i,p][1,4,11,15]-tetraoxa-[7,19]diazacyclohenicosine-5,16(6H,13H)-dione.

In the 200 ml flask containing 150 ml of n-butanol as solvent the reaction by adding dropwise 1,3- dichloropropan-2-ol dissolved in 15 ml of n-butanol to NaOH mixture of N,N'-((ethane-1,2-diylbis (oxy)) bis (ethane-2,1-diyl)) bis (2-hydroxybenzamide) was carried. Reaction was conducted during 25 hours and obtained product after dissolving in water was extracted in to chloroform.

XRD - X-ray diffraction analysis was performed on Rigaku Mini Flex 600 XRD dif-fractometer in ambient. In all the cases, CuKα- radiation from a Cu X-ray tube (run at 15 mA and 30 kV) was used.

FTIR The functional groups, present in the powder samples of MC @ Fe_3O_4 were identified by Fourier Transform Infrared (FTIR) spectros-copy. FTIR spectra were recorded on a Varian 3600 FTIR spectrophotometer in KBr tablets. The spectrum was taken in the range of 4000 - 400 cm-1 at room temperature.

Scanning Electron Microscope (SEM) and Energy-Dispersive Spectrum (EDS) analysis SEM and EDS analysis of prepared samples of MC @ Fe_3O_4 nanoparticles were taken on Field Emission Scanning Electron Microscope.

^{1}H and ^{13}C NMR spectra were recorded on Brucker AC-300 (300 and 75 MHz, respectively), Varian VXR-400 (399.97 and 100.613) instruments, the internal standard everywhere was tetramethylsilane.

UV Spectroscopy. The UV spectra have been recorded on Spectrophotometer Specord 250 Plus. UV spectra were recorded at 278 nm for standard solutions of with different concentrations.

RESULTS AND DISCUSSION

When examining the NMR spectrum of the resulting intermediate synthon (fig.3), we found that we get a product that has functional groups for further synthesis based on it. İn further synthesis, we based on the reactions that we carried out earlier and now we can construct new supramolecular assemblies.

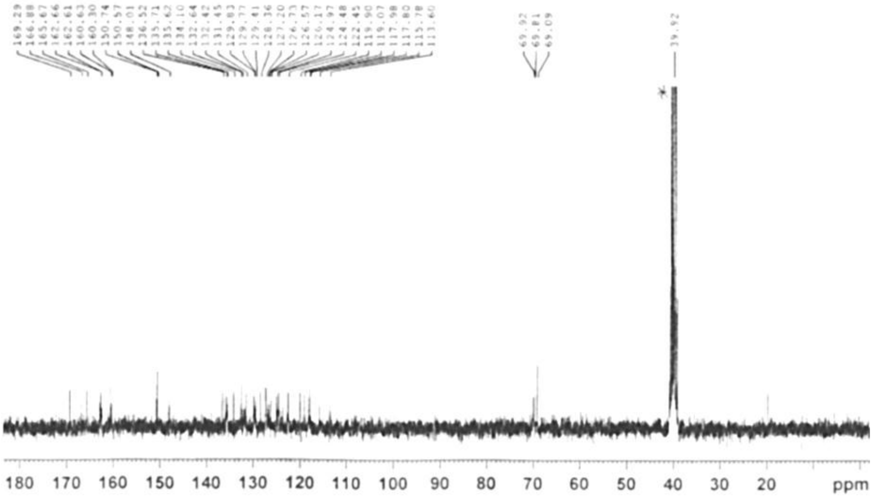

Fig . 3. ^{13}C NMR spectrum of intermediate sintone N,N’-((ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl))bis(2-hydroxybenzamide).

Structural morphology of macrocycle binded to magnetite (MC@Fe_3O_4) was determined by the scanning electron microscopy method and result is depicted on figure 4. It was determined that, obtained structures have size of 6-13 nm.

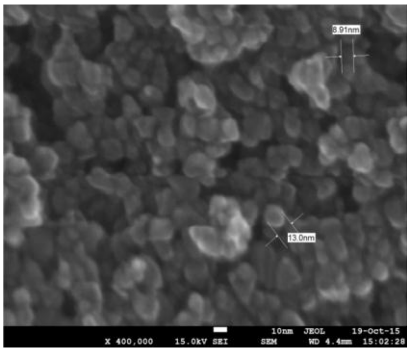

Fig.4. Scanning Electron Microscopy image of MC@Fe_3O_4.

CONCLUSION

We determined and matched the macrocycle of an azacrown ether containing a peptide bond in its structure with magnetite nanoparticles and studied the structure of the resulting supramolecular ensemble, which will become a good basis for the synthesis of new composite materials containing a peptide bond, which, as a result, can be good natural siderophores. Nanotechnology creates suitable conditions for decreasing of single dosage of medications and consuming drug of same class with acceptable minimal side effects.

REFERENCES

1. Thanh N.T.K., Robinson I., Tung L..Magnetic nanoparticles for biomedical applications: synthesis, characterization and uses, Dekker Encyclopedia of Nanoscience and Nanotechnology .2007, № 1, pp.1-10
2. Li, M., Gou H., Al-Ogaidi, I., Wu, N Nanostructured Sensors for Detection of Heavy Metals A Review, ACS Sustainable Chemistry Engineering .2013, № 1, pp. 713–723
3. Wu, W., He, Q., Jiang, C. Magnetic iron oxide nanoparticles: synthesis and surface functionalization strategies, Nanoscale Research Letters. 2008, № 3, pp. 397–415
4. Fegtle F., Webe E., Chemistry of “Guest-Host” Complexes. Synthesis, Structure and Applications, Moscow: Mir. 1988, pp. 513
5. Voronin D.V., Sadovnikov A.V., Beginin E.N., Shchukin D.G., Gorin D.A. Magnetic Composites with Embedded Magnetite Nanoparticles: Control of physical properties, applications, Journal Proceedings of the Saratov University, New episode. Series Physics. 2013,Vol.13, №2, pp. 50-54

СИНТЕЗ НАНОАНСАМБЛЕЙ НА ОСНОВЕ КРАУН-ЭФИРОВ

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Нами синтезировано соединение класса азакраунов макроциклического строения. На основе синтезированных макроциклических структур были структурированы супрамолекулярные ансамбли с наночастицами. Структурированные азакраун макроциклы были исследованы методами ЯМР, масс- спектроскопии. Полученные наночастицы анализировали и изучали их струтуры методами сканирующей электронной микроскопии, FTIR, а также рентгеноструктурным анализом. Для определения количественного состава наночастиц применялся метод на основе закона Ламберта–Бугера-Бера методом УФ-спектроскопии. Изучен механизм реакции с диамином содержащим в своей структуре кислородные атомы.

Ключевые слова: *азакраун эфир, макроцикл, супрамолекулярный ансамбль, композитный материал.*

KRAUN EFIR ƏSASINDA NANOANSAMBLLARIN SINTEZI

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Biz azakraun sinifinə aid olan makrotsiklik birləşməni sintez etdik. Sintez olunmuş makrotsiklik birləşmənin əsasında supramolekulyar ansambllar qurulmuşdur. Qurulmuş azakraun makrotsikllar NMR və kütlə spektroskopiya metodları vasitəsilə öyrənilmişdir. Əldə edilmiş nanohissəciklər SEM, FTIR metodları və həmçinin rentgen analiz vasitəsi ilə tədqiq edilmişdir. Nanohissəciklərin kəmiyyət tərkibini öyrənmək məqsədi ilə Lambert-Buger-Bere prinsiplərinə əsaslanan UB spektroskopiya metodundan istifadə olunmuşdur. Həmçinin əlavə olaraq tərkibində oksigen atomu daşıyan diaminlər ilə ilə reaksiya tədqiq olunmuşdur.

Açar sözlər: *azakraun efir, makrotsikl, supramolekulyar ansambl, kompozit material.*

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EFFECT OF STEAM ON CATALYTIC PYROLYSIS PROCESS

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In this paper, research is being conducted to improve the thermal cracking process and to alleviate the rigid process regime. It is known that the rigid thermal pyrolysis process in the petrochemical industry makes it one of the most economically and technologically difficult processes. In this regard, the intensification of the process is constantly being studied by specialists. The application of catalysts to the process of thermal pyrolysis and its transition to a mild mode can be an important factor. Given the urgency of the process, it is important to select catalysts that can be used at high temperatures for the catalytic pyrolysis process, to study its mechanism of action, to study the effect of yield and quality of the products obtained and to study the effect of water vapor applied to the selected catalyst. Taking these into account, in our research, for the first time in the process of thermal pyrolysis, using the natural Azerbaijani zeolite mordenite-type catalyst, we analyzed the results of this process with or without the presence of water vapor. Thus, the yield of ethylene in the process of thermal pyrolysis with the presence of a catalyst without water vapor at 650^{0}C was 10.03% (mass), and with the presence of water vapor was 11.44% (mass). At the appropriate temperature and conditions, the yield of propylene was 29.13% (mass) and 32.25% (mass). Thus, the natural Azerbaijani zeolite mordenite, which we used for the first time, was selected with its selectivity in the process of catalytic pyrolysis due to its more perfect structure than the catalysts known from the literature, and positive results were obtained.

Keywords: *thermal pyrolysis, catalytic pyrolysis, zeolite catalyst, mordenite, water vapor, straight run gasoline.*

INTRODUCTION

Acquisition of a wide range of chemical products from hydrocarbon raw materials through petrochemical synthesis is associated with the perspective development of the national economy. In this regard, the development of this sector is always relevant.

The main raw materials in the modern chemical industry are low-molecular olefins. The main source of low-molecular olefins is the pyrolysis process, which is a thermo-catalytic process of hydrocarbon gases and petroleum products.

At present, the pyrolysis of petroleum fractions in petrochemical industry in the world is carried out in a tubular furnace with the presence of water vapor. Although the pyrolysis process has been continuously updated since the introduction of the first industrial unit, the apparatus of the technological unit, as well as various technological junctions, has resulted in increased productivity. Besides, significant work has been done to increase the selectivity and efficiency of the process. Despite all this work, the indicators of this process are limited. From this point of view, the demand for the pyrolysis process makes it urgent to increase its raw material base, to improve the process economically in the petrochemical industry and to work on modifying the process.

The aim of this paper was to investigate the intensity of the catalytic pyrolysis process. Numerous catalyst systems have been studied as catalysts for the pyrolysis process. Among them, zeolite catalysts gave better results[7]. As a result of the application of these catalysts, an increase in the yield of propylene and butene was observed. However, during the application of the catalytic pyrolysis process, thanks to the catalyst supplied to the process, either the yield of the target product was increased or the temperature regime of the process was reduced. So far, both cases have not been possible at the same time. From this point of view, the investigation of the application of various catalysts continues

The use of a catalyst with a basic micro spheric zeolite for the production of low-molecular olefins has been studied in more detail.

EXPERIMENTAL PART

It is known that there are eight types of natural zeolites: - clinoptilolite, mordenite, erionite, shabazite, phillipsite, ferritite, limonite analsim. These are available in large natural deposits. Among these types of catalysts, clinoptilolite and mordenite zeolites are mostly used in the petrochemical industry. There are large deposits of both zeolites in our country. Natural zeolites are usually found in the form of tuff. Clinoptilolite tuff contains 70-90% clinoptilolite. At the same time, it contains various mineral mixtures - montmorillonite, celadonite, cristobalite, feldspar quartz, biotite, etc. available. "Aydagh" clinoptilolite is more popular in Azerbaijan [2].

The composition of Azerbaijani zeolite applied to the catalytic cracking process is shown in Table 1. The composition of mordenite, an Azerbaijani zeolite, was analyzed by “Derivatograph”, “Phase X-ray” and “Electromicroscope” methods. The main method of studying zeolite-related minerals in zeolite deposits is the "Diffrometric X-ray" method. In this way, in addition to mordenite, it contains clinoptilolite, montmorillonite, kvarsin, etc. it is possible to determine their existence. The amount of water, temperature resistance and dehydration area in mordenite were determined by "thermographic" analysis [3].

Table 1

Composition of Azerbaijani zeolite

№	Components	%, wt.
1	SO_2	59.48
2	$Al\ _2O_3$	25,67
3	Fe_2O_3	2.78
4	FeO	0.56
5	CaO	7.08
6	MgO	1.49
7	TiO_2	0.19
8	Na_2O	1.40
9	K_2O	3.01

It was determined that, high content of Ca and Mg components in zeolite contributes to its performance and dehydration temperature, temperature resistance. The authors show that hydration of mordenite zeolite is completed at a temperature of 600^0C . As a result of X-ray analysis, it was determined that The structure of mordenite is stable at temperatures up to 1000^0C. When the temperature rises from 1000^0C to 1300^0C, X-ray analysis shows a breakdown of the microstructure of mordenite[8].

Taking into account that, in the process of thermal pyrolysis, the direct pyrolysis of gasoline is carried out at a temperature of 700-900^{0}C[8].Then, The application of Azerbaijani zeolite to this process can be considered favorable. Regarding to this, we used mardenite- an Azerbaijani zeolite- in our research

First of all, we determined the indicators of disposable distillate gasoline obtained from the EUSD-AV unit operating at the Baku Oil Refinery named after H. Aliyev (table 2). Traditionally, the density of direct-run gasoline was determined by pycnometric method, the fraction composition was determined in the device "ARN-2".

Table 2

Indicators of disposable distillate gasoline

Indicators	Disposable distillate gasoline
Density, ρ	0.744
The composition of the faction	
Boiling point, T °C	38 °C
10% Distillate, T °C	67 °C
50% Distillate, T°C	104 °C
90% Distillate, T°C	151 °C
End of boiling T °C	166 °C
Amount of Sulphur, %(wt).	1.01
Hydrocarbon composition, %(wt)	
Paraffins	55.2
Naphthene	42.7
Aromatics	2.6

We studied catalytic pyrolysis process in a flow-type reactor unit, which we have compiled below.

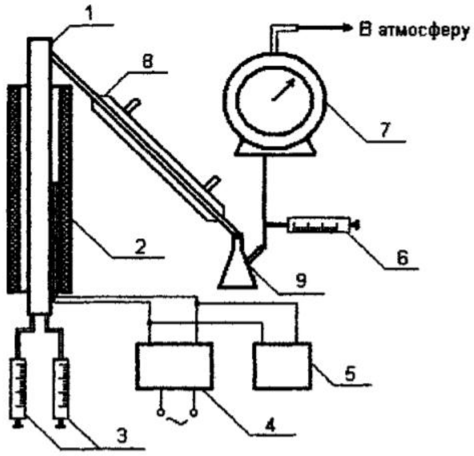

Fig.1. Scheme of the laboratory device of the catalytic pyrolysis process with a flow reactor.

1-reactor, 2-electric furnace, 3-piston dosing, 4-BRT-3, 5-resistor, 6-sampling; 7-gas meter; 8-refrigerator; 9-condensate receiver

First of all, we carried out catalytic pyrolysis of disposable gasoline using Azerbaijani zeolites without water vapor. It is known that the use of water vapor leads to the process of coking and in some cases increases the yield of the target product. However, the literature we studied showed that water vapor reduces the activity of the catalyst without changing the selectivity [1]. For this reason, we made our presentation without water vapor, and the results are shown below.

Table 2

Effect of catalyst and steam on catalytic prolysis process

Components	Concentration of gaseous products (C1-C4) in the reaction zone at different temperatures, T^0C					
	600	650	700	600	650	700
	Without water vapor			In the presence of water vapor		
	3.5 san			3.5san		
Hidrogen	0.78	0.79	1.06	1.52	1.29	1.99
Metan	6.52	9.70	15.72	6.31	8.74	15.15
Etan	10.62	5.53	9.08	2.22	3.29	4.78
Propan	10.35	8.16	4.67	6.59	4.99	2.16
Butan	9.93	9.08	5.36	9.61	8.69	3.26
i-butan	17.54	11.61	4.49	10.59	6.74	3.18
Etilen	6.45	10.03	17.14	7.94	11.44	20.01
Propilen	27.74	29.13	25.41	36.64	32.25	32.75
Σbuten	10.08	15.98	16.32	18.59	22.06	14.56
Divinil	0	0	0.75	0	0	2.15
The amount of olefin in the gas, %(wt).	44.26	55.13	58.87	63.17	65.76	67.32
Yield of olefin, (C_1-C_4) %(wt).	9.62	16.51	28.21	11.19	18.87	37.94
Yield of ethylene and propylene,% (wt).	7.43	11.72	20.39	7.90	12.54	29.74
Gas formation, %(wt).	21.73	29.94	47.92	17.72	28.70	56.36

RESULTS AND DISCUSSION

When applying zeolite and zeolite-containing catalysts to the pyrolysis process, the authors [2-6] showed that there are two types of acid centers on the surface of catalysts: Brensteda-based and Huisa-based.

Brenstov centers predominate on the surface of the catalyst. These centers are characterized as potentially bransted acid centers. The relative surface area decreases when the catalytic pyrolysis process is carried out at high temperatures without the presence of water vapor. This process mainly applies to amorphous alumysilicate catalysts. The reason for this is the dehydrogenation process, in which hydroxyl groups combined with aluminum atoms are released from the surface of the catalyst. In this case, a certain amount of water vapor is obtained. This reduced the activity of the catalyst. Thus, first the strong acid centers weaken on the surface of the catalyst. At this point, only Lewis centers begin to form and acid vapors are formed, which weakens the catalyst - negatively damaged centers are formed, as shown in the table above.

When the process is carried out with the participation of water vapor, the Brandstov acid centers are restored, and the balance between the two types of centers is restored.

On the other hand, in the process of pyrolysis without the presence of water vapor, carbon ions or radicals are more likely to collide with each other, surrounded by other reaction particles. When the process is carried out with water vapor, the mixture dissolves in each other and the recovery of radicals is weakened. When comparing the presence of water vapor and the process of pyrolysis without water vapor, we see that the amount of olefins in the pyrolysis gas during the same contact period is higher than the yield from pyrolysis pyrolysis without water vapor. Based on the obtained results, it can be said that such a good result can be obtained with or without the presence of water vapor by changing the structure of the acid center of the catalyst at high temperatures.

CONCLUSİON

The analysis of the research shows that it is possible to get such a good result by changing the structure of the acid center of the Azerbaijani zeolite catalyst at high temperatures, both in the presence of water vapor and without the presence of water vapor. The application of Azerbaijani zeolite to this process can play an economic and effective role in reducing the temperature of the process. This is facilitated by the fact that the selected catalyst maintains its structure stable at a temperature of 1000 ^{0}C.

REFERENCES

1. Sukhanov V.P. Catalytic processes in oil refining. –M.: Chemistry, 1979, 344 p
2. Boreskova G.K. The use of zeolites in catalysis. Publishing house Science Siberian department. 1977, 192 p
3. Movsumzade E.M., Pavgyuv M.L. and other Natural and synthetic zeolites, their production and use.Ufa: Reagent. 2000, 230 p
4. Reyts B., Ketzir J., Lluyt G. Chemistry of catalytic processes. Per. From English. Ed. A.F. Plato. - M .: Mir.981,551 p
5. Jacobs P. Carbonaceous activity of zeolites. Per. From English. / Ed. A.A. Slinkin. - M .: Chemistry.1983,144 p
6. Levinter M.E., Akhmetov S.A. Deep processing of oil: a textbook for universities. - M .: Chemistry.1992, 224 p
7. Sukhanov V.P. Catalytic processes in oil refining,-M.: Chemistry, 1979,344 p.
8. Yusif-zade A.A., Dadaeva G.Ch. “Study of catalytic pyrolysis of a fraction at a temperature of 130-230^{0}C. "Bulatov Readings”. Materials of the IV International Scientific and Technical Conference (March 31, 2020) Technical and technological developments. Vol.6, №3, Krasnodar 2020, pp.234-237

ИССЛЕДОВАНИЕ ВЛИЯНИЯ ВОДЯНОГО ПАРА НА ПРОЦЕСС КАТАЛИТИЧЕСКОГО ПИРОЛИЗА

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Известно, что термический пиролиз проведенный в жестком режиме в нефтехимической промышленности является одним из наиболее сложных процессов как экономически, так и технологически. В связи с этим интенсификация процесса постоянно изучается специалистами. Важным фактором может быть применение катализаторов в процессе термического пиролиза и его переход в мягкий режим. С этой точки зрения, принимая во внимание селективность различных системных катализаторов, проводятся постоянные исследования для улучшения процесса. Учитывая актуальность процесса, выбор катализаторов, которые могут быть использованы при высоких температурах для процесса каталитического пиролиза, изучение механизма его действия, влияния на выход и качество целевых продуктов и влияние применяемого водяного пара к выбранному катализатору при термическом пиролизе являются важными факторами. Принимая это во внимание, в нашем исследовании, впервые в процессе термического пиролиза, были проанализированы результаты этого процесса с использованием катализатора типа морденита, природного азербайджанского цеолита, с водяным паром или без него. Таким образом, выход этилена в процессе термического пиролиза с участием катализатора без водяного пара при 650°C составил 10,03% (по массе), а с участием водяного пара - 11,44% (по массе). При подходящих температурах и условиях выход пропилена составил 29,13% (по массе) и 32,25% (по массе). Таким образом, природный азербайджанский цеолит - морденит, который был использован впервые, имеет более совершенную структуру, чем катализаторы, известные из литературы, поэтому он был выбран в процессе каталитического пиролиза и были получены положительные результаты.

Ключевые слова: *термический пиролиз, каталитический пиролиз, цеолитный катализатор, морденит, водяной пар, прямогонный бензин.*

SU BUXARININ KATALITIK PIROLIZ PROSESINƏ TƏSIRI

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Məlumdur ki, neftkimya sənayesində termiki piroliz prosesinin sərt rejimdə getməsi onun həm iqtisadi və həm də texnoloji cəhətdən ağır proseslər sırasına salır. Bu baxımdan prosesin intensivləşdirilməsi daim mütəxəsislər tərəfindən araşdırılır. Termiki piroliz prosesinə katalizatrların tətbiqi və onun mülayim rejimə keçməsi üçün önəmli faktor ola bilər.Bu baxımdan müxtəlif sistemli katalizatorların seçiciliyini nəzərə alaraq prosesin təkmilləşdirilməsi istiqamətində daim tədqiqatlar aparılmadaddır. Prosesin aktuallığını nəzərə alaraq katalitik piroliz prosesi üçün yüksək temperatur şəraitində istifadə oluna bilən katalizatorların secilməsi, onun prosesə təsir mexanizminin öyrənilməsi, alınan məqsədli məhsulların çıxım və keyfiyyətinə təsirini öyrənmk və termiki piroliz prosesində tətbiq edilən su buxarının seçilmiş katalizatora təsirinin öyrənilməsi vacib amlılərdən hesab edilir. Bunları nəzərə alaraq tədqiqat işimizdə termiki piroliz prosesində ilk dəfə olaraq təbii Azərbaycanın seoliti olan mordenit tipli katalizatordan istifadə edərək, bu prosesin su buxarının iştirakı və su buxarının iştirakı olmadan aparmaqla alınmış nəticələrinin analizini təhlil etmişik. Beləki, etilenin çıxımı su *buxarı olmadan katalizatorun iştirakı ilə aparılan termiki piroliz prosesində 650^{0}C də 10.03% (küt.), su buxarının iştirakı ilə isə 11.44% (küt.) təşkil etmişdir. Uyğun temperatur və şəraitdə isə propilenin çıxımı 29.13% (küt.) və 32.25%(küt.) çıxım əldə edilmişdir. Beləliklə, ilk dəfə istifadə etdiyimiz təbii Azərbaycan seoliti olan mordenit ədəbiyyatlardan məlum olan katalizatorlardan daha mükəmməl struktura malik oldugu uçun katalitik piroliz prosesində öz seçiciliyi ilə seçilmiş və müsbət nəticələr əldə olunmuşdur.*

Acar sözlər: termiki piroli, *katalitik piroliz, seolit katalizatoru, mordenit, su buxarı, birbaşa qovulma benzini.*

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WATER TREATMENT USING GRAPHENE OXIDE AND ZEOLITE

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In this scientific work, we described how the medium was prepared from solutions with several salts to create an imitation of the environment with NaCl equal concentration of the Caspian Sea. Zeolite nanoparticles and graphene oxide were used for water purification. In our research, the optimal conditions for the production of graphene oxide by an improved method are established and the results of FTIR analyzes and the results of SEM of nanoparticles are presented. The procedure for creating a carrier with nanoparticles is also disclosed and the results of calculations are presented. Graphene oxide nanoparticles were synthesized and their morphology was studied, after that they were used for water purification. According to the obtained results, GO nanoparticles on a Schott filter without a membrane showed the best results in comparison with zeolite.

Keywords: *zeolite, graphene oxide, water purification, FTIR, SEM, nanoparticles.*

INTRODUCTION

Where is water, there is life. At all times, man used water in everyday life for various purposes. As you know, most of the earth's surface is covered with oceans and seas, whereas it became clear that, the most of the water resources are rather salty. İn today's era potable water resources are reducing day by day and it is one of the most important problems that is increasing at an alarming rate in all over the world. The main reason of this problem is tossing of contaminants like chemicals, undesired mechanical impurities and etc. to the environment. As you know, the main sources of environmental pollution are engineering plants, thermal power plants and transports which are necessary for humanity for everyday life. In the last decade of the development of nanotechnology, water purification has become quite real for their use to improve the composition of water and chemical purification [1,2]. Various kinds of nanostructured membranes (mainly carbon based nanomaterials) are used for the purification processes.

The key indicator is the reason for the high reactivity of nanoparticles due to their large specific surface area. So from the literature it is known that a number of studies indicate the toxicity of some nanomaterials, as a result of which we decided to use graphene oxide for water purification, which has good antimicrobial properties and which is also environmentally friendly. Graphene oxide has a very complex chemical composition [3,4]. There are different methods of synthesis of GO nanoparticles in laboratory conditions. The most commonly used method is the Hammer method, It is a modified and improved method. We used a modified Hammer method to get a more effective product in the world of nanomaterials. The most commonly used water purifiers for heavy metals, microbiological contaminants, metals and salts are carbon nanotubes (UNT), graphene and graphene oxide [5]. Each of them has a different effect on the purification of water, and the most suitable is graphene oxide [6,7]. Comparing the characteristics of graphene, carbon nanotubes and graphene oxide, we can see a large number of functional groups in graphene oxide. Membrane production using graphene and carbon nanotubes is more expensive and requires too much time for synthesis. It contains various functional groups such as hydroxyl, epoxy, carboxyl, aldehyde, ketone, and it has no chemical formula yet. There are several ideas about the structure of GO.

Hydroxyl and epoxy groups are the main components of GO. They are located in the basal layers. It is also important to emphasize that the basic rules of organic chemistry are not appropriate for GO chemistry. Although controlled chemistry has not yet been completed for GO, functional groups can directly enter into some reactions. GO's chemistry can help us understand why water can be treated with these nanoparticles. There are several reactive functional groups on GO, and it is very likely that Na^+ and Cl^- ions in water will be attracted by functional groups. However, it is a little tricky to predict where or the exact functional group to which the ions will attach. Scientists are looking for an analytical method to find a controlled chemical composition and detect all sides of GO after a reaction. And also for comparison, we carried out an analysis with a zeolite of a certain structure, which was decoded by the SEM method. There are many types of natural zeolites like clinoptilolite, mordenite, phillipsite, chabazite, stilbite, analcime and lomontite. Among them, clinoptilolite (ZC) is the most widespread natural zeolite and is widely used in the world, it perfectly removes toxins, it is also a good antioxidant and anti-inflammatory agent.

EXPERIMENTAL PART

Procedure:
Desalination part: NaCl
- mineral zeolite is prepared as a fine powder
- morphology of zeolite powder investigated using SEM
- taken powder FTIR
- the filter device was washed with DW, then 15 g of zeolite was added to it in the form of a layer
- 200 ml. DZ and 2. 4 g of NaCl was added to a beaker and 100 ml of this solution was carefully placed over the layer of zeolite powder.
- after 2 hours the conductivity of the treated water was measured and compared with that which was measured before the experiment.

$$\mathrm{Na_2Ze + CaCl_2 \rightarrow CaZe + 2NaCl}$$
$$\mathrm{Na_2Ze + MgCl_2 \rightarrow MgZe + 2NaCl}$$
$$\mathrm{CaZe + 2NaCl \rightarrow CaCl_2 + 2NaZe}$$

Synthesis of graphene oxide.

Basically graphene is obtained by the restoration of GO in the presence of hydrazine. In this case, we get graphene with less C / O correlation and less quality of functionality of layers by comparison with GO. The high cost of obtaining graphene, carbon nanotubes and many other properties of graphene oxide make us choose graphene oxide for water purification, which attracts ions to water. Graphite is enriched with sodium nitrate, which is oxidized by potassium permanganate and hydrogen peroxide. The purpose of oxidation is the acquisition of a large number of functional groups, which help to attract ions. the ions cannot pass from the layer of graphene oxide because of the chemical reactions and the sizes. The surface of GO is too wide and it is the main thing which makes retention and reaction time higher. Water desalination with GO.

Three plastic sample holders containing 2 g of graphite, 1 g of $NaNO_3$ and 6g of $KMnO_4$ have been weighted. The 46 ml of sulfuric acid (H_2SO_4) 95 - 98% has been poured into the 250 ml volumetric cylinder. The ice bath has been filled with ice for experiment. This procedure has been implemented for 2 times since 2 reactions has been we discussed in the chemistry planned. After the preparation of the sample, 3 necked and 2 necked flasks have been taken, as well as convenient thermometers for the flasks.

Necked flasks have been put into the ice bath. Subsequently, weighted graphite, $NaNO_3$ and H_2SO_4 have been added respectively. Thermometer has been put into the flask and the stirring process started. We have waited 20 minutes to reach the temperature of 0 °C. After reaching 0 °C, we got rid of an ice bath and the temperature of mixture started increasing.

During this process the hot plate has also been used in order to reach the temperature of 20 °C in a shorter time period. After reaching 20 °C, the $KMnO_4$ has been added gradually for two hours. Since the temperature was increasing with addition of $KMnO_4$, we were keeping the temperature between 20-25 °C using ice bath. After adding all $KMnO_4$ during 2 hours, we have let the mixture to be stirred for more 4 hours.

During these hours the temperature has been kept between 20-25 °C. When temperature was increased to 35 °C, the mixture has been stirred at this temperature for 30 minutes. The mixture was put in the ice bath. 92 ml of DW has been poured into the sample gradually. During this process, temperature increased suddenly till 90 °C and decreased till 70 °C. The temperature has been kept between 70-75 °C for 15 minutes and the hot plate was used in order to keep the temperature between 70-75 °C. The mixture in the necked flask has been poured into the 1 l Erlenmeyer flask. Then, the necked flask has been washed with 280 ml DW in order to help dispersion and to decrease the loss of products.

For this step, we prepared 500 ml 3% H_2O_2 , poured it into the mixture and stirred it for 10 minutes. Then, we let the mixture rest for 12 hours. In the end, we have started the filtering process. During filtering process we have washed our product with DW in order to get rid of the sulfuric acid inside it been added to beaker 1.2 g of NaCl has been added to the beaker and stirred for 20 minutes 12 g/l concentrated water has been prepared 1 g of GO has been put on the filtration device and this device has been put into the Buchner system 100 ml of concentrated water has been added to GO gradually.

Materials:

Distilled water, Filter paper, Wastewater from the lake, Putty knife, Clinoptilolite, Measuring cylinder 250 ml Ice bath Sodium chloride (NaCl), Sodium nitrate ($NaNO_3$), Potassium permanganate ($KMnO_4$), Sulfuric acid (H_2SO_4), H_2O_2 30%.

Characterization of structure.

FTIR spectrophotometry**.** The functional groups, present in the powder samples of hybrid nanostructures in combination with ILs, will be identified by Fourier Transform Infrared (FTIR) spectroscopy. FTIR spectra were recorded on a Varian 3600 FTIR spectrophotometer in KBr tablets. The spectrum was taken in the range of 4000 - 400 cm^{-1} at room temperature.

Scanning Electron Microscope (SEM**).** SEM analysis of prepared samples NPs were taken on Field Emission SEM JEOL JSM-7600F at an accelerating voltage of 15Kv.

RESULTS AND DISCUSSION

In the pores of zeolite, there are cations and water. Zeolites have a rigid three-dimensional structure. The crystal structure of zeolite composed of a network connected between tunnels and cells. Water enters and exits these pores unhindered, but the zeolite framework remains rigid.

Another feature of this structure is that the pore and channel sizes are almost the same, which allows the crystal to act like a molecular sieve. Porous zeolite contains water molecules and ions.

Before starting our procedure part, we obtained SEM (scanning electron microscopy) images of our zeolite powder in order to determine the characterization and porous structure clinoptilolite as a sorbent. (table1,2, fig.1)

Table1

General composition of clinoptilolite

Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	FeO	MnO	Fe_2O_3
1.37	0.99	12.13	65.95	1.95	3.63	0.07	0.02	1.22

Table 2

Composition of used zeolite

Element	Weight %	Atomic %	Compound %	Formula
Na	3.09	2.78	4.17	Na_2O
Mg	2.03	1.72	3.37	MgO
Al	7.61	5.82	14.38	Al_2O_3
Si	33.41	24.55	71.48	SiO_2
K	2.39	1.26	2.88	K_2O
Ca	0.65	0.34	0.91	CaO
Fe	2.18	0.81	2.81	FeO
O	48.63	62.72		
Sum	100			

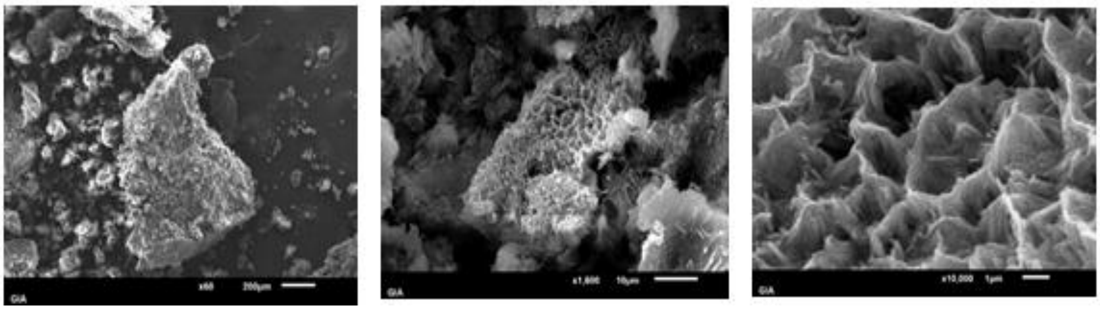

Fig. 1. SEM image structure clinoptilolite.

Then FTIR of zeolite was taken, and we noticed that we don't have OH groups in our image but actually we should have some picks because this group is one of the strongest one.

Desalination part: NaCl. We have checked the conductivity values of NaCl solution after and before the zeolite treatment. Before the zeolite layer, the conductivity of salty water was 21.4 mS/cm, after the zeolite treatment this value decreased to 19 mS/cm.

Considering that there is a linear relationship between the conductivity and concentration (lower conductivity, smaller the concentration). Finally, we got 12% of purification, according to the conductivity values.

CONCLUSION

In conclusion, we note that we conducted several experiments to find out which nanoparticle has a good effect on water purification. It can be said that GO nanoparticles are more efficient and economical in reducing Cl^- ions, but zeolite also showed good results. Our project was based on calculating the efficiency of nanoparticles on a Schott filter without a membrane, so that we can establish how these nanoparticles can be useful in membranes.

REFERENCES

1. Fu F, Wang Q (2011) Removal of heavy metal ions from wastewaters: A review. J. Environ. Manage. 92 : 40 Erdem, E.2011, pp. 407-418
2. Karapinar, N., Donat, R., 2004 . The removal of heavy metal cations by natural zeolites. Journal of Colloid and Interface Science 280,2004, pp. 309– 314
3. Wang, Shaobin; Peng, Yuelian . Chemical Engineering Journal, ISSN: 1385-8947.Vol. 156, Issue: 1, 2010, pp.11-24
4. Ayrat M, Dimiev Siegfried Graphene oxide fundamentals and applications. 2016, pp. 39- 60
5. Ayrat M, Dimiev, Siegfried Graphene oxide fundamentals and applications. 2016, pp. 175 - 192
6. Peter J. Cragg. Supramolecular Chem. // Biol. Inspiration to Biomedical Appl. 2010, Vol.4, pp. 109–156
7. Lili Liu and Shimou Chen. Theoretical Study on Cyclopeptides as the Nanocarriers for Li+, Na+, K+ and F−, Cl−, Br− // Journal of Nanomater. 2015, Vol.2, №3,pp. 18–26

ОЧИСТКА ВОДЫ С ИСПОЛЬЗОВАНИЕМ ОКСИДА ГРАФЕНА И ЦЕОЛИТА

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В этой научной работе мы описали, как растворами нескольких солей была приготовлена среда для создания имитации среды с NaCl концентрации равной концентрации Каспийского моря. Для очистки воды использовались наночастицы цеолита и оксид графена. В нашем исследовании установлены оптимальные условия получения оксида графена улучшенным методом и представлены результаты FTIR-анализов и результаты SEM наночастиц. Также раскрыта процедура создания *носителя с наночастицами и представлены результаты расчетов. Синтезированы наночастицы оксида графена и изучена их морфология, после чего они применены для очистки воды . По полученным результатам наночастицы графен оксида на фильтре Шотта без мембраны, показали наилучшие результаты по сравнению с цеолитом.*

Ключевые слова: *цеолит, оксид графена, очистка воды, FTIR, SEM, наночастицы.*

QRAFEN OKSİD VƏ SEOLİTDƏN İSTİFADƏ EDƏRƏK SUYUN TƏMİZLƏNMƏSİ

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Bu elmi işdə biz, NaCl konsentrasiyası ilə Xəzər dənizinin konsentrasiyasına bərabər süni mühit yaratmaq üçün bir neçə duzun məhlulundan mühitin necə hazırlandığını təsvir etdik. Suyun təmizlənməsi üçün seolit nanohissəciklərindən və qrafen oksiddən istifadə edilmişdir. Tədqiqatımızda qrafen oksidin yaxşılaşdırılmış bir metodla əldə edilməsi üçün optimal şərtlər qurulmuş və FTIR analizlərinin nəticələri və nanohissəciklərin SEM nəticələri təqdim edilmişdir. Beləliklə, nanohissəciklərlə daşıyıcı düzəldilməsi mexanizmi və hesablamaların nəticələri göstərilmişdir. Qrafen oksid nanohissəcikləri sintez edilmiş və onların morfoloji tərkibi öyrənilmiş, daha sonra isə suyun təmizlənməsi üçün istifadə edilmişdir. Alınmış göstəricilərə görə, membransız Şotta filtrində qrafen oksid nanohissəciklərinin nəticələri seolitlə müqayisədə daha yaxşı olmuşdur.

Açar sözlər: *seolit, qrafen oksid, suyun təmizlənməsi, FTIR, SEM, nanohissəciklər.*

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ENVİRONMENTAL ASPECTS OF PETROLEUM OİLS. RESULTS OF LABORATORY-EXPERİMENTAL RESEARCHES

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The study improved the quality of synthetic motor oils (Zic A Plus 10W – 40 SL / CF, Texaco Havoline Extra 10W-40SJ / CF, Ravenol TSI 10W-40SM / CF) on a photoelectrocalorimetre apparatus using the technique of direct photometry, which is belonging to the methods of physical and chemical analysis. A mercury lamp was used as a light source. The wavelength of the spectrum is set at 510-550 nm in the green part and 30 µm in the infrared part. In this case, the viscosity of the oil sample taken from the engine oil system in the volume of 10 ml, other physical and chemical parameters were determined and photometric oil products corresponding to the light absorption coefficient (Kp = 0.37 units) were obtained. When the absorption coefficient of the obtained products exceeds the permissible limit (Kp> 0.51 units), the aging products of oils are formed. To purify these substances from oils, a centrifuge separation method is used. Photometry is a new method for oil quality control and is considered promising in the petrochemical industry.

Keywords: *environmental safety, photometric analysis, regeneration, refined oil products, pure oils received from petroleum, economic aspects of oil production, clean environment.*

INTRODUCTION

The study of the ecological purity of petroleum oils, as well as their impact on the ecological situation and the environment, leads us to the conclusion that this effect is quite large.

The penetration of oil and its components into the environment, such as air, water or soil, disrupts the natural biochemical processes and causes changes in their physical, chemical and biological properties. During transformation, petroleum hydrocarbons can form toxic compounds that are dangerous properties to human health, including carcinogens that are resistant to microbiological degradation. The complexity of the problem lies not only in its scale, but also in the development of criteria and methods to combat this complex and variability in the pollution of the composition [3].

Given that virtually the entire ecosystem of the environment suffers from the effects of waste as a result of the need for oil refining and regeneration of petroleum products, it is not difficult to assess the theoretical and practical significance of the research. It should also be noted that a significant part of the observed damage is inflicted on the soil cover. Thus, if the discharge of waste oil products into the hydrosphere and lithosphere continues, this will inevitably lead to the destruction of not only animals, but also human settlements. Such an effect can not be completely excluded, but it can be minimized and waste oils can be used. This can be done by creating rational technologies for the use and complete recovery of waste oil products. When developing technologies, there is a need for a comprehensive assessment, including an assessment of their quality and an assessment of their impact on the environment [4].

The processes of extraction, transportation, processing and disposal of oil and petroleum products are accompanied by the release of harmful substances into the environment. Environmental pollution also occurs as a result of unauthorized discharges of oil products into water bodies, man-made accidents and industrial production. Streams from urban areas, seaports and various industries are also polluted with these substances. Thus, oil and oil products entering the environment cause great ecological damage to it. Due to the development and use of oil resources, the problem of their environmental pollution is becoming increasingly important [4].

Contamination with oil and oil products is found everywhere: in the soil, in the hydrosphere, in the atmosphere. Due to the deterioration of the ecological situation in the contaminated area, we observe a significant deterioration of both flora and fauna [3].

The chemical composition of the oil contains several thousand liquid hydrocarbons. Their percentage reaches 80-90%. The oil also contains other organic compounds such as resins, mercaptans, naphthenic acids, asphaltenes and other substances. In addition, the oil contains up to 10% water and up to 4% gas. Mineral salts and trace elements are found in small quantities. It is known that the chemical composition of the oil contains the most aliphatic hydrocarbons, about 57%. The less aromatic hydrocarbon content is about 29%, asphaltenes and other compounds 14% [6].

During the extraction and processing of oil are produced about 48% of hydrocarbons and 44% of carbon monoxide. These substances have a negative impact on the environment, as they are polluting. In addition, the oil contains about 30 metals. Thus, oil pollution is complex. It has a harmful effect on all elements of the environment, thereby causing a negative reaction.

The lightest part of the fat, which is in the soil, water or air environment, the most active part, has the most toxic effect on living organisms. Thus, with a decrease in the content of this fraction, the toxicity of the oil will be lower. But the reverse side of the coin is an increase in the content of aromatic compounds and, as a result, an increase in their toxicity. Let's consider in more detail the impact of oil and petroleum products on the state of various components of the ecosystem [4].

When soils are contaminated with petroleum products, a number of their signs and characteristics change. First of all, it suffers from changes in the physical properties that affect the morphological properties of soils. Thus, the air exchange in the soil is disrupted, the flow of water and, accordingly, the various nutrients necessary to ensure the vital activity of soil animals and plants is hindered. Soils lose their productivity. Vegetation degradation affects other elements of the ecosystem [6].

According to the sources, the production of essential oil is carried out according to the classical one - stage purification scheme, which combines vacuum distillation of oil, selective purification of distillates, wax purification of refineries, hydro-or adsorption purification of paraffinized oils in itself to obtain the target oil product and the by-product of the extract of the first stage. The main drawbacks are classic technology and method - the use of a “fresh” solvent. From the classic technology it is impossible to obtain group II base oil with 0.03% sulfur content; The usage of resolvent is needed at each extraction stage, which leads to a high overall ratio of the solvent for the separated raw material, the presence of four solvent recovery blocks and a high specific energy consumption, which ultimately increases the cost of production. In addition, the second stage of extraction is characterized by poor separation of raffinate and extract solutions due to insignificant differences in the density of the interacting products, which is confirmed by numerous laboratory experiments in purification of the extract with N-methylpyrrolidone [2].

The diversity of petroleum products involves the complexity of the problem of their monitoring: each product has its own defined chemical composition, as well as individual solution and biological decomposition. For example, the solution is 10 - 50 mg / l for oils, 9 - 505 mg / l for gasoline, 23-5 mg / l for kerosene, 8-22 mg / l for diesel fuel [2].

The development of struggle methods to combat pollution of the environment with oil and oil products is extremely difficult, because the reaction of the soil, for example, is not the same as the reaction of air or water. Even the reaction of soils to oil and oil products pollution, their sensitivity to these pollutants, varies in different soil zones and adjacent landscapes [3].

The problem with water is that oil pollution in natural waters tends to disintegrate and migrate. The difference is also observed in the behavior of aquatic objects - surface, groundwater and soil. Thus, for example, the composition of petroleum products under the influence of evaporation and intensive chemical and biological decomposition in surfacewaters undergoes rapid changes in a short period of time, and in groundwater, on the contrary, hinders the destruction process [2].

Experts and researchers classify solutions to the problems facing the oil and oil refining industry as follows:

1) modernization of old oil refineries and construction of new modern oil refineries, improvement of oil refining and quality of oil products;
2) maximum possible collection of oil from operating wells and reduction of losses during transportation;
3) development of new promising fields.

The oil extraction and refining industry is very harmful and has a negative impact on the environment. The reasons for the harmful effects of the oil industry on the environment are known as non-compliance of environmental safety requirements of technologies used for oil production and transportation, low percentage of financial investments in the development and implementation of scientific research, low ecological production culture, isolation of industry from the state and society [4].

EXPERIMENTAL PART

Monitoring of oil pollution in the environment is one of the most difficult tasks. It is impossible to ensure reliable economic control without the development and application of modern measurements. According to experts, without the application of measurement and monitoring methods based on innovative innovations in modern science and technology, it is impossible to ensure the development and control of a reliable organizational and legal, as well as economic basis of environmental protection in the context of production and processing of oil and oil products [3].

The following principles can be used to assess the compliance of petroleum products with several environmental requirements. According to these rules, during laboratory studies, the considered effect of the relevant technology should be evaluated simultaneously for all indicators, regardless of the overall environmental situation, ie the unit of measurement and the range of values. Each new technology offered for application has an environmental assessment that reflects the characteristics of this technology compared to those previously available. It is necessary to form an environmental assessment of the technology for all indicators. The evaluation formed should not depend on the technology under consideration, in other words, if two technologies are described with the same set of indicators with the same values, both should receive the same evaluation. All ratings must be in the same range. An interval of 0 to 1 is considered to be the most favorable interval. Moreover, the higher the value of the assessment, the higher the environmental friendliness of the technology and the lower the environmental impact (table 1).

Table 1

Analysis of oil product quality

Goal	Expansion of the raw material base of ecologically clean oil from petroleum			
Position	Creation of new, selective and stable catalysts for processing of renewable raw materials into intermediate and petrochemical products			
Stages of the process	Synthesis of catalysts	Physical and chemical certification of catalysts	The test of catalysts	Analysis of catalytic reaction products

It has led to the creation of an Environmental Assessment Index (PE) of implemented and already used technologies and the creation of a system for calculating the degree of environmental impact (SV) based on it. This technique allows you to perform all the necessary procedures and obtain an activity assessment that adequately reflects the characteristics of the technology under consideration in terms of its impact on the environment. Calculation of the effect of SV is carried out in three stages. The calculation of ecological purity of the investigated technology is based on the results of patent and scientific literature analysis, as well as laboratory research. The evaluation is carried out on the basis of average measured values [2].

In order to assess the environmental efficiency of quality indicators of petroleum oils, the formation of a mathematical model is carried out in the following manner. All environmental criteria are assigned coefficients (k_{pi}). In this case, it is accepted that the sum of the weight coefficients is equal to one. For each criterion, the dependence of the ecologically cleanness of technology on the value of the indicator is established (PEi – i criterion as an indicator of environmental compatibility). We build this relationship on the basis of the results of patent and literature analysis, as well as laboratory research. For each criterion obtained according to the relevant method, the value of the environmental compliance indicator is from 0 to 1. The optimal value of the indicator corresponds to one, the worst value of the indicator is zero [2].

The calculation of ecological purity of the technology based on the studied model is based on the results of patent and literature analysis, as well as laboratory research. Here the evaluation is based on the average measured values. At this stage, the value of the REi indicator is determined for each i criterion (according to the histogram - analytically or graphically). As a result, the environmental compliance indicator (PE) is defined as the weight coefficient of the PEi value products and the corresponding k_{pi}:

$$PE = \sum_{i=1}\left(k_{pi} \cdot PE_i\right)$$

The cost of assessing the impact of technology (SV indicator) is equal to the ratio of this technology (PE) to the environmental compliance indicator, which is equal to one of the environmental compliance indicators ($PE_{opt} = 1$):

$$SV = PE_{opt} / PE$$

It is necessary to formulate the value of the PEi indicator for each criterion. This value varies between 0 and 1 ($0 \leq PEi \leq 1$). It is necessary to determine the optimal value of the criterion in the range of values, with which we will compare the indicator equal to one ($PEi = 1$) and the worst values of the indicator ($PEi = 0$). We divide the range of all values into the range m according to the level of reduction of environmental cleanliness. We believe that the value of the ecological balance in the same range is reduced equally, that is, for the case when the right end of the range is higher than the ecological value observed in the left end of the environmental range:

$$PE_{m\_int} = PE_{m\_sol} + (PE_{m\_int} - PE_{m\_sol}) / PE_{m\_\text{sağ}} - PE_{m\_sol}$$

If the environmental value at the left boundary of the range is higher than the ecological value observed at the right boundary of the range, we obtain [2]:

$$PE_{m\_int} = PE_{m\_\text{sağ}} + (PE_{m\_\text{sağ}} - PE_{m\_int}) / (PE_{m\_\text{sağ}} - PE_{m\_sol})$$

RESULTS AND DISCUSSION

The oil refining industry in our country and beyond its borders has long been making efforts to protect the environment, working together with the authorities in the field of creating environmental legislation. However, to date, no basic directive or effective general line for environmental protection has been established. In Western countries, there has been an increasingly intensive consolidation of a large number of companies to address environmental issues over the past few years. In this case, it is inevitable that different views on the solution of the problem will emerge. This situation prompted the British Petroleum Institute to prepare a key document on environmental protection- the "Main Directions of Environmental Protection during Oil Refining" - especially to help oil producers and consumers, to provide an understanding of the environment, to accept different points of view, to minimize the impact on the environment in the most economical way, to predict the situation for the future [5].

In the study, partial synthetic motor oils derived from petroleum - Zic A Plus 10W–40 SL/CF, BPVisco 300010W–40 SJ/CF, Texaco Havoline Extra10W-40SJ/CF, Ravenol TSI10W – 40SM/CF, TNK Super 5W – 40 SL/CF and Esso Ultra 10W – 40SJ/CF were selected. These oils were discharged at the maintenance station during the planned shift and were used in various types of gasoline engines of passenger cars with different degrees of wear.

Laboratory monitoring of the quality of oils obtained from these oils on environmental parameters is based on the method of processing experimental data [1].

Analysis of samples of petroleum-based partial synthetic motor oils by direct photometry shows that their optical properties, estimated by the luminous flux absorption coefficient, are between 0.17 and 0.51 units (table 1).

The results of their photometry were statistically processed to determine the limited state of the partially synthetic motor oils used during the planned change.

Any petroleum-based oil has a potential energy determined by the quality of the base and a number of additives that give it the necessary properties, but during engine operation, this energy is spent on resisting external influences. As a result of resistance, the base wears out, the concentration of additives decreases and the internal energy of the lubricant decreases [5].

In this case, testing oils with different internal energies at the same temperature causes a change in the absorption coefficient of the light flux K_p. The absorption coefficient of K_p light flux can be explained by differences in the composition of obsolete products, the technical condition of the cylinder-piston group, filter elements of the lubrication system, fuel equipment and the concentration of incomplete combustion products included in the cartridge [1].

Table 1

Research results of petroleum-based partially synthetic motor oils

№	Brand of the petroleum-based oil	Moving distance of the car, km.	Duration of action of petroleum-based oil, km	Depreciation of product concentration		
				K_p	K_{pr}	K_{pn}
1.	Zic A Plus 10W–40 SL/CF	161 450	8000	0,23	0,11	0,12
2.	Zic A Plus 10W–40 SL/CF	184 190	16000	0,40	0,26	0,14
3.	Zic A Plus 5W–30 SL/CF	173 190	11500	0,51	0,29	0,22
4.	Zic A Plus 10W–40 SL/CF	135 290	8000	0,29	0,12	0,17
5.	BP Visco 3000 10W–40 SJ/CF	164 500	9000	0,33	0,19	0,14
6.	BP Visco 3000 10W–40 SJ/ CF	135 500	10000	0,19	0,12	0,07
7.	BP Visco 3000 10W–40 SJ/ CF	98 700	10700	0,17	0,11	0,06
8.	BP Visco 3000 10W–40 SJ/ CF	114 000	7000	0,17	0,13	0,04
9.	Texaco Havoline Extra10W–40 SJ/CF	66 800	8800	0,41	0,37	0,04
10.	Texaco Havoline Extra10W–40 SJ/CF	176 500	10000	0,27	0,12	0,15
11.	Texaco Havoline Extra 10W–40 SJ/CF	188 460	9800	0,25	0,21	0,04
12.	Texaco Havoline Extra10W–40 SJ/CF	85 242	10000	0,33	0,15	0,18
13.	Texaco Havoline Extra10W–40 SJ/CF	103 000	12500	0,37	0,23	0,14
14.	Ravenol HCS 5W–40 SL/CF	195 130	10000	0,24	0,13	0,11
15.	Ravenol TSI 10W–40 SM/CF	319 666	10000	0,22	0,13	0,09
16.	Ravenol TSI 10W–40 SM/CF	30 820	11000	0,17	0,10	0,07
17.	ТНКСупер 5W–40 SL/CF	76 200	10000	0,24	0,10	0,08
18.	ESSO Ultra 10W–40 SJ/CF	156 215	6000	0,24	0,08	0,16
19.	ESSO Ultra 10W–40 SJ/CF	135 066	10000	0,29	0,11	0,18
20.	ESSO Ultra 10W–40 SJ/CF	158 550	6000	0,24	0,08	0,16

Analysis of the results of direct photometry showed that the total concentration of aging products of synthetic motor oils used is 0.06 - 0.61 units, and the concentration of insoluble aging products is between 0.02 - 0.28 units. These data confirm the imperfection of the current system for changing oils per kilometer, since the individual working conditions and technical condition of the engines, the frequency of fillingulmo due to oil depletion and the condition of the cylinder-piston group, which affects the aging speed , are not taken into account, which confirms the urgency of the problem solved in the work [1].

CONCLUSION

In the modern world there are various methods that ensure effective protection of the environment from pollution by oil and petroleum products. The most common methods include: mechanical, chemical, physical, physicochemical, microbiological, in addition, new methods and technologies are being developed. Examples include biosorption methods, water ozonation, magnetic purification, flotation-cavitation purification, magnetic nanoparticle purification, biological purification, and so on.

Mankind is constantly looking for an opportunity that allows us to actively fight against oil pollution most effectively and has a relatively low cost.

REFERENCES

1. Vereshchagin V.I., Yanovich V.S., Kovalsky B.I. Methods of control and results of the study of the state of transmission and motor problems in their oxidation and tribotechnical tests. Krasnoyarsk. 2017, pp.128-208
2. Ivanyuk S.V. Evaluation of the impact of regeneration technologies used on the surrounding environment. 2011, № 3, pp.20-65
3. Saxonov M.N., Abalakov A.D., Danko L.V., Barkhatova O.A., Stom D.I. Environmental monitoring of the oil and gas industry. Physicochemical and biological methods. Irkutsk. 2005, pp.110-114
4. Tarasov V.V. Environmental aspects of the need to regenerate used lubricants.2010, pp.15
5. Mang T., Wilfried D. Lubricants and Lubrication, 2017, Vol. 2, № 3, part XVII, onlinelibrary.wiley.com / doi / pdf / 10.1002/9783527645565, pp.843-880
6. Privalova N.M. Impact of oil and oil products on the environment. 2017, № 125(01), scientific journal, pp.7-10

ЭКОЛОГИЧЕСКИЕ АСПЕКТЫ НЕФТЯНЫХ МАСЕЛ. РЕЗУЛЬТАТЫ ЛАБОРАТОРНО-ЭКСПЕРИМЕНТАЛЬНЫХ ИССЛЕДОВАНИЙ

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В результате исследования с использованием методики прямой фотометрии, относящемся к методам физико-химического анализа, на фотоэлектрокалориметрическом аппарате улучшилось качество синтетических моторных масел (Zic A Plus 10W - 40 SL / CF, Texaco Havoline Extra 10W-40SJ / CF, Ravenol TSI 10W-40SM / CF). В качестве источника света использовалась ртутная лампа. Длина волны спектра в *зеленой части установлена на уровне 510-550 нм и в инфракрасной части 30 мкм. При этом из масляной системы двигателя в объеме 10 мл пробы масла определены вязкость, а также другие физико-химические параметры и получены фотометрические нефтепродукты, соответствующие коэффициенту светопоглощения (Кп = 0,37 ед.). Когда коэффициент поглощения полученных продуктов превышает допустимый предел, образуются продукты старения масел. Чтобы очистить эти вещества из масел, используется метод разделения на центрифуге. Для контроля качества нефти фотометрия является новым методом и считается перспективной в нефтехимической промышленности.*

Ключевые слова: *экологическая безопасность, фотометрический анализ, регенерация, рафинированные нефтепродукты, чистые масла полученные из нефти, экономические аспекты добычи нефти, чистая окружающая среда.*

NEFTDƏN ALINAN YAĞLARIN EKOLOJİ ASPEKTLƏRİ. LABORATOR-EKSPERİMENTAL TƏDQİQATLARIN NƏTİCƏLƏRİ

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Tədqiqatda fiziki-kimyəvi analiz metodu olan birbaşa fotometriya üsulundan istifadə olunaraq sintetik motor yağlarının (Zic A Plus 10W– 40 SL/CF, Texaco Havoline Extra 10W-40SJ/CF, Ravenol TSI 10W-40SM/CF) fotoelektrokalorimetr aparatında keyfiyyətinin yaxşılaşdırılmasına nail olunmuşdur. Aparatda işıq mənbəyi kimi civə lampasından istifadə olunmuşdur. Spektrin dalğa uzunluğu yaşıl hissədə 510-550 nm, infraqırmızı hissədə isə 30 mkm aralığında təyin edilir. Bu zaman mühərrik yağları sistemindən 10 ml həcmində götürülmüş yağ nümunəsinin özlülüyü və digər fiziki-kimyəvi göstəriciləri müəyyən edilmiş, işığın udma əmsalı göstəricisinə cavab verən (K_p=0,37 vahid) fotometrik yağ məhsulları əldə edilmişdir. Əldə olunan məhsulların udma əmsalı limit həddini keçdikdə (K_p>0,51 vahid) yağlarda aşınma məhsulları əmələ gəlir. Həmin maddələri yağlardan təmizləmək üçün sentrafuqa aparatında ayrılma üsulundan istifadə olunur. Yağların keyfiyyətinə nəzarət sahəsində bəhs olunan fotometriya üsulu yeni üsuldur və neft-kimya sənayesində perspektivli hesab olunur.

Açar sözlər: *ekoloji təhlükəsizlik, fotometrik analiz, regenerasiya, emal olunan neft məhsulları, neftdən alınan təmiz yağlar, neft istehsalının iqtisadi aspektləri, təmiz ətraf mühit .*

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DEVELOPMENT OF A MULTI-STAGE PURIFICATION PROCESS OF ENGINE OIL

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The process of multi-stage selective purification of motor oil fractions 320-400°C, 440-500°C is investigated with using N-methylpyrrolidone as a selective solvent, followed by hydroparaffinization process of the obtained refined products, also optimal purification conditions were found. The results showed that this purification method of engine oil from aromatic hydrocarbons, oxygen-containing compounds, sulfur and polycyclic aromatic hydrocarbons with short side chains under appropriate experimental conditions increased the viscosity index above 93 and reduced the base number to 0.05 mg KOH/g. In contrast to many polar solvents, N-methylpyrrolidone interacts with undesirable hydrocarbons and hetero-impurities during the purification of oil fractions, both due to van der waals forces and complexation due to acceptor properties. The removal of resinous substances and polycyclic arenes with short side chains contributed to a decrease in the coking ability of oils, which from an environmental point of view reduces the risk of environmental pollution from toxic compounds. The removal of resinous substances and unsaturated hydrocarbons significantly increased the thermal-oxidative capacity.

Keywords: *engine oil purification, N-methylpyrrolidone, liquid- liquid purification, aromatic hydrocarbons.*

INTRODUCTION

Currently, the oil production and refining industry is one of the most intensively developing areas of the Azerbaijani economy. Every year, about 6 million tons of petroleum products enter the planet's biosphere, more than 50% of which are used engine oils. Pollution of the environment by hazardous components of used engine oil becomes global. Atmospheric pollution occurs as a result of evaporation and, mainly, the burning of waste oil. The main requirements for the quality of motor oil are the low content of sulfur and aromatic hydrocarbons. High content of aromatic hydrocarbons in the fuel composition leads to increasing the emission of solid particles, which is extremely dangerous for the health of living organisms. From an environmental point of view, the most dangerous aromatic hydrocarbons are polycyclic aromatic hydrocarbons, which have a high toxicity. Their combustion leads to increasing of carbon dioxide, soot etc. harmful compounds [1, 2].

Extraction as an alternative method of cleaning engine oils. Along with hydrogenation methods to improve the quality of engine oil, alternative methods of raw material purification are widely used – liquid extraction, adsorption, oxidative desulfurization, precipitation, etc., among which the main place is occupied by the method of extraction purification. The use of liquid extraction as an alternative to hydrogenation methods for cleaning engine oil is associated with the following advantages of this method: extraction is carried out under milder conditions, low temperatures and pressure, there is no need to use expensive catalysts and hydrogen, easy to remove PAHs, nitrogen compounds that are difficult to remove during hydro treatment are extracted more efficiently [3, 4].

The purpose of the selective purification process is to remove resinous substances and polycyclic aromatic hydrocarbons from oil in order to increase their viscosity index and reduce coking ability (on the basis of the extraction of an undesirable component, it can be called the dearomatization process of oil) [5].

The global solvent market was estimated at US $ 47.37 billion in 2018 and is expected to reach US $ 64.32 billion by 2026. Solvents allow you to clean, apply, process, or separate substances. A number of scientists are involved in the manufacture of new solvents. A team of nearly 100 scientists is investigating the potential of ionic liquids at Queen's University Belfast. These solvents are called "super solvents", which are salts that remain liquid at room temperature and do not form vapors. The global solvent market is stimulated by a number of factors, such as the growing demand for solvents from emerging market economies, government regulation for the use of biological solvents [6]. Ionic liquids are a new group of solvents of great interest and are being studied as potential "green solvents". Their near-zero vapor pressure and temperature stability make them attractive solvents in many applications. IL are widely recognized as new solvents in chemistry, although they are not new, for example, $[EtNH_3]^+$ NO^{3-}, was discovered in 1914. They are also known as anhydrous IL, molten salts, liquid organic salts. The first example of a new IL, which is currently receiving much attention as a new medium for homogeneous catalysis, is ethylmethylimidazolium tetrafluoroborate [7].

In the process of selective purification of oil distillate fractions and deasphaltisates, phenol and furfural are traditionally used as a solvent. Furfural exhibits high selectivity, but relatively low solubility, so the process requires a higher solvent consumption compared to phenolic purification. However, due to its physical and chemical properties, it is more preferable than phenol. The main disadvantage of furfural is its low thermal and oxidative stability. N-methylpyrrolidone (NMP) is increasingly being used as a solvent in refineries [8]. Analysis of the physicochemical properties of furfural and NMP shows that the solvents have some common properties: the thermal stability of furfural and NMP is less than that of phenol, so the regeneration of these solvents should be carried out at reduced pressure; furfural and NMP are easily oxidized, and they should be stored under a layer of inert gas. At the same time, NMP is less toxic and has a higher solvent capacity than furfural. The process of extraction of hydrocarbons with selective solvents is multifactorial: the results of purification are influenced by the chemical composition and quality of the raw material, the nature and amount of the solvent, the temperature and the efficiency of the extraction equipments [9].

EXPERIMENTAL PART

We used two samples of oil fractions from a mixture of Baku Oil as raw materials. The total sulfur content in the oil fractions boiling at 320-400°C, 440-500°C, and the obtained raffinates and extracts was determined by the lamp method according to GOST 19121-73. The physical and chemical properties of oil fractions are presented in the table 1.

Table 1

Properties of raw materials for selective purification

№	Sample Fraction	Fraction $T_{boiling}$ 320-400°C	Fraction $T_{boiling}$ 440-500°C
	Indicators	General physical and chemical parameters	
1	Density at 20 °C, kg/m^3	860	890
2	Kinematic viscosity at 50 °C, mm^2/s	26.5	44
3	Kinematic viscosity at 100 °C, mm^2/s:	5.5	8.7
4	Viscosity index	83	75
5	Base number, mg KOH/g	2.8	4.9
6	Flash point, °C	135	181
7	Yield loss temperature, °C	-9	-2
8	Coking ability, %	1.2	3.7
9	Sulfur content, % wt.	0.29	0.32
10	Aromatic carbon content , % wt.	24	32

Table 2

The hydrocarbon composition of the oil fractions

Hydrocarbons	Fraction $T_{boiling}$ 320-400 °C		Fraction $T_{boiling}$ 440-500 °C	
	Yield, wt%	n_d^{20}	Yield, wt%	n_d^{20}
Paraffin naphthenic	75	1.4640	66.7	1.4770
Aromatic	21.7	-	30	-
- light	6.3	1.5100	9.5	1.5200
-medium	10.5	1.5485	12.5	1.5499
-heavy	4.9	1.5925	8.0	1.5970
Resins	2.6	-	2.4	-
Losses	0.7	-	0.9	-

Table 3

The results of refining raffinate, corresponding to the fraction of 320-400 °C

Indicators		Process temperature, °C			
		300	350	300	350
		Mordenite Weight, %			
		20	20	27	27
1	Density at 20 °C, kg/m^3	865	863	864.5	864
2	Kinematic viscosity at 40 °C, mm^2/s	20.7	20.2	20	19.5
	Kinematic viscosity at 100 °C, mm^2/s	5.4	5.35	5.36	5.33
3	Viscosity index	93	93	95	96
4	Base number, mg KOH/g	0.14	0.12	0.10	0.005
5	Solidification point, °C	-29	-36	-35	-41
6	Flash point, °C	137	136	135	134.5

The experimental part of the hydroparaffinization of raffinates was carried out on a laboratory installation. The reactor was loaded with a catalytic system: Al-Ni-Mo and high-silica modified mordenite. Zeolite catalysts are designed for hydroparaffinization process of oil fractions and Al – Ni-Mo for hydrodesulfurization and hydrogenation. The table shows the results of refining raffinate, corresponding to the fraction of 320-400 °C.

RESULTS AND DISCUSSION

As a result of laboratory studies, it was found that the use of NMP allows to increase the yield of raffinate by 4-5% compared to other solvents. In this work, the influence of the ratio of solvent and temperature to raw materials was investigated. The critical solution temperature of N-methylpyrrolidone in the studied oil fractions was determined (table 3).
In tab. 4. the yield of raffinate, acidity and viscosity index, as well as the ratio of solvent to raw material in the range from 1:1 to 3:1 are shown as the main criteria.

Table 4

The critical solution temperature of the oil fractions

Critical solution temperature, °C	Fractions	
	320-400°C	440-500°C
	78	82.5

Table 5

Quality of raffinate fraction 320-400 °C

№	Indicators	Solvent-to-raw material ratio			
		1:1	2:1	2,5:1	3:1
1	Density at 20 °C, kg/m^3	870	867	866.5	865.1
2	Kinematic viscosity at 100 °C, mm^2/s	5.66	5.61	5.5	5.4
3	Viscosity index	81	83	85	86
4	Base number, mg KOH/g	2.9	2.7	2.5	2.5
5	Flash point, °C	137	137	136	136
6	Coking ability, %	0.80	0.5	0.4	0.2
7	Yield, %	88.6	87.5	86	85

Table 6

Quality of raffinate fraction 440-500 °C

№	Indicators	Solvent-to-raw material ratio			
		1:1	2:1	2,5:1	3:1
1	Density at 20 °C, kg/m^3	876	872	872	871
2	Kinematic viscosity at 100 °C, mm^2/s	7.65	7.50	7.45	7.40
3	Viscosity index	80	82	83	83.6
4	Base number, mg KOH/g	2.80	2.60	2.45	2.35
5	Flash point, °C	183	182	181	181
6	Coking ability, %	2.60	2.20	1.70	1.35
7	Yield, %	88.2	87.0	86.5	84.0

Table 7

Quality of raffinates and extracts from fractions 320-400 °C и 440-500 °C

№	Indicators	Raffinates		Extracts	
		320-400°C	440-500°C	320-400°C	440-500°C
1	Density at 20 °C, kg/m^3	865	870	935	973
2	Kinematic viscosity at 40 °C, mm^2/s	22	55	-	-
	Kinematic viscosity at 100 °C, mm^2/s	5.7	8.5	12.0	15.0
3	Viscosity index	87	82	-	-
4	Base number, mg KOH/g	2.5	2.3	4.5	10.0
5	Flash point, °C	138	179	-	-
6	Coking ability, %	0.4	1.7	-	-

The optimum conditions for the hydrodeparrafinization process is T= 320°C, the volumetric feed rate of 0.7-0.9 g^{-1}, the quantity of hydrogen 195-200 nm^3/m^3. As a result, we obtained engine oil with a high viscosity index and a low solidification point. According to these indicators, it is clear that there is no need for additional thickening additives.

After the above studies, the oil with better physical and chemical properties were obtained, which are indicated in the table 8.

Table 8

Physical and chemical properties of finished oil

№	Indicators	Oil from fractions	
		320-400 °C	440-500 °C
1	Density at 20 °C, kg/m^3	864	868
2	Kinematic viscosity at 40 °C, mm^2/s	19.8	51
3	Kinematic viscosity at 100 °C, mm^2/s	5.4	8.35
4	Viscosity index	95	93
5	Base number, mg KOH/g	0.0006	0.05
6	Flash point, °C	133	178
7	Solidification point, °C	-38	-26
8	Coking ability, %	1.2	3.7
9	Sulfur content, % wt.	0.003	0.006

CONCLUSION

It is shown that the oil fractions boiling out in the range of 320-400° C and 440-500° C contain 77 and 66.7 % paraffin-naphthenic, 21 and 28.5 % aromatic hydrocarbons, the acid number is 3,1 and 2.2 mg KOH/g.

An effective selective solvent for the purification of oil fractions, N-methylpyrrolidone, is proposed, which increases the oil viscosity index and significantly reduces the amount of aromatic hydrocarbons.

The catalytic hydroparaffinization with the using of Al/Co/Mo catalyst and mordenite was investigated.

REFERENCES

1. Ostrikov, V.V., Tupotilov, N.N., Kornev, A.Yu. The method of cleaning of used synthetic motor oil. Patent № 2437923, Russia. 2011,pp.8-9
2. He L., Li H., Zhu W. Deep Oxidative Desulfurization of Fuels using Peroxophosphomolybdate Catalysts in Ionic Liquids. Indust. Eng. Chem. Res. 2008, Vol.47 (18),pp. 6890-6895
3. Sergun V. P., Korol I. S., Min R. S. Organosulfur compounds of high-sulfur oil of the Nizhnepervomayskoye field. Chemistry for sustainable development. 2014,№ 22, pp. 175-180
4. Gao S., Chen X., Abro R., Abdeltawab A.A., Al-Deyab S.S., Yu G. Desulfurization of fuel oil: conductor-like screening model for real solvents study on capacity of ionic liquids for thiophene and dibenzothiophene. Indust. Eng. Chem. Res. 2015,54(38), pp. 9421-9430
5. Bosmann A., Datsevich L., Jess A. Deep desulfurization of diesel fuel by extraction with ionic liquids. Chem.Commun. 2001, № 23, pp. 2494-2495
6. Gaile A. A., Somov V. E., Zalishchevsky G. D. Selective solvents. Separation and purification of hydrocarbon-containing raw materials. St. Petersburg: Khimizdat. 2008, 736 p
7. Bilal Benobidi, Gayle A. A., Zhiganova A. G., Kuzichkin N. V., Lisitsyn N. V. Selectivity of solvents with respect to arenes with different numbers of aromatic cycles. Oil refining and petrochemicals. 2015, №.12, pp. 15-18
8. Pykhalova N. V., Appazov A. Yu., Balamedova U. A. Investigation of the influence of the conditions of liquid extraction of the diesel fraction with N-methylpyrrolidone on the environmental performance of diesel fuel. Oil refining and petrochemicals. 2011, №12, pp. 19-23
9. Kolbin V. A., Dezortsev S. V., Telyashev E. G. Extraction refinement of the heavy component of diesel fuel with N-methyl-pyrrolidone. Bashkirs. chem. Sib. 2016, T. 23,№ 1, pp. 3-6

РАЗРАБОТКА МНОГОСТУПЕНЧАТОГО ПРОЦЕССА ОЧИСТКИ МОТОРНОГО МАСЛА

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Исследован процесс многоступенчатой селективной очистки моторных масел фракций 320-400°С, 440-500°С с использованием N-метилпирролидона в качестве селективного растворителя с последующей гидродепарафинизацией полученных рафинатов и найдены оптимальные условия очистки. Результаты показали, что этот метод очистки моторного масла при соответствующих экспериментальных условиях от ароматических углеводородов, кислородсодержащих соединений, серы и *полициклических ароматических углеводородов с короткими боковыми цепями увеличил индекс вязкости выше 93 и снизил основное число до 0.05 мг КОН/г. В отличие от многих полярных растворителей, N-метилпирролидон при очистке масляных фракций взаимодействует с нежелательными углеводородами и гетеро-примесями как за счет ван-дер-ваальсовых сил так и комплексообразования благодаря акцепторным свойствам. Удаление смолистых веществ и полициклических аренов с короткими боковыми цепями способствовали понижению коксуемости масел, что с экологической точки зрения снижает риск загрязнения окружающей среды от токсичных соединений. Удаление смолистых веществ и непредельных углеводородов значительно увеличило термоокислительную способность.*

Ключевые слова: *очистка моторного масла, N-метилпирролидон, ароматические углеводороды.*

MÜHƏRRİK YAĞLARININ ÇOXPİLLƏLİ TƏMİZLƏMƏ PROSESİNİN TƏDQİQİ

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Motor yağlarının 320-400°C, 440-500°C, fraksiyalarının həlledici qismində N-metilpirrolidondan istifadə etməklə və alınmış rafinatların hidrodeparafinizasiyası ilə çoxpilləli selektiv təmizləmə prosesi tədqiq edilmiş və optimal şərtləri tapılmışdır. Nəticələr göstərmişdir ki, aromatik karbohidrogenlərdən, oksigen tərkibli birləşmələrdən, kükürddən və qısa yan zəncirli polisiklik aromatik karbohidrogenlərdən müvafiq eksperimental şəraitdə mühərrik yağının təmizlənməsi üsulu 93-dən yuxarı özlülük indeksini artırmış və qələvilik ədədini 0.05 mq KOH/q endirmişdir. Bir çox qütb həlledicilərindən fərqli olaraq, N-metilpirrolidon yağ fraksiyalarının təmizlənməsi zamanı arzuolunmaz karbohidrogenlərlə və hetero-qatışıqlarla həm van-der-vals qüvvələrinin hesabına, həm də akseptor xassələrinə görə kompleks əmələgəlmə hesabına qarşılıqlı təsir göstərir. Qısa yan zəncirli qətranlı maddələrin və polisiklik arenlərin aradan qaldırılması yağların kokslaşmasının azalmasına səbəb olmuşdur ki, bu da ekoloji baxımdan ətraf mühitin zəhərli birləşmələrdən çirklənməsi riskini azaldır. Motor yağlarının qətranlı maddələrdən və doymamış karbohidrogenlərdən təmizlənməsi onların termooksidləşmə qabiliyyətini artırmışdır.

Açar sözlər: *mühərrik yağının təmizlənməsi, N-metilpirrolidon, aromatik karbohidrogenlər.*

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PHASE RELATIONS IN THE $CuSbS_2$-Cu_3SbS_4-Sb_2S_3 SYSTEM

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The phase relationships in the $CuSbS_2$-Cu_3SbS_4-Sb_2S_3 *system were determined experimentally over the entire concentration range by means of differential thermal analysis (DTA) and powder x-ray diffraction (PXRD) techniques. Two quasi-binary boundary, two internal polythermal sections, and a liquidus surface projection of the system were constructed. Primary crystallization fields of existing phases, the types and coordinates of non- and monovariant equilibria were determined. It was defined that, the concentration triangle under study is an independent subsystem of the Cu-Sb-S ternary system and belongs to the eutectic type with limited solid solutions on basis of the primary compounds.*

Keywords: *phase diagram, stibnite, copper antimony sulfides (CAS), chalcostibite, fematinite, solid solutions.*

INTRODUCTION

In recent years, research in the development of less-toxic, earth-abundant functional materials is highly pursued to reduce the cost for the possibility of their manufacture at large scales. An attractive class of materials composed of sustainable, inexpensive, non-toxic elements is the ternary phases of the copper-antimony-sulfide system [1-3]. Copper antimony sulfide (CAS) exists mainly in four naturally occurring mineral phases, which are intensively studied due to their versatile properties and cost consideration: $CuSbS_2$ (Chalcostibite), $Cu_{12}Sb_4S_{13}$ (Tetrahedrite), Cu_3SbS_3 (Skinnerite), and Cu_3SbS_4 (Fematinite) [4-7]. Wherein, the primary focus of researchers has been in exploring photovoltaic, photoelectric, thermoelectric, optoelectric, detector, absorber, etc. properties of Cu-Sb sulfosalts in order to identify their main application areas [1-4, 8-11].

There are numerous works dedicated to the study of phase relations in the system Cu-Sb-S [12-20]. Authors of [12] reported about the phase formation along the Cu_2S-Sb_2S_3 section of this system in 1912. The results on the preparation and determination of the melting temperatures of synthetic analogs of famatinite, chalcostibite, and tetrahedrite minerals are given in [13].

In [14] ternary compounds $CuSbS_2$ and Cu_3SbS_3 are reflected in the phase diagram of the Cu_2S-Sb_2S_3 system. A little later, Kuliyev R.A. et al. reported on the existence of only one compound - $CuSbS_2$ in this section [15]. A comprehensive re-study of phase equilibria in the Cu_2S-Sb_2S_3 section [16,17] showed the existence of a complex interaction near Cu_3SbS_3. Phase diagrams of the Cu_2S-Sb_2S_3 section constructed by different authors are significantly different. These works have been collected and systematized by [18].

Phase relations in the Cu-Sb-S system in the 570-870K temperature range are presented in [7, 19,20]. The isothermal section of the phase diagram presented by them at 770 K reflects Cu_3SbS_4, $CuSbS_2$, $Cu_{12}Sb_4S_{13}$, and Cu_3SbS_3 phases.

Despite the numerous available data on the phase diagram of the section Cu_2S-Sb_2S_3 and solid-phase equilibria in the Cu-Sb-S system, we have not found any information about its T-x-y diagram and liquidus surfaces of phases.

The information accumulated in phase diagrams of the corresponding systems is always helpful in materials science for the development of advanced materials [21-23]. In the context of the foregoing, we have undertaken a new, complex study of phase equilibria and the thermodynamic properties of the Cu– Sb–S system. Here we report about phase relations in the subsystem CuSbS2-Cu_3SbS_4-Sb_2S_3 (A).

Constituent phases of the subsystem (A) have been studied in detail. Sb_2S_3 (stibnite) melts congruently at 823 K [24] and crystallizes into orthorhombic structure with the space group P*nma*: *a* = 11.3107; *b* = 11.2285 Å; *c* = 3,8363 [25].

$CuSbS_2$ melts congruently at 828 K [18] and crystallizes into orthorhombic structure (Sp.gr. P*nma*): *a* = 6.018(1), *b* = 3.7958(6), and *c* = 14.495(7) Å [26,27].

Cu_3SbS_4, known as fematenite mineral melts congruently at 908 K [18] and crystallizes into tetragonal lattice (Sp.gr. $I\bar{4}2m$); *a* = 5.391(1), *c* = 10.764(1) [28].

EXPERIMENTAL PART

The Sb_2S_3, $CuSbS_2$, and Cu_3SbS_4 compounds were initially synthesized to prepare different alloys of the system under study. Simple substances of high purity from *Evochem Advanced Materials GmbH* (Germany) were used for synthesis: copper granules (Cu-00029; 99.9999%), antimony granules (Sb-00002; 99.999%), sulphur pieces (S -00001; 99.999%).

Compounds were synthesized by fusion of the elemental substances in stoichiometric ratios in evacuated up to ~10^{-2} Pa and sealed quartz ampoule of the 15x1.5 cm size in a two-zone inclined furnace. The temperature of the hot zone of the furnace was gradually increased to ~50^0C higher than the melting point of the corresponding compound in 3-4 hours. At that time, the temperature of the upper, "cold" zone of the furnace was 650 K, which is slightly below the boiling point of sulphur (718 K [29]). The synthesis was continued in this mode for another 3-4 hours and the ampoules were then completely transferred into the hot zone. The resulting liquids were mixed by shaking the alloys and the oven was gradually cooled. After synthesis, the ampoules were kept at 750 K for 100 h.

The individuality of the synthesized compounds was monitored by differential thermal analysis (DTA) and powder X-ray diffraction (PXRD), obtained data well coincided with the literature [18, 25-28].

Two sets of samples (0.5 g by mass each) were prepared by co-melting of different proportions of the preliminarily synthesized compounds in evacuated quartz ampoules. After melting, most of the alloys were annealed at about ~$40\text{-}50^0$ below the solidus temperature for ~1000 hours in order to achieve complete homogenization.

Obtained equilibrium samples were examined by DTA and PXRD methods. DTA of the samples was carried out in evacuated quartz ampoules on a differential scanning calorimeter of the 404 F1 Pegasus System (NETZSCH). Results of measurements were processed using the NETZSCH Proteus Software. The accuracy of the temperature measurements was within ±2 ^{0}. X-ray analysis was carried out at room temperature on the Bruker D2 PHASER diffractometer with CuKα_1 radiation. The diffraction patterns were indexed using the Topas 4.2 Software (Bruker).

RESULTS AND DISCUSSION

To determine the nature of phase equilibria in the system under study, a number of synthesized samples were studied in boundary systems Cu_3SbS_4-Sb_2S_3 and Cu_3SbS_4-$CuSbS_2$, as well as, within the concentration triangle. A full description of phase equilibria in the system (A) was obtained by co-analysis of the obtained experimental results and literature data for the boundary system $CuSbS_2$-Sb_2S_3 [18].

Below, on the phase diagram of the system (A) and its various sections, the compositions of the compounds are expressed in equal numbers of atoms using the corresponding coefficients in front of their formulas. This is identical to the expression of composition in atomic percent and allows this data to be used in the general phase diagram of the Cu-Sb-S system without recalculation of composition.

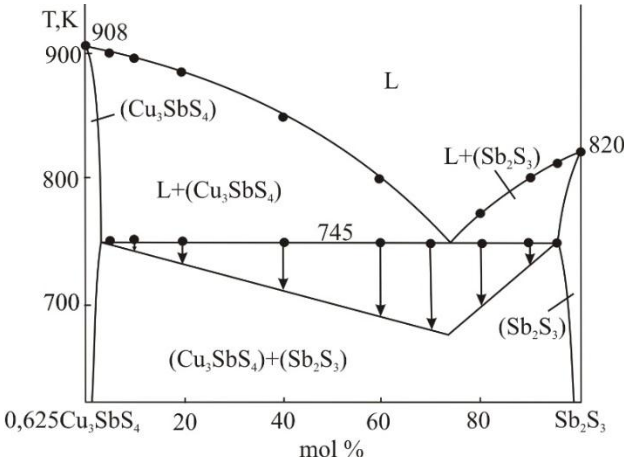
1.1. Boundary quasi-binary systems.

The DTA results of the thermally treated alloys of the Cu_3SbS_4-Sb_2S_3 and Cu_3SbS_4-$CuSbS_2$ systems are given in table 1. T-x diagrams of the systems are constructed based on these experimental results (fig.1a,b).

Table 1.

DTA results of the $0.625Cu_3SbS_4$-Sb_2S_3 and $0.5Cu_3SbS_4$-$CuSbS_2$ systems

System	Composition, mol% Sb_2S_3	Thermal effects, K	System	Composition, mol% $CuSbS_2$	Thermal effects, K
0.625 Cu_3SbS_4-Sb_2S_3	0	908	$0.5Cu_3SbS_4$-$CuSbS_2$	0	908
	5	750-903		5	815-904
	10	745-897		10	816-898
	20	743-882		20	814-890
	40	745-863		40	815-873
	60	746-798		60	816-842
	70	745		70	818-832
	80	744-770		80	816
	90	745-800		90	816-820
	95 100	778-813 820		95 100	817-823 825



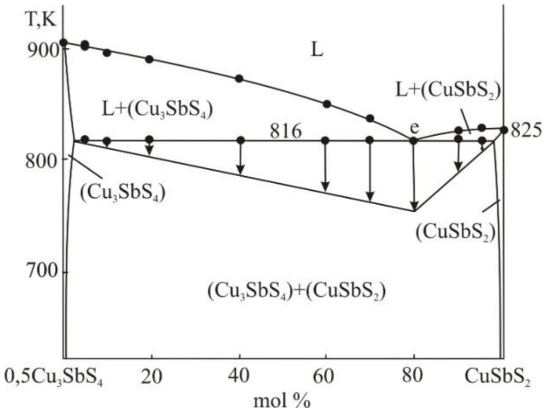


Fig. 1. The T-x phase diagram of the systems Cu_3SbS_4-Sb_2S_3 (a) and Cu_3SbS_4-$CuSbS_2$ (b).

Both systems are quasi-binary and form a eutectic phase diagram. Eutectics in the Cu_3SbS_4-Sb_2S_3 system has a ~73 mol% Sb_2S_3 composition and crystallizes at 745K, while the eutectics in the Cu_3SbS_4-$CuSbS_2$ system has ~80 mol% $CuSbS_2$ and 816K coordinates. The composition of eutectics and the solubility on the bases of primary compounds in both systems were specified by constructing Tamman's triangles. It was defined that, solubility on the basis of primary compounds does not exceed 5 mol% in both systems.

Constructed phase diagrams were confirmed by the PXRD method (fig.2). As can be clearly seen from fig.2, samples of both systems are two-phase alloys. Their diffraction patterns are composed of the diffraction lines of the constituent compounds. There is no significant shift in the diffraction lines of alloys relative to the primary compounds. This indicates that the solubility based on those compounds does not exceed 1-2 mol% at room temperature.

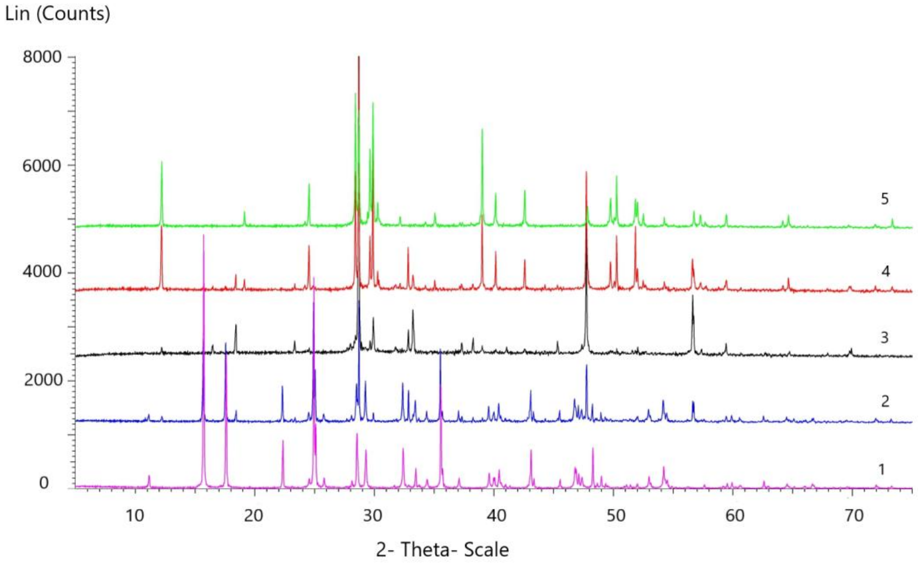


Fig. 2. X-ray images of some alloys of the Cu_3SbS_4-Sb_2S_3 and Cu_3SbS_4-$CuSbS_2$ systems: 1- Sb_2S_3; 2 – 70 mol% Sb_2S_3 + 30 mol% Cu_3SbS_4; 3 - Cu_3SbS_4; 4 – 30 mol% Cu_3SbS_4 + 70 mol% $CuSbS_2$; 5 - $CuSbS_2$.

Projection of the liquidus surface (fig.3)

The projection of the liquidus surface of the $CuSbS_2$-Cu_3SbS_4-Sb_2S_3 system on the concentration triangle is given in fig. 3, where liquidus isotherms are given in blue. It is an independent subsystem of the Cu-Sb-S system and belongs to the eutectic type. The liquidus surface consists of three fields corresponding to the crystallization of the initial compounds (fig.3). The latter occupies a small region near the appropriate corner of the concentration triangle. These phase areas are bordered by 3 eutectic curves reflecting monovariant co-crystallization of those phases:

e_1E curve: $L \leftrightarrow (CuSbS_2) + (Sb_2S_3)$ T=765-733K (1)

e_2E curve: $L \leftrightarrow (CuSbS_2) + (Cu_3SbS_3)$ T=816-733K (2)

e_3E curve: $L \leftrightarrow (Cu_3SbS_4) + (Sb_2S_3)$ T=745-733K (3)

These curves converge in the triple eutectic point E:

$L \leftrightarrow (CuSbS_2) + (Cu_3SbS_3) + (Sb_2S_3)$ T=733K (4)

In equations (1) - (4) and on the T-x diagrams (fig.1.4), chemical formulas of the compounds are given in parentheses, which indicates solid solutions based on them.

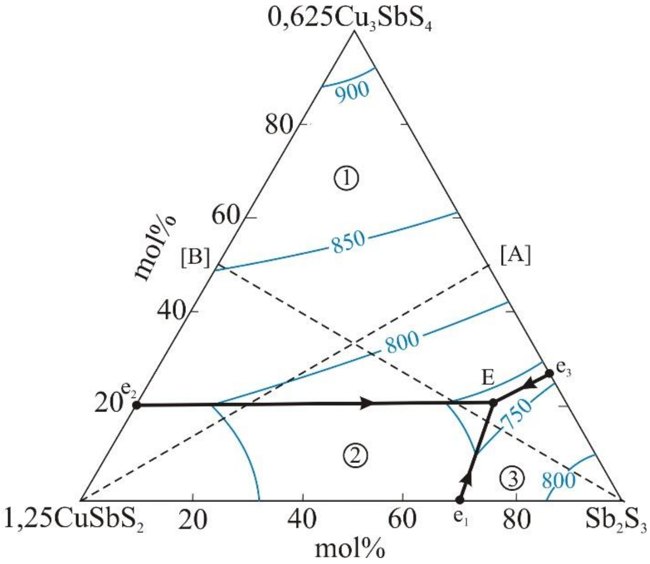


Fig.3. Projection of the liquidus surface of the system $CuSbS_2$-Cu_3SbS_4-Sb_2S_3. Primary crystallization fields: 1 – Cu_3SbS_4, 2 – $CuSbS_2$; 3 – Sb_2S_3. Dotted lines are studied polythermal sections.

1.2. Polythermal sections (fig.4 a,b)

Two polythermal sections of the phase diagram of the system $CuSbS_2$-Cu_3SbS_4-Sb_2S_3 are given below (fig.4 a,b) and analyzed in context with the projection of the liquidus surface (fig.3). Here, [A] and [B] are 1:1 mix ratios of the constituent compounds of the $0.625Cu_3SbS_4$-Sb_2S_3 and $1.25CuSbS_2$-$0.625Cu_3SbS_4$ boundary binary systems, consequently.

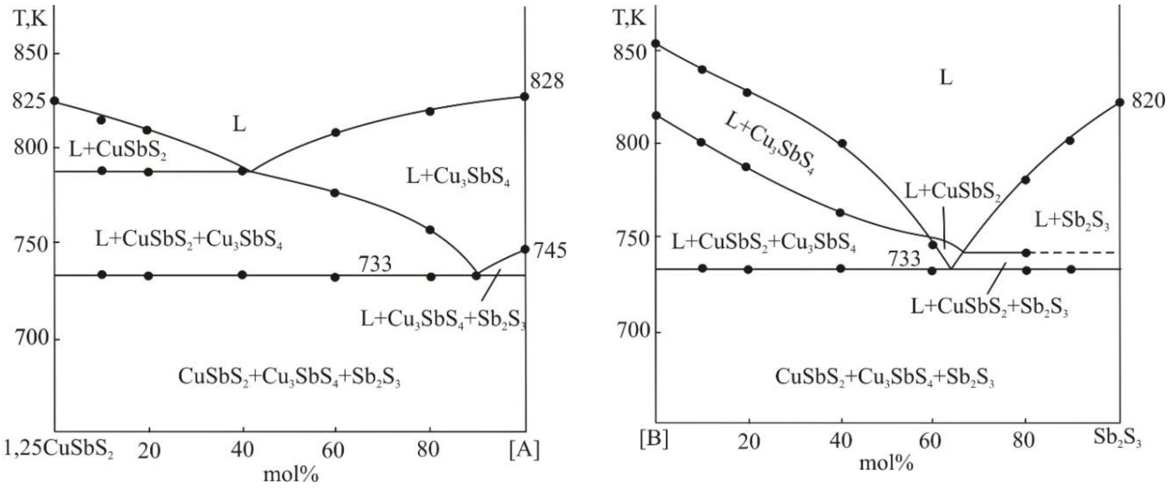


Fig.4. T-x phase diagrams of the systems 1.25$CuSbS_2$-[A] (a) and [B]- Sb_2S_3 (b).

1.25$CuSbS_2$-[A] polythermal section (fig.4a) passes through the primary crystallization areas of the ($CuSbS_2$) and (Cu_3SbS_4) phases. In a wide composition region (<90 mol% [A]) after primary crystallization of mentioned phases, the monovariant eutectic reaction (2) occurs. In the >90 mol% [A] phase area crystallization continues by the eutectic scheme (3). Crystallization in the system is completed by the nonvariant reaction (4) at 733K.

[B]- Sb_2S_3 polythermal section (fig.4b*).* The liquidus of the system [B]- Sb_2S_3 consists of 3 curves. The phases based on the Cu_3SbS_4, $CuSbS_2$, and Sb_2S_3 compounds primarily crystallize from a liquid solution along these curves. Below liquidus, crystallization continues by the monovariant (2) and (1) eutectic reactions and ends with the formation of a three-phase eutectic mixture at 733K.

Thereby, a comparative analysis of all elements of the phase diagram (fig. 1,3,4) indicates their compatibility with each other. Presented results can be used to prepare phases based on the primary compounds of the system $CuSbS_2$-Cu_3SbS_4-Sb_2S_3, as well as and their eutectic composites.

CONCLUSION

For the first time, the nature of the physicochemical interaction of the stibnite, chalcostibite, and fematinite minerals was determined using DTA and powder X-ray methods. The Cu_3SbS_4-Sb_2S_3 and Cu_3SbS_4-$CuSbS_2$ boundary systems, 2 isopleth sections, as well as, the surface of the liquidus surface of the $CuSbS_2$-Cu_3SbS_4-Sb_2S_3 system were constructed. It was established that the system is of eutectic type and is characterized by the formation of limited solid solutions on the basis of constituent minerals.

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REFERENCES

1. Peccerillo E., Durose K. Copper–antimony and copper–bismuth chalcogenides—Research opportunities and review for solar photovoltaics // MRS Energy & Sustainability. 2018,Vol.5,№ 9, pp. 1-59
2. Yang B., Wang L., Han J., Zhou Y., Song H., Chen S., Zhong J., Lv L., Niu D., Tang J. $CuSbS_2$ as a Promising Earth-Abundant Photovoltaic Absorber Material: A Combined Theoretical and Experimental Study // Chem. Mater. 2014, Vol.26, № 10, pp. 3135–3143
3. Ramasamy K., Sims H., Butler W. H., Gupta A. Selective Nanocrystal Synthesis and Calculated Electronic Structure of All Four Phases of Copper–Antimony–Sulfide // Chemistry of Materials. 2014, Vol. 26, № 9, pp. 2891–2899
4. Rabinal M.H.K., Mulla R. Copper Sulfides: Earth-Abundant and Low-Cost Thermoelectric Materials // Energy Technology. 2019, Vol.7, № 7.,pp. 1800850
5. Mindat.org: Open database of minerals, rocks, meteorites, and the localities they come from. Available at http://www.mindat.org (accessed August 23, 2018)
6. Filippou D., St-Germain P., Grammatikopoulos T. Recovery of metal values from copper—arsenic minerals and other related resources // Miner. Process. Extr. Metall. Rev. 2007, Vol.28, № 4, pp. 247-298
7. Skinner B.J., Luce F.D., Makovicky E. Studies of the sulfosalts of copper III. Phases and phase relations in the system Cu-Sb-S // Econ. Geol. 1972, Vol. 67, pp. 924−938
8. Krishnan B., Shaji S., Ernesto Ornelas R. Progress in development of copper antimony sulfide thin films as an alternative material for solar energy harvesting // J. Mater. Sci: Mater. Electron. 2015, Vol 26, № 7, pp. 4770–4781
9. Vinayakumar V., Shaji S., Avellaneda D., Aguilar-Martínez J.A., Krishnan B. Copper antimony sulfide thin films for visible to near infrared photodetector applications // RSC Adv. 2018, Vol 8, № 54, pp. 31055–31065
10. Anthony V. Powell. Recent developments in Earth-abundant copper-sulfide thermoelectric materials // J. Appl. Phys. 2019, Vol.126, pp. 100901
11. Chetty R., Bali A., Mallik R.C. Tetrahedrites as thermoelectric materials: an overview // J. Mater. Chem. C. 2015, Vol.3, pp. 12364-12378
12. Parravano N., de Cesaris P., I solfoantimoniti ramose // Chimica Italiana. 1912, Vol.42, № 2, 189 p
13. Wernick J.H., Benson K.E. New semiconducting ternary compounds // J. Phys. Chem. Solids. 1957, Vol. 3, pp. 157-159
14. Cambi L., Elli M. Processi idrotermali. Sintesi di solfosali da ossidi di metallic e metalloidi // Chimica Industria. 1965, Vol.47, № 2, pp. 136-147
15. Kuliyev R.A., Krestovnikov A.N., Glazov V.M. Enquire into phase equilibria between Cu and Sb chalcogenides // Izv. An. SSSR, Inorganic Materials. 1969,Vol. 5, № 12, pp. 2217-2218
16. Godovikov A.A., Ilyasheva N.A., Nenasheva S.N. New synthetic copper and silver sulfosalts // J. Soc. Mining Geol. Japan, Spec. 1971, Iss. 2, pp. 32-34
17. Ilyasheva N.A. Study of the Cu_2S-Sb_2S_3 system at 320-400^{0}C // Neorg. Mater. 1973, Vol. 9, № 10, pp. 677-679
18. Babanly M.B., Yusibov Yu.A., Abishev V.T. Trekhkomponentnye halkogenidy na osnove medi i serebra (In Russian). Baku: BGU. 1993, 342 p.

19. Braga M.H., Ferreira J.A., Lopes C., Malheiros L.F. Phase Transitions in the Cu-Sb-S System // Mater. Sci. Forum. 2008, Vol.587-588, pp. 435-439
20. Tesfaye F., Taskinen P. Phase Equilibria and Thermochemistry of Selected Sulfide Systems in the Pyrometallurgy of Ni and Cu. Espoo: Aalto University Publications in Materials Science and Engineering. 2012,39 p.
21. Babanly M.B., Chulkov E.V., Aliev Z. S., Shevelkov A.V., Amiraslanov I. R. Phase diagrams in materials science of topological insulators based on metal chalcogenides // Russ. J. Inorg. Chem. 2017, Vol. 62, № 13, pp. 1703–1729
22. Babanly M.B., Mashadiyeva L.F., Babanly D.M., Imamaliyeva S.Z., Tagiev D.B., Yusibov Yu.A. Some issues of complex studies of phase equilibria and thermodynamic properties in ternary chalcogenide systems involving EMF measurements (review) // Russ. J. Inorg. Chem. 2019, Vol. 64, № 13, pp. 1649-1671
23. Babanly D.M., Tagiyev D.B. Physicochemical aspects of ternary and complex phases development based on thallium chalcohalides // Chemical Problem. 2018. Vol. 16. № 2. pp.153-177
24. Massalski T.B., Okamoto H. Binary alloy phase diagrams. Materials park, Ohio: ASM International, 2nd ed. 1990, Vol. 3, 3589 p.
25. Bayliss P., Nowacki W. Refinement of the crystal structure of stibnite, Sb_2S_3 // Z. Kristallogr. 1972, Vol. 135, pp. 308-315
26. Kyono A., Kimata M. Crystal structures of chalcostibite ($CuSbS_2$) and emplectite ($CuBiS_2$): Structural relationship of stereochemical activity between chalcostibite and emplectite // Am. Mineral. 2005, Vol. 90, № 1, pp.162-165
27. McCarthy C.L., Cottingham P., Abuyen K., Schueller E.C., Culver S.P., Brutchey R.L., Earth-abundant $CuSbS_2$ thin films solution-processed from thiol–amine mixtures // J. Mater. Chem. C. 2016, Vol. 4, № 26, pp. 6230-6233
28. Pfitzner A., Reiser S. Refinement of the crystal structures of Cu_3PS_4 and Cu_3SbS_4 and a comment on normal tetrahedral structures // Z. Kristallogr. Cryst. Mater. 2002, Vol. 217, № 2, pp. 51-54
29. Emsley J. The elements. New York: Oxford University Press, 3rd ed. 1998, 300 p

ФАЗОВЫЕ РАВНОВЕСИЯ В СИСТЕМЕ $CuSbS_2$-Cu_3SbS_4-Sb_2S_3

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Фазовые соотношения в системе $CuSbS_2$-Cu_3SbS_4-Sb_2S_3 в полном диапазоне концентраций были определены методами дифференциального термического анализа (ДТА) и рентгенофазового анализа (РФА). Построены две квазибинарные границы, два внутренних политермических сечения и проекция поверхности ликвидуса системы. Определены поля первичной кристаллизации существующих фаз, типы и координаты *нон- и моновариантных равновесий. Установлено, что исследуемый концентрационный треугольник является самостоятельной подсистемой тройной системы Cu-Sb-S и относится к эвтектическому типу с ограниченными твердыми растворами на основе первичных соединений.*

Ключевые слова: *фазовая диаграмма, антимонит, сульфиды меди сурьмы, халькостибит, фематинит, твердые растворы.*

$CuSbS_2$-Cu_3SbS_4-Sb_2S_3 SİSTEMİNDƏ FAZA ÇEVRİLMƏLƏRİ

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$CuSbS_2$-Cu_3SbS_4-Sb_2S_3 *sistemində faza tarazlıqları diferensial termal analiz (DTA) və rentgen-faza analizi (RFA) üsulları ilə tam qatılıq intervalında müəyyən edilmişdir. Sistemin iki sərhəd kvazi-binar, iki daxili politermik kəsiyi və likvidus səthinin proyeksiyası qurulmuşdur. Mövcud fazaların ilkin kristallaşma sahələri, nonvariant və monovariant tarazlıqların tipləri və koordinatları təyin edilmişdir. Müəyyən olunmuşdur ki, tədqiq olunan qatılıq üçbucağı Cu-Sb-S üçlü sisteminin müstəqil alt sistemi olub ilkin birləşmələr əsasında məhdud bərk məhlul sahəsinə malik evtektik tipə aiddir.*

Açar sözlər: *faza diaqramı, stibnit, mis stibium sulfidləri, xalkostibit, fematinit, bərk məhlullar.*