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Development of technology obtainment of paints based on modified bitumen

ABSTRACT

on dissertation for the Doctor of Philosophy degree (PhD)
on the specialty 6D072100 - Chemical technology of organic substances

Timelines. The quality and durability improvement of bituminous materials exploiting in atmospheric conditions acquires particular relevance in modern conditions, characterized by an increase in energy, material and labor expenses, especially in the construction and operation of oil and gas pipelines and industrial and civil facilities.

The most important of the tasks of modern industrial and civil construction, housing and communal services is the use of reliable anti-corrosion materials of domestic production with maximum import substitution. In this regard, ability to use the domestic bitumen in new modern technological scheme acquires relevance, in order to product composite bitumen materials (CBM). This technology will allow to solve the environmental and economic aspects of the industry.

Bituminous paint-and-lacquer materials (PLM) have very good water resistance, but they do not sufficiently resist the atmospheric influences and especially the solar radiation. To increase the atmospheric resistance, oils and resins are included in the composition; however it reduces their water resistance.

The factors restraining the widespread use of bituminous paints and varnishes are low indicators of hardness, adhesion and strength, preferably depending on the technological conditions of the bitumen production process - temperature, air consumption and process duration, and the group chemical composition of the feedstock. It should be noted that bituminous paints have a good perspective, as their properties can be significantly improved by the addition of surfactants, corrosion inhibitors, some polymers and oligomers. All this facts make it possible to reduce the consumption in oil and to make these paints more bituminous, therefore more accessible and cheaper. Consequently, additional opportunities appear to improve the quality of bituminous paint-and-lacquer materials, and to organize the development of technology for new PLM production with high running abilities. In this reason, the development of obtainment technology of paint-and-lacquer materials is an actual task.

A review of literary sources and an analysis of the technology development level indicate the high relevance of the chosen theme for the

performance of dissertation research aimed to develop the production technology of paint-and-lacquer materials based on modified bitumen.

Relationship with research scientific works and government programs: The work was carried out within the framework of the fundamental research program of state funding - 16-03-05 "Development of obtainment technology for equipment and pipelines of refineries corrosion protection combined coatings" (2015-2020).

Targets of research. Domestic petroleum bitumen of RPB 70/100 grade (road petroleum bitumen), produced by the Shymkent bitumen plant LLP "Gazpromneft-Bitumen Kazakhstan" and bitumen varnishes based on them.

Scope of research is the obtainment process of paint-and-lacquer materials based on modified bitumen, formulation of bituminous paint-and-lacquer materials, the research of the physical and mechanical characteristics of composite paint-and-lacquer materials based on domestic bitumen.

The objectives and problems of the thesis work are:

- development of a method for obtaining paint-and-lacquer materials based on modified bitumen;
- research of the influence of the modifier Kulantau vermiculite on the rheological and physical-mechanical properties of bituminous paint-and-lacquer materials (BPLM);
- formulation and technologies development for modified BPLM obtainment;
- development of the principle technological scheme production for bituminous paint-and-lacquer materials.

The resulting effect definition of modification, determined by qualitative and quantitative regularity, a number of accompanying processes with the participation of other individual components determined the need for appropriate research.

The research scientific novelty concludes in that the most important are the following results:

- the development of new paint-and-lacquer on the basis of modified domestic bitumen and formulations of bituminous paint-and-lacquer materials with improved running ability;
- the regularities of various nature modifying additives influence on the running abilities of bituminous paint-and-lacquer materials were determined and their optimal concentrations were defined to ensure the spatial dispersed structure of the required quality;
- the development of different nature raw materials preparation methods with the purpose of high quality bituminous paint-and-lacquer materials production;
- the development of the bituminous paint-and-lacquer materials formulation with improved physical-chemical and operational characteristics based on modified bitumen. A patent for a utility model of the Republic of

Kazakhstan "Bitumen composition with a mineral filler" was obtained No. 4530 dated 06.03.2019.

The practical significance of the work:

- the use of raw materials - domestic petroleum bitumen - for obtaining bituminous paint-and-lacquer materials;

- justification of the choice of production technology parameters and the creation of bituminous paint-and-lacquer materials formulations by modifying their constituent components;

- analysis of modern scientific and technical achievement and the results of developments, taking into account the action mechanism of various additives to bituminous materials made it possible to create an original classification of additives and components, allowing effectively regulate the quality of stocks, materials and products at each of the production technological stages and technological complex of bitumen production;

- the use of Kulantau vermiculite in the composition of anticorrosive bituminous varnish provides stable adhesion in a wide temperature range, preservation of high plasticity and protective properties during long-term operation, does not require a high degree of metal surface preparation before using;

- the formulation of bituminous paint-and-lacquer materials with improved physicochemical and operational characteristics were developed based on modifying their properties with additives that combine structuring and plasticizing properties; that is features of technological schemes for the production of bituminous varnishes;

- the technology for obtaining anticorrosive bituminous paint-and-lacquer materials with good running ability, which can be used for corrosion protection of the outer surfaces of main- and oil-, gas-pipelines and pipelines for various purposes and tanks.

The main provision to be defended:

- the systematization of modern ideas about the structure of petroleum bitumen and regulation of physical and mechanical properties of bitumen by modifying additives;

- the research of paint-and-lacquer materials current state trends in the Republic of Kazakhstan;

- the research of physical-chemical features of composite bitumen materials obtainment based on RPB70/100 bitumen and mineral fillers;

- the research of physical-mechanical and protective properties of bituminous paint-and-lacquer materials;

- the development of a technological scheme for obtainment PLM based on modified petroleum bitumen.

In the analytical review the modern ideas about the structure of petroleum bitumen and regulation of physical-mechanical properties of bitumen by modifying additives, modified bitumen and paint-and-lacquer materials on their basis were considered.

Petroleum bitumen is one of the most widely used products of petroleum processing due to a number of valuable running abilities and increasing production scale. Despite of the fact that the increasing volumes of production and expansion of the range, the demand for bitumen is not fully satisfied, as well as the level of consumer requirements for the quality of petroleum bitumen is increased.

As it is known, bitumen is a complex mixture of high molecular hydrocarbons of petroleum origin, as well as their derivatives, containing oxygen, sulfur, nitrogen and metals complex compounds. Bitumens are obtained as a result of heavy oil residues processing, such as tar, fuel oil, deasphaltization asphalt, cracking residues and petroleum fractions selective distillation extracts.

Bitumen, being oil high molecular compounds, have a complex chemical composition, which is determined by the nature of petroleum feedstock, oil refining technology and bitumen production technology. Physical-chemical properties of petroleum bitumens are given in the table 1.

In accordance with the theory of high-molecular compounds, depending on external conditions, bitumens can be in different thermodynamic states, successively passing through all stages from true solutions (at high technological temperatures) to colloidal solutions of asphaltenes supramolecular structures (associates) and tars to plastic ones, and then solids states.

Table 1 - Properties of petroleum bitumens

Indicator	Type of bitumen		
	Semi-solid	Solid	Liquid
$T_{softening}$, °C	25-50	60-90	—
Penetration (25°C), mm	4-20	0-5	—
Extensibility (25°C), sm	40-60	1-5	60
T_{flash}, °C	180-200	>230	65-120

The presence of paramagnetic free radical particles is very important for the formation and strengthening of asphaltene associates.

The method of constructing a hypothetical structure of the asphaltene molecule was developed by I. Posadov and Y. Pokonov on the basis of complex analysis IR-, VMR-, UV-, EPR-spectroscopy, ray-structural and electron diffraction method, mass spectroscopy, gas chromatography and determination of structural group parameters. It is in accordance with the values of the structural-group characteristics of asphaltenes (figure 1).

This model gives an idea about formation of an associate in supramolecular formations of asphaltenes and metal ions arrangement in the form of porphyrin-similar complexes.

A promising direction for improving the bitumen quality is the developnet of a bitumen production technology based on a scientific approach to the selection and use of mixed raw materials and activating, modifying and intensifying additives to oxidized stocks. The stocks preparation is an effective way to increase the stability of the fractional, group chemical and elemental composition of stocks for bitumen production. However, nowadays at some refineries the approach to the stocks preparation by compounding is associated mainly with the need to dispose the production waste, and not to ensure the optimal stocks composition for bitumen production, what leads to the production of petroleum bitumen, that does not meet the requirements of the actual State Standart 22245-90 on one or several indicators. The bitumen properties, as it was proved by the authors, depend on their component composition. Physical-chemical properties and running ability are determined by the optimal composition. It is achieved at a certain ratio of asphaltenes, tar and oils with the required content of aromatic components and in the absence of significant amounts of solid paraffinic compounds. Consequently the bitumen properties can be regulated by selection of the feedstock formulation, the parameters of the technological process of their production, by stocks activating (modifying) and modifying the properties of the commercial product.

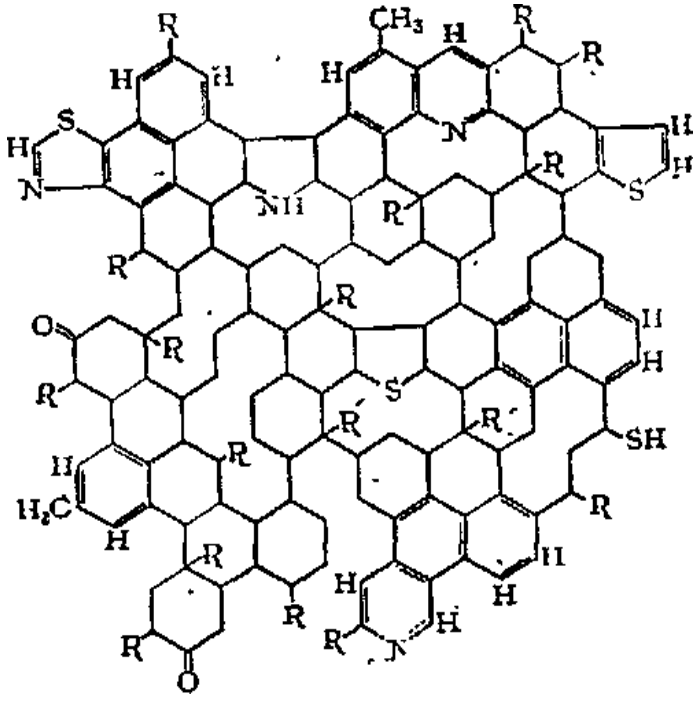


Figure 1 - Model of the hypothetical structure of the asphaltene molecule

This model gives an idea about the process of associates formation in supramolecular asphaltenes compounds and how metal ions position in the form of porphyrin-similar complexes.

Bitumen production technology development, based on a scientific approach to the selection and use of mixed stocks and activating, modifying and intensifying additives to oxidized stocks, is a promising direction for improving the quality of bitumen. Stocks preparation is an effective way to increase the stability of the fractional, group chemical and elemental composition of stocks for bitumen production. However, nowadays at some refineries, the approach to the stocks preparation by compounding is associated mainly with the need to dispose of production waste, and not to ensure the optimal stocks composition for bitumen production, what leads to the production of petroleum bitumen that does not meet the requirements by one or several indicators of the current State Standart 22245-90. The properties of bitumen, as the authors have shown, depend on their component composition. The optimal composition, which determines the physicochemical and running abilities of bitumen, is achieved at a certain ratio of asphaltenes, tar and oils with the required content of aromatic components and in the absence of significant amounts of solid paraffinic compounds. Consequently, bitumen properties can be regulated by the feedstocks formulation, technological process parameters of their production, by stocks activating (modifying) and commercial product properties modifying.

Nowadays, the quality of the produced bitumen and the volume of their production do not fully meet the market requirements. Demand for high-quality bitumen for repair and application of new coatings is satisfied only by 40-65%. Sharp cyclical temperature drops typical for our country lead to their rapid destruction of composite coatings during their exploitation, cause rapid changes in the values of linear expansion.

The production of modified bitumen - component of asphalt concrete - has been started in Kazakhstan. It makes the road surface resistant to dynamic and temperature loads, elasticity, and prevents deformation during cars' moving.

Start of equipment using for modified bitumen production with a capacity of 120 thousand tons per year and the release of the first pilot industrial product consignment took place at the Aktau bitumen plant LLP "JV "CASPI BITUM", whose products are used at "Western Europe - Western China" international highway construction objects and road sections of republican significance.

Modified bitumen is obtained by SBS polymer component (modifier) addition into the composition of oil road bitumen. The presence of the polymer increases the operating temperature range of the roadway up to 100°C, what is significantly higher than that of a conventional one, and increases its wear resistance.

Kazakhstan in the framework of the innovation-industrial policy covers a wide spectrum of petrochemistry development, included a number of tasks, what will allow to rapidly increase deep processing of products for the

related industries of oil and gas, and this procedure will undoubtedly accelerate the development of the RK economy in the future, what is defined in the Development Strategy of the Republic of Kazakhstan-2050.

Bitumen is the largest type of petroleum products in Kazakhstan and abroad. Tightening requirements for bitumen quality and an increase in bitumen consumption lead to the need to improve and increase the capacity of technological processes for oxidized bitumen obtaining. The range of bitumen application is wide; it is used for the construction and repair of roads, airfields, in civil and industrial construction (roofing materials production, insulating pipelines from soil corrosion, paints and varnishes).

Significant amounts of metal consumption and hard operating conditions of oil and gas production equipment make the problem of increasing the durability of equipment one of the central problems, that determine the growth rate and technical- economic efficiency of oil and gas production and transportation.

One of the perspective directions on the reliability and efficiency of oil equipment is the insulation of equipment surfaces with paint-and-lacquer materials. Products with paint-and-lacquer materials successfully combine strength and rigidity proper for metals with chemical resistance, wear resistance and a number of other special properties characteristic of polymers.

Paint-and-lacquer industry produces a wide range of paints and varnishes (varnishes, enamels, paints, primers, putties, various auxiliary materials), which are widely used in various industries, in construction, in transport, in everyday life. They are used for anti-corrosion protection of various products and equipment, automobiles, agricultural machines and mechanisms, in order to increase weather resistance, to make products with a decorative look and for many other purposes. Using a new polymers for paint-and-lacquer materials production, as well as the modification of commonly used film-forming materials contribute to the creation of paints and varnishes of improved quality, as well as with specific properties.

The consumption volume and structure are growing slowly, but steadily. Figure 2 shows the growth rates of the main indicators of paint-and-lacquer materials market in the RK in 2015-2019 according to the Ministry of Finance of the RK, the Ministry of National Economy of the RK, TebizGroup for such as production, import, export and market volumes.

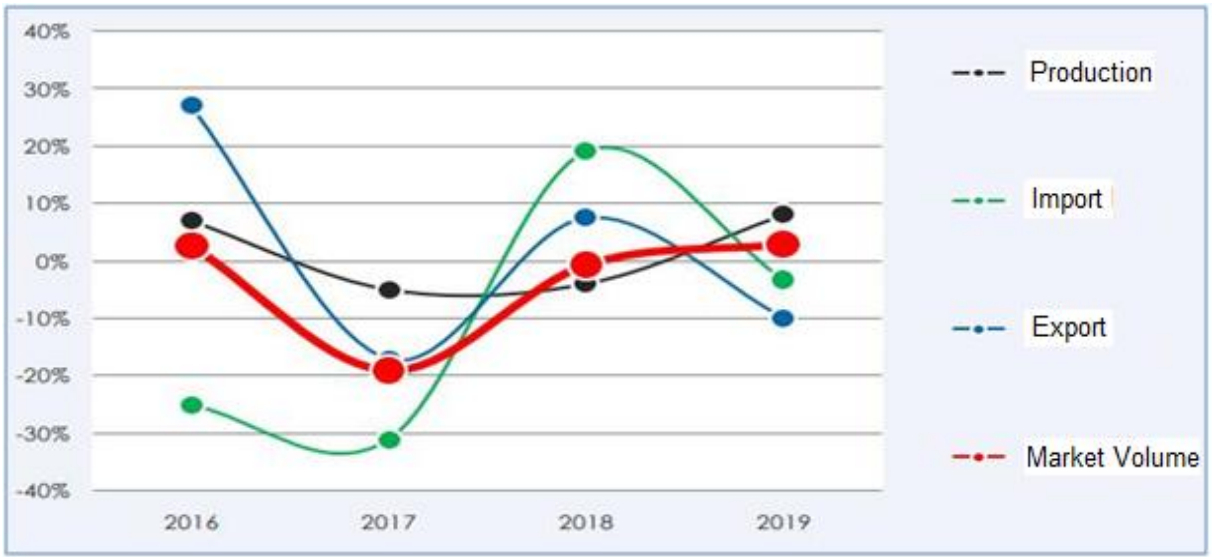


Figure 2 - Main indicators growth rates of the paint-and-lacquer materials market in the RK in 2015-2019

Paint-and-lacquer materials for construction purposes are in the greatest demand and their share in weigh is from 60 to 70%, according to various estimates. The greatest demand is for interior paints (45-50%), approximately 25% of the consumption volume is for facade paints, the third position (15-20%) is occupied by varnishes for wood (parquet, furniture), and various auxiliary materials (primers, putties, mastics etc.) are about 10%.

However, in recent years the volume of domestic production of this paints type has begun to grow, and at present the share of PLM imported from abroad is less than half of the total consumption. The most interesting classification is based on the characteristics of "cost" and "quality".

Analysts note that our consumer still prefers cheap and not very high quality paint-and-lacquer products (mostly of domestic production), which occupy approximately 50% of the consumed volume. This category should include also oil paints, alkyd and water-soluble PLM by domestic manufacturers. At the same time, there is a steady growth in the volume of the average price (and quality) segment.

Every year the content of construction work in the RK is growing. This will give an impetus to an increase in demand for paints and varnishes. Most of the organizations for the PLM production are concentrated in the following areas: (figure 3).

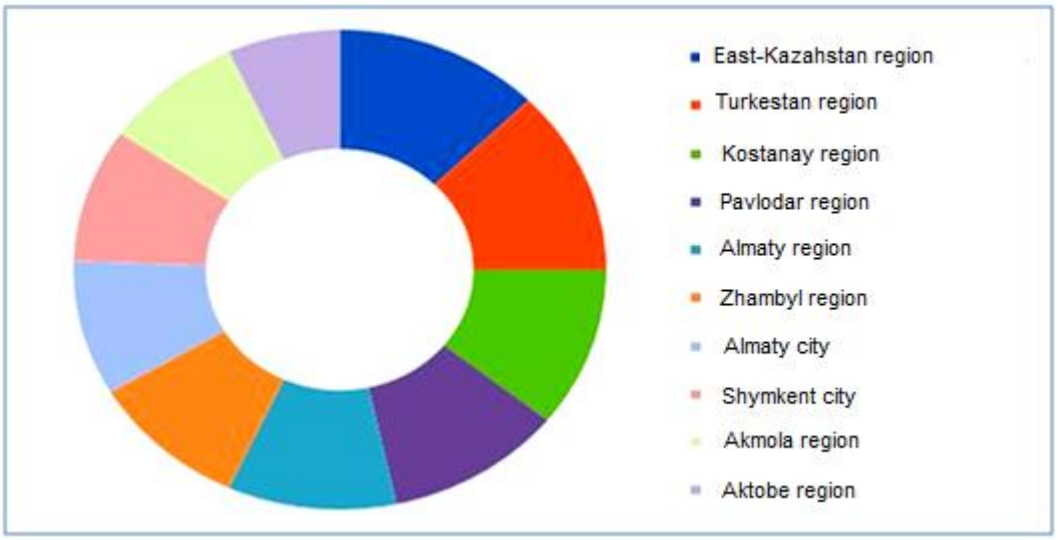


Figure 3 - Producers distribution structure by Kazakhstan's regions

Production volume of paints and varnishes in Kazakhstan in 2016 increased in comparison with 2015 on 15037 tons. The increase over the last three years was 55,7%. The volume of PLM imports to Kazakhstan continued to decline. In Kazakhstan, the production of paints and varnishes has an upward trend. This is evidenced by the figure 4, compiled on the basis of data of the Agency on Statistics of the RK.

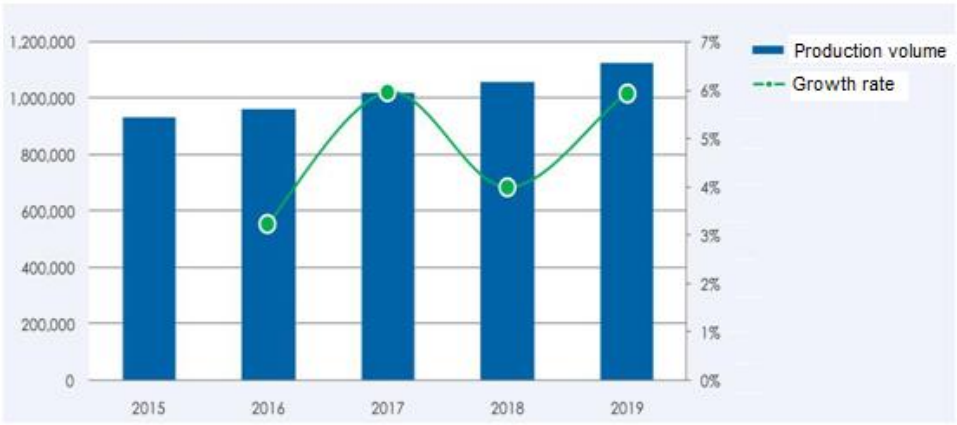


Figure 4 - Annual growth rates of paints and varnishes production in the RK

Thus, the figure 4 shows that the paints and varnishes production volume in Kazakhstan in 2019 increased compared to 2015 by 44%. The increase over the last five years has been 50%. So it is possible to make the following conclusion: paint-and-lacquer materials production has been and remains one of the most promising and profitable investments. Varnishes and paints are the most widespread and one of the most affordable finishing materials. Despite on the fact that the domestic industry is enough actively developing in this segment, the competition is still not so high and the new business has every chance for success.

Nowadays such countries as Russia, Germany, Finland, Denmark are the main suppliers of PLM to Kazakhstan. One of the main problems of the branch is the lack of domestically produced paints and varnishes.

The analysis of literary sources proved that bituminous paint-and-lacquer materials have very good water resistance, but they do not sufficiently resist atmospheric influences and especially solar radiation. In order to increase the weather resistance, oils and tar are added into their composition, what, however, reduce their water resistance.

Factors constraining the widespread use of bituminous paint-and-lacquer materials are low hardness, adhesion and strength, largely depended on both the technological conditions of the bitumen production process (temperature, air consumption and the duration of the process) and on the group chemical composition of the feedstock.

It is necessary to note, that bituminous paints have a good perspective, since their properties can be noticeably improved by addition of surfactants, corrosion inhibitors, some polymers and oligomers. All this facts make it possible to reduce the demand for oil and make these paints more bituminous, more accessible and cheaper. In addition, there is an opportunity to improve the quality of bitumen during its synthesis. Consequently, there are additional opportunities to improve the quality of bituminous paint-and-lacquer materials.

Bituminous varnish is a special solution made on the basis of polymer tar and various bitumen, which improve running ability and physical-chemical properties. It can be applied for materials such as concrete, ferrous metals, wood, brick.

The bonding component which is a basis of the bitumen varnish is natural petroleum bitumen. We know bitumen as a black solid material or one of its shades (figure 5). Natural bitumen can be a solid or fluid state depending on the ambient temperature.

Figure 5 – Bitumen appearance

Bitumen melts and turns into a liquid state at temperatures above 1000°C. By this way the production of asphalt concrete mixtures takes place.

As bituminous varnishes have an excellent water-repellent properties, they found an application in construction works of the foundation part of

buildings and constructions. After the bituminous varnish hardening, a water-repellent glossy film is formed, usually has black color (figure 6a, 6b).

Figure 6a - Bituminous varnished wooden structures

Figure 6b - Bitumen coated metal products

The main technical characteristics are: relative viscosity according to the B3-4 viscometer at 20°C, the content of non-volatile substances, the drying time of the layer at a certain temperature are given in (table 2).

Table 2 - Grades and technical characteristics of bitumen varnish

Grade of varnish	Viscosity on VZ – 4 at 20 °C, not less	Content of non-volatile substances,%, not less	Temperature, °C	Time of drying
BT-99	39-60	42-47	20±224	15 min
BT-123	30-70	38-42	200±10	50 min
BT-142	120-180	55-58	120	2 h
BT-566	—	38-44	90	1 h
BT-569	50-90	40-50	200±3	50 min
BT-577	18-35	37-41	20±2	24 min
			100-110	20 min
BT-783	60-100	45-55	20±2	48 h
			100	2,5 h
BT-980	30-60	40	100-110	10 h
BT-987	30-60	40	105-110	6 h
BT-988	30-60	40	105-110	3 h
BT-5100	25-40	43-48	20±2	2 h
			60	30 min

In our country it happened so, that the oil refining industry is more interested in deepening the process of light fractions maximum selection,

while there is no oil refining base that would specifically produce oil bitumen of good quality.

Thus, the trends of the current state of paint-and-lacquer materials production are analyzed in the Republic of Kazakhstan. The volume and structure of consumption are growing slowly but steadily. An analytical review of bituminous paint-and-lacquer materials proved that the factors that restrain the widespread use of bituminous paints and varnishes are low hardness, adhesion and strength, which largely depend on the technological conditions of the bitumen production process.

Analysis of modern scientific-technological achievements and the results of developments, taking into account the mechanism of different additives action to bitumenous materials, allowing to regulate effectively the quality of stocks, materials and products on each of the technological stage of production-technological complex of bitumen production.

With increasing energy, material and labour expenses, especially at the construction and exploitation oil- and gas- pipelines and objects of industrial and civil purposes, in current state using of domestic bitumen in development on their basis modern technology of composite bitumen materials production, which should solve ecological and economic aspects of industry, is gathering actuality.

In experimental part of the doctoral thesis the characteristic of research objects is given.

The objects of scientific-research work are:

1. Petroleum road bitumen marked PRB 70/100. Bitumen PRB 70/100 is a bitumen of Shymkent bitumen enterprise LLP “Gazpromneft’-Bitum Kazakhstan” is a large-capacity product of oil refinery, has a complex of valuable technical properties. Production capacity is 500 tons of bitumen per day. The stocks for bitumen production is a tar (heavy petroleum residue of vacuum distillation), provided from Omsk refinery LLP «Gazpromneft’-Omsk Refinery”. In the table 3 physical-mechanical properties of the bitumen are given.

Table 3 – Physical-mechanical properties of PRB 70/100

Indicator	Value
Needle penetration depth, 0,1 mm:	
at 25 °C	75
at 0 °C	22
Ring and ball softening point, °C	48
Extensibility at 25°C, sm	115
Fragility temperature, °C	-20
Flash point, °C	240

Vermiculite of Kulantau oilfield.

For the research purpose Kulantau vermiculite was used. Picture of the sample of expanded vermiculite is given on the picture 7.

The following crystal chemical formulas are proposed for vermiculites.

According to Barshard: $(H_2O)_x$ $(Mg, Ca)_y(Al, Fe, Mg)$ $(Si, Al, Fe)_4O_{10}$ $(OH)_z$, where y - varies from 0,22 to 0,36, z – 3.

According to Gruner: $22MgO \cdot 5Al_2O_3 \cdot Fe_2O_3 \cdot 22\ SiO_2 \cdot 4\ H_2O$.

Picture 7 – Expanded vermiculite of the Kulantau deposit (Turkestan region)

The qualitative characteristics of the vermiculite of the Kulantau deposit are shown in Table 4.

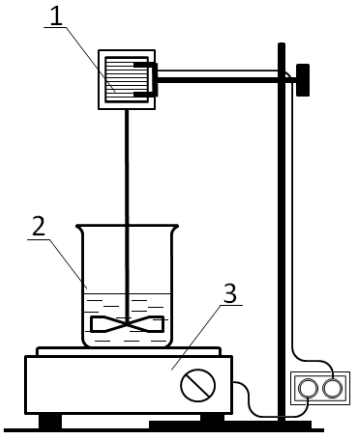
Table 4 - The qualitative characteristics of the vermiculite of the Kulantau deposit

№ sample	Humidity, %	Hydration degree, %	Volume weight, kg/m^3	Vermiculite content, %
1	6,2	65	178	30
2	9,0	70	200	35
3	3,7	60	130	28
4	3,1	75	140	26

Microscopic research and the results of X-ray diffraction analysis of vermiculite samples from the Kulantau deposit showed that the main component is kochubeite - $(Mg, Fe, Al)_6$ $(Si, Cr)_4O_{10}$ $(OH)_8$, a product of biotite alteration with a reduced content of K_2O and an increased content of H_2O, represented by flakes of brown mica. The following impurities are observed: calcite, crystals of chlorite, quartz.

Method of preparing bituminous paint materials

For the preparation of bituminous paint materials a laboratory installation was assembled (fiigure 8). The initial bitumen is heated, melted at a temperature of 100-120 °C, and loaded in an amount of 300 g into a metal container preheated to the same temperature. Next, a plasticizer is added in the amount of 3% of the mass volume of bitumen. When the temperature reaches 140-150 °C, expanded Kulantau vermiculite (fraction 0,5-1 mm) is added with constant stirring. For the resulting composition, the penetration depth of the 0.1 mm needle at 25 °C, the softening temperature, the brittleness temperature, the plasticity temperature and the extensibility at 25 °C were determined.



1– electric mixer; 2 – metal container; 3 – electric heater with temperature controller

Figure 8 - Scheme of a laboratory mixing installation for the preparation of bituminous paint materials

The research of the physical and mechanical properties of bitumen and the resulting bituminous paint materials were carried out in the laboratory of the Oil Refining and Petrochemistry Department and IRLRP of Auezov SKU.

In the experimental part of the work, the physicochemical features of obtaining composite bitumen materials based on RPB 70/100 bitumen and mineral filler are considered.

The following is an approach Ring and Ball method to the development of basic formulations of paint materials using the example of bitumen resin and the development of bituminous paint materials with Kulantau vermiculite.

Analysis of literature data and existing patents showed that, we need to develop mineral-filled bitumen varnish in order to expand the range and versatility of their coating applications in structures in industrial construction.

The problem is solved by using oil bitumen RPB 70/10 for bitumen in the manufacture of the claimed varnish and Kulantau vermiculite of domestic production in manufacture of mineral filler.

The technical objective of this invention is elimination of the shortcomings of the prototype and further improvement of the operational properties, in particular, the stabilization of adhesion with an increase in the temperature range, an increase in the adhesion of the composition to the metal surface over time, the preservation of high plasticity and protective properties during prolonged operation, the possibility of using an anti-corrosion material as a repair material without a high degree of preparation of the metal surface before application. The technical problem posed is achieved due to the fact that the bitumen varnish, including bitumen, a mineral component, a solvent, according to the invention, as bitumen contains petroleum bitumen with a temperature according to the Ring and Ball method of at least 90 °C, a mineral filler is a domestic Kulantau vermiculite, a solvent is white spirit, with the following ratio of components, wt%:

petroleum bitumen RPB 70/100 – 35 % mass;

vermiculite – 5,5 % mass;

siccative NF-1 – 4,5 % mass;

white spirit – 55 % mass;

Examples of bituminous varnishes with mineral filler are shown in table 5.

Table 5- Examples of bitumen varnishes with mineral filler

Components	Proposed composition,% mass.					Prototype
	1	2	3	4	5	
petroleum bitumen PRB 70/100	35	40	45	50	55	
petroleum bitumen PRB 70/30	-	-	-	-	-	48-68
oil sludge	-	-	-	-	-	30-15
Kulantau vermiculite	5,5	5,5	5,5	5,5	5,5	-
Siccative NF-1	4,5	4,5	4,5	4,5	4,5	4,5
Solvent (white spirit)	55	50	45	40	35	17,5-12,5

When the content of the bitumen varnish is less than 40% of the mass, the adhesion of the coatings obtained decreases, and with the content of 45% of the mass, the fragility of the resulting coatings increases, especially at low temperatures and, accordingly, the water resistance decreases. The factors restraining the widespread use of bituminous paints and varnishes are low hardness, adhesion and strength, which largely depend on both the technological conditions of the bitumen production process (temperature, air consumption, process duration) and the group chemical composition of the feedstock.

The physical and mechanical properties of the prepared bitumen varnish according to the invention and the prototype are shown in Table 6.

The technical result of the claimed bitumen varnish consists in stable adhesion in a wide temperature range, maintaining high plasticity and

protective properties during long-term operation, simplicity of its implementation, which does not require special highly qualified personnel.

Table 6 - Comparative physical and mechanical properties of bituminous varnishes

Indicators	The proposed composition, % mass					Prototype
	1	2	3	4	5	
Apparent viscosity according to VZ-4 at 20^0C, sec	32	34	33	35	34	39
Drying time of the film to degree 3						
at $20\pm0,5^0$C, hrs.	12	12	12	11	11	13
at $100\text{-}110^0$C, hrs.	2,0	2,2	2,3	2,4	2,2	2,0
The content of non-volatile substances in varnish, %	39,77	40,01	39,56	39,48	40,05	54,2
Flexural elasticity, mm	3,2	3,2	3,3	3,2	3,2	3,0
Film hardness by M-3 device, st. un.						
-in 3 days	0,06	0,05	0,06	0,05	0,04	0,04
- in 7 days	0,36	0,35	0,39	0,34	0,32	0,31
-after water saturation	0,21	0,20	0,22	0,20	0,23	018
Film strength on impact, N-s	420	440	460	440	465	460
Adhesion, points	0,6	1	1	1	1	1
Shine, mA	0,175	0,180	0,165	0,170	0,175	0,159

With similar costs for comparable bituminous varnishes with this claimed one, it is possible to get a universal material for different applications - for coatings, including anti-corrosion ones for industrial construction. When compared with known similar bituminous varnishes, the claimed one is characterized by increased parameters in terms of environmental friendliness and energy saving while reducing the cost of transportation.

Thus, the developed composition of anticorrosive bitumen varnish is durable, increases operational properties by improving protective properties, increasing adhesion to metal, and can be used to protect the outer surfaces of trunk and oil and gas pipelines, pipelines of various other purposes and reservoirs from corrosion. Bituminous varnish with mineral filler provides stable adhesion in a wide temperature range, preservation of high plasticity and protective properties during long-term operation, does not require a high degree of preparation of the metal surface before application.

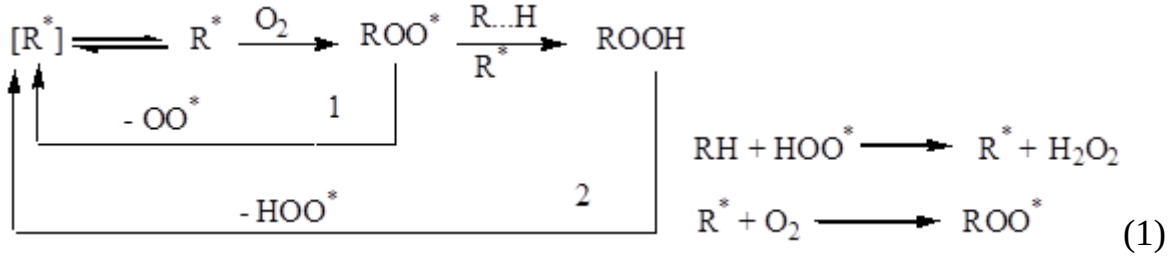
Further, a study of the structural-group formulation of composite bituminous materials was carried out when modified with Kulantau vermiculite. Expanded vermiculite, depending on the size and particles, is divided into several fractions, the bulk density of which, depending on the expansion of the raw material, can vary within fairly wide limits.

Expanded vermiculite low volume weight is not only its advantage. Vermiculite particles are elastic. Expanded vermiculite has elasticity

expressed in a partial restoration of the height of a previously compressed sample after removing the load from it. Total deformation of expanded vermiculite during axial compression due to air trapped between the plates is composed of elastic and residual. Expanded vermiculite is characterized by anisotropic properties: in the direction perpendicular to the cleavage plane, vermiculite grains have lower strength than in the direction parallel to the cleavage plane. In accordance with it, the first determines the deformation properties, and the second determines the brittleness of expanded vermiculite.

When changing the solvent capacity of bitumen, an anomaly of the viscosity, softening temperature and penetration of bitumen is usually observed. Abnormal phenomena increase with an increase in the quantitative ratio of asphaltenes to resins in bitumen and a decrease in the solvent capacity of the oil component. These data indirectly confirm the fact that bitumen at normal temperatures, are structured substances. The colloidal structure of bitumen is determined by the concentration of components forming supramolecular structures and their chemical nature, which is used to classify bitumen. There is a relationship between the supramolecular structure of bitumen and its rheological properties. Free radicals are concentrated in asphaltenes, which contribute to the association of asphaltenes and the formation of supramolecular structures. The plasticizing effect is provided by the resin fractions. The plasticity and solubility of asphaltenes largely determine the operational properties of bitumen. The content of asphaltenes determines the temperature stability, viscosity and hardness of bitumen. There are two types of supramolecular structures in tar and bitumen. When the temperature changes, a periodic rearrangement of the supramolecular aggregates is observed, hence it follows that the initial substance, depending on the chemical nature, group composition and temperature, can be either in the state of a molecular solution, or represent a colloidal system.

The mechanism of oxidation of the components in the dispersed phase can be influenced by the nature of the components of the dispersion medium, primarily the content of substances with mobile hydrogen atoms in it. This effect is illustrated by the diagram:



(1)

[R*] - a substance and a radical in the form of an associate, RN - the initial substance.

The nucleation of the chain occurs as a result of the action of oxygen with free radicals leaving the particles of the dispersed phase in the dispersion

medium. The components of the oils are converted into mainly resin components. It is possible that in the initial oxidation period, the resin associates may act as a trap for free radicals, which recombine in the associates to form molecules or less active radicals. Within the boundaries of the next stage, the least polar components of the resins are primarily oxidized, which turn into asphaltenes, which undergo structural changes as they accumulate. The structural rearrangement in oil residues is caused by the dynamic ordering of aliphatic chains and aromatic hydrocarbons in the environment of particle nuclei in the dispersed phase.

According to the analysis of the process, it can be seen that intermolecular interactions occur between the polar components of bitumen and vermiculite, leading to the formation of dispersed structures. Such structures are quite stable and persist under the conditions of thermal and oxidative processes of bitumen production. When such processes are carried out, there is a change in the quantity and quality of the ingredients in the dispersed phase and the dispersion medium, which affects the reactivity of the components of the dispersed system, which differ in the mechanism of chemical transformations

Analysis of the structure and properties of expanded vermiculite proved the possibility of using it as a damping additive in bitumen.

The data of physical-chemical research of the properties of compositions modified with expanded Kulantau vermiculite, depending on the amount of expanded Kulantau vermiculite for PRB70/100 bitumen are given in the table 7.

Table 7 – Physical-chemical properties of modified by expanded Kulantau vermiculite compositions

The amount of expanded Kulantau vermiculite, % mass	Compositions properties		
	Viscosity, conventional degrees	Softening temperature, ^{0}C	Extensibility
PRB 70/100 Bitumen			
0	108	44	68
0,5	104	49	64
1,0	98	50	61
1,5	97	52	58
2,0	85	53	57
2,5	76	56	49
3,0	77	48	60
3,5	74	49,5	60
4,0	72	48,5	61
4,5	70	48	61
5,0	68	49	60

The characteristics of the bitumen - vermiculite composition (BVC), depending on the amount of expanded vermiculite for bitumen PRB70/100, are given in the table 7. As can be seen from the data in table 7, with an increase in the content of expanded vermiculite in the composition of the bitumen composition, the viscosity and softening temperature increase.

The viscosity increase and softening temperature of modified bitumen means that under conditions of elevated temperatures in summer, the possibility of plastic deformation will significantly decrease. The research have shown that the optimal amount of expanded vermiculite in the bitumen composition is 4 ± 0,5 %.

Due to the fact that IR-spectroscopy is one of the most informative and sensitive methods for instrumental analysis of complex mixtures of organic compounds, such as oxidized bitumen and their modification products, this method to research changes in the qualitative and quantitative composition of bitumen PRB 70/100 and the resulting bitumen compositions containing different amounts of vermiculite (from 2% to 25%), containing different amounts of vermiculite (from 2% to 25%) were used. After PRB70/100 samples preparation and samples from the obtained bitumen compositions, IR-spectra of structures initial bitumen PRB70/100 were obtained (figure 9), with the addition of different amounts of vermiculite (5%, 10%, and combined IR-spectra of bitumen compositions, containing different amounts of vermiculite (from 2% to 25%) (figure 10).

The IR spectra of the compounds were recorded on a Shimadzu IR Prestige-21 IR Fourier spectrometer with a Miracle ATR attachment (Pike Technologies) in the average IR range (4000-600 cm^{-1}), (optical resolution 4 cm^{-1}, registration time 16 s). The registration of the IR spectra of bitumen was carried out directly between KBr holes, heated to 50-60 °C without the use of vaseline oil, because the consistency of bitumen at this temperature makes it possible to obtain a capillary film of the required thickness. The results of IR spectroscopy of the initial and modified with expanded vermiculite bitumen are given in figures 9 and 10. In this case, in accordance with the procedure for comparative analysis of the chemical composition of compounds using IR-spectroscopy, the received spectra were superimposed with scaling for CH_2-groups, the content of which does not depend on the experimental conditions. Such a comparison makes it possible to track changes in their number relative to each other.

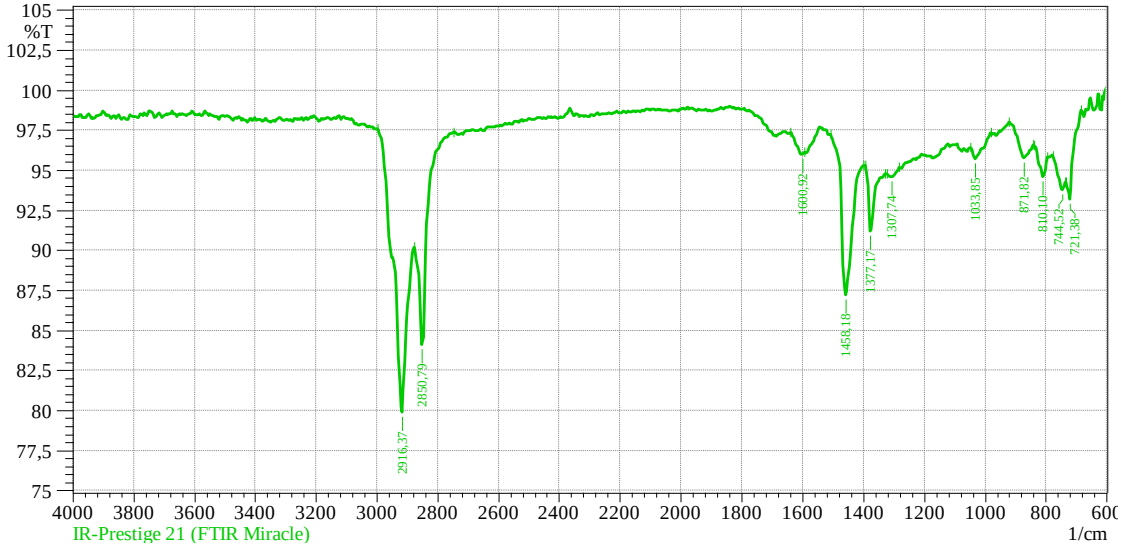


Figure 9 - IR spectrum of the PRB70/100 bitumen structure

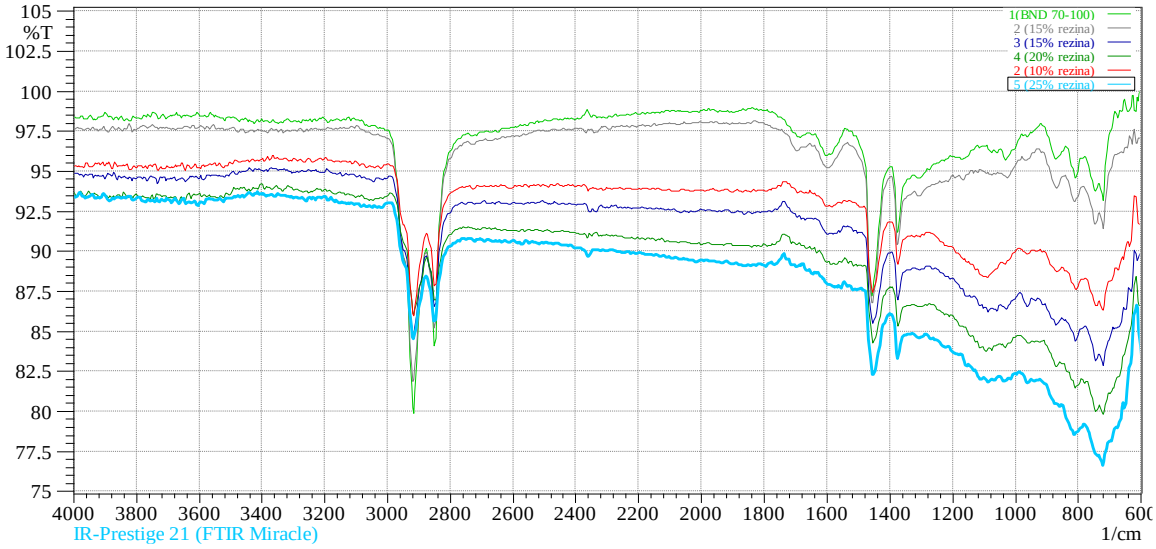


Figure 10 - Combined IR spectra of bituminous compositions containing different amounts of vermiculite (from 2% to 25%)

Received results research analysis of PRB 70/100 bitumen proved the presence of intense strips characteristic of bitumen in the range of 3000-2800 cm^{-1} (stretching vibrations of n(CH) and CH_2 groups), 1470 cm^{-1} (deformation vibrations 5 (CH_2)) and 1377 cm^{-1} (bending vibrations 5(CH_3)). These strips are always present in the spectra of saturated hydrocarbons, paraffins, oils (figure 9). The spectra of the components clearly show the pass strip at 722 cm^{-1}, which corresponds to the bending vibrations of 5(CH_2) - groups in free paraffin chains. The characteristic triplet 740, 722, and 820 cm^{-1} is clearly manifested is a feature of the aromatic structures presence.

The transmission bands in the range of 1380-1480 cm^{-1} are characterized by significantly higher intensity, indicating the presence of

oxygen-containing compounds. The 1600 cm^{-1} strip characterizes the stretching vibrations of unsaturated C=C bonds, mainly of cyclic structure, and primarily of benzene rings. The large half-width and complex structure of this strip indicates a wide compositional distribution of aromatic compounds - asphaltenes in bitumen. In the area of 1688 cm^{-1}, there are bands of carbonyl and carboxyl C=O groups that appear during the oxidation of organic compounds. The characteristic absorption strip of the carbonyl group, which in the spectrum of modified bitumen has a higher intensity than in the spectrum of the original one, and shifts from 1458 to 1600 cm^{-1} (figure 10). It is known that free radicals are concentrated in asphaltene substances, which are one of the factors determining the tendency of asphaltenes to associate. The presence of free radicals is due to the fact that the most condensed aromatic structures are concentrated in asphaltenes, creating the phenomenon of paramagnetism. This leads to intermolecular interaction, which promotes the formation of supramolecular structures. Obviously, the changes in the region of stretching vibrations of n(OH) and partly according to the bands (C=O) characterize the hydrogen bonds of carboxyl groups and the formation of intermolecular hydrogen bonds can be assumed.

The analysis of given spectra indicates an increased content of high-molecular-weight asphaltenes in modified bitumen with a slight increase in structuring resins, since there is an increase in the absorption bands of the carbonyl group at 1458 cm^{-1} (shift in modified bitumen to 1600 cm^{-1} and aromatic rings at 1602 cm^{-1}). Moreover, during expanded vermiculite in bitumen interaction, the content of the oil fraction, in particular, paraffin-naphthenic hydrocarbons, characterized by paraffin chains with a spectral band at 718 cm^{-1} decreases.

The concentration decrease of paraffin-naphthenic hydrocarbons in bitumen leads to an increase in the lyophilicity of asphaltenes, which solvate and swell in aromatic hydrocarbons and are insoluble in paraffin-naphthenic hydrocarbons. Such bitumen is different by the fact that asphaltenes can interact with their polar (lyophobic) surface areas, forming aggregates and nucleus of a coagulation structure, and resins are orientedly adsorbed on the lyophilic outer side of asphaltenes.

The next step of the research was to study the physical, mechanical and protective properties of bitumen paints and varnishes. The results of research of the physical and mechanical properties of bituminous paints and varnishes are given in (table 8).

So water absorption changes by almost 3,2 times (from 0,03% to 0,8%), and their viability in the investigated temperature range remains sufficient to apply several layers of film from the prepared compositions. Moreover, all of them in terms of impact strength and in terms of water absorption are much superior to unmodified ones (table 8, column H).

Table 8 - Physical and mechanical properties of samples of bituminous paint and varnish materials with different fillers

Indicator	Coating				
	1*	2*	3*	4*	H
Drying from "dust", min	20	20	20	20	20
Practical drying, hour	3	3	3	3	3
Impact strength, N.M	3,8	5	5,5	5	3
Elasticity	1	1	1	1	2
Pendulum hardness device	0,5	0,7	0,8	0,8	0,8
Water absorption, % mass	0,03	0,08	0,037	0,051	0,17
Viability, day	+25°C	>7	>7	>7	>7
	+60°C	>7	>7	>7	>7

Fillers1* - kaolin, 2* - mica 3* - talc, 4* - Kulantau vermiculite

Thus, the water absorption changes from almost 0,01% to 0,08%, and their viability in the studied temperature range remains sufficient for applying several layers of film from the prepared compositions. At the same time, all of them in terms of impact strength and water absorption are much higher than the unmodified ones (Table 8, Column H).

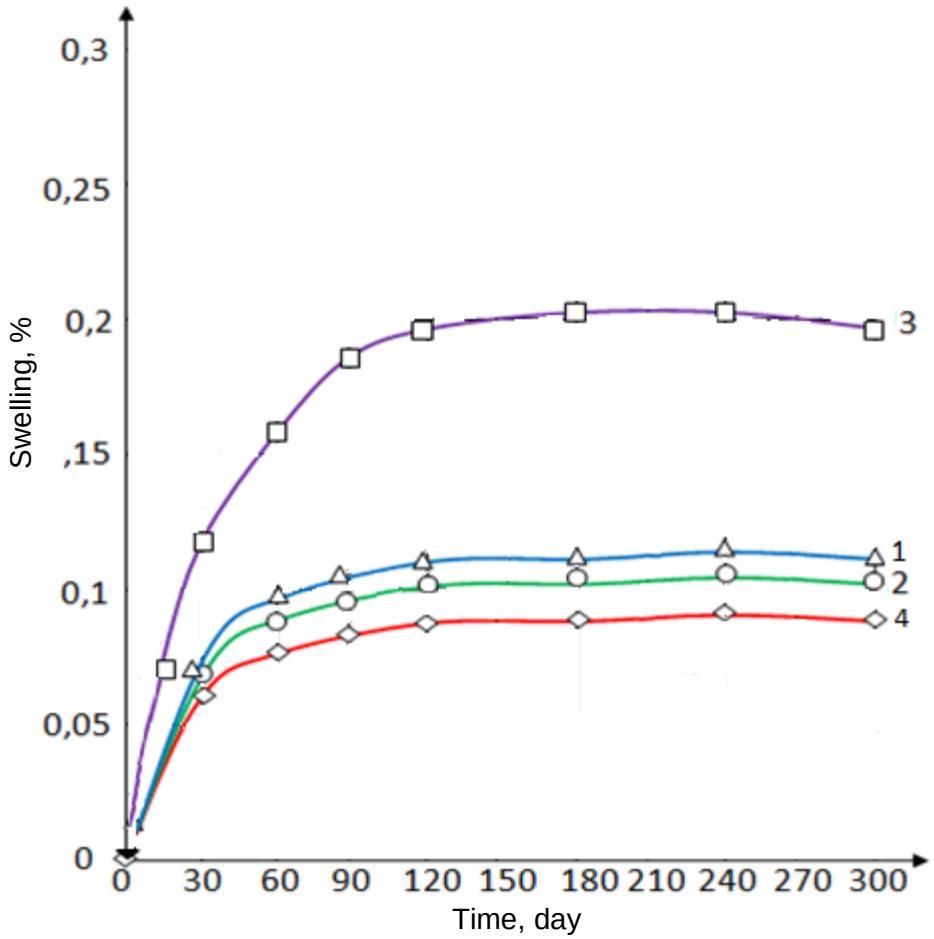
The heat resistance of the coatings is not reduced, and its value is within the permissible temperature limits used in the conduct of technological processes.

The conducted research shows that all compositions have high physical and mechanical properties.

The research of protective properties of bitumen paints and varnishes was carried out in some aggressive media, such as 3% NaCl solution, simulator of petroleum products (50% isooctane according to State Standart 4095 – 75, 30% xylene according to State Standart 9949-76 and 20% toluene according to State Standart 9880-76) and technical water, solutions of which have contact with the most extensive areas of equipment and pipelines that should be protected.

The protective properties were evaluated based on changes in appearance and weight, physical and mechanical properties and adhesion, as well as on the value of electrical resistance and the presence of sub-film corrosion after exposure of the samples in aggressive environments. The study of the protective properties of bituminous coatings showed their high protective properties both at 25°C and at 50°C (Fig. 11).

The results of the study of changes in the amount of swelling over time at temperatures of 25 and 50°C showed that coatings No.1, No.2, No.4, after reaching 30 days of the swelling value from 0.06 to 0.12% of the original mass, stabilize and remain constant for the next 300 days, and coatings No. 3 continue to swell up to 90-100 days.

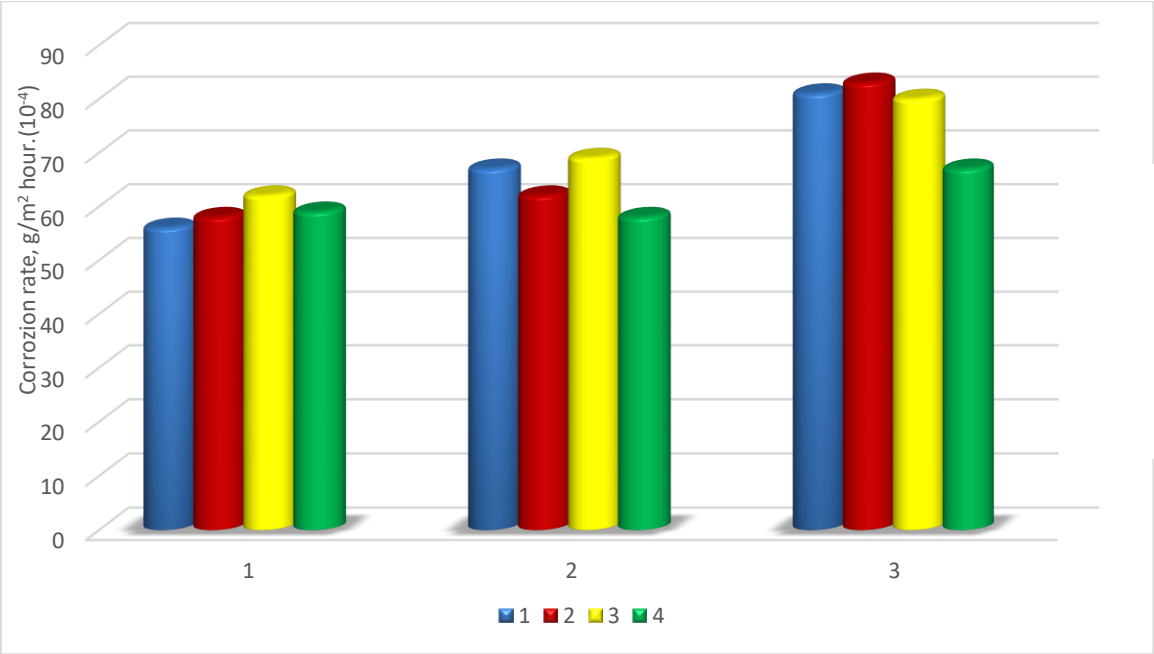


Bituminous coatings with fillers:1-kaolin, 2-mica, 3-talc, 4-Kulantau vermiculite.

Figure 11 - Swelling of bituminous coatings in water at 25°C

When bitumen coatings are immersed in water, the dependence of the swelling (%)of the coatings on the time(day), for example, 30 days, is observed for the following coatings with fillers: with vermiculite-0.65% (curve 1),mica-0.70%, with kaolin-0.86%. with talc - 0.12 %, .Further, the curves of the swelling-time dependence of bituminous coatings with various fillers in water at 250C remained almost unchanged for the next 300 days. A slight initial increase in the mass of the samples is explained by the penetration of water into the pores of the surface layer, after which a mobile equilibrium is established in the system and the state of the coatings is stabilized, which is expressed in the horizontal component of the curves of the swelling value.

The increase of the test temperatures in water up to 50% increases the coatings swelling. In this case, the period increases for all coatings to maximum swelling. But if for coatings №1, №4 there is a slight increase in swelling (up to 0,125%), then for coatings №2 and №3 the swelling reaches 0,23% and 0,31%, respectively.

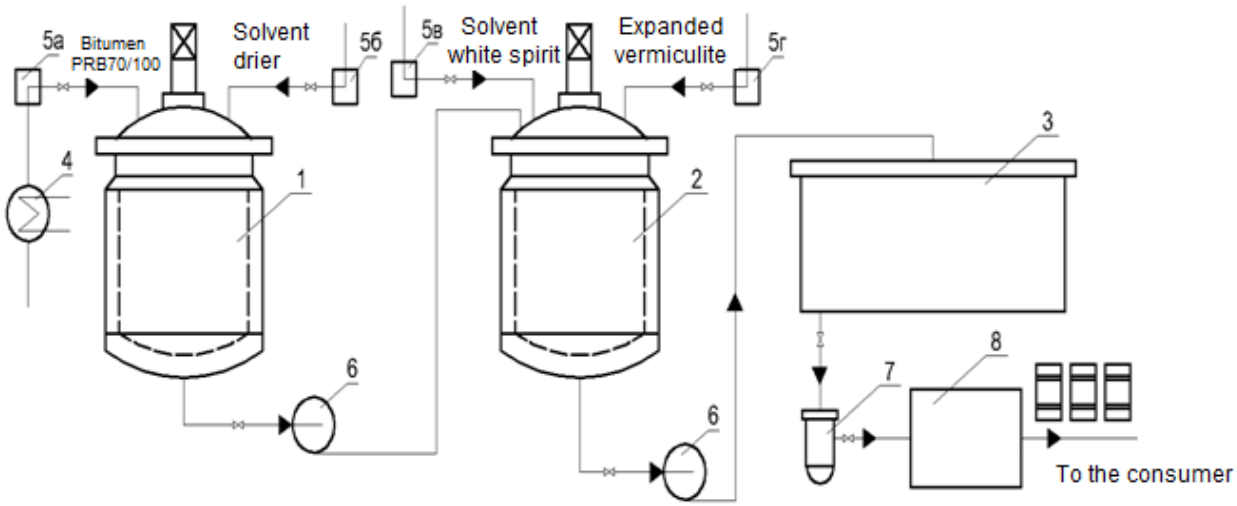


1-with kaolin, 2-with mica, 3-with talc, 4 - with vermiculite
A-the upper part of the pipeline; Б-the middle part of the pipeline;
B-lower part of the pipeline

Figure 12 – Metal corrosion rate with different bituminous coating after 6 months of testing

The highest corrosion resistance in atmospheric conditions was shown by coating №4 with vermiculite, and the lowest one by coating №1 with addition of kaolin as a filler.

Based on the experimental data obtained for the production of bitumen varnish based on PRB 70/100 bitumen, a basic technological scheme of the process was developed and the optimal technological parameters of the process were selected (Fig. 13).



1 - reactor; 2 - mixing tank; 3 - receiver; 4 - heat exchanger; 5a - bitumen dispenser; 5b - desiccant dispenser; 5c - white spirit dispenser; 5g - expanded vermiculite dispenser; 6-pumps; 7- Kuno filter; 8- container for finished products

Figure 13 - Bituminous varnish production scheme

Bitumen PRB 70/100 heated in a heat exchanger (4) is loaded into the reactor (1) (170-180 °C), by air through a distribution grid (1000-1500 m^3/h). Then the varnish resin is cooled up to a temperature of 120-130 °C, then it is pumped into the mixer (2) (purging with nitrogen). Part of the solvent is poured through a dispenser (5b, 5c) into the reactor, where the lacquer resin is mixed with the remaining solvent and a desiccant at a temperature of 15–25 °C for 1 hour. The resulting varnish is fed to the receiver (3) and then for filtration into the «Kuno» filter (7), from where the bitumen varnish independently enters the container for finished products (8), then for packaging. Thus on the basis of bituminous tar a new target products were obtained, required in human life, where there is a solution of the problem of energy and resource conservation.

CONCLUSION

1. The trends of the current state of the production of paint and varnish materials in the Republic of Kazakhstan are considered and analyzed. An analytical review of bituminous paint materials showed that the factors hindering the widespread use of bituminous paint materials are low indicators of hardness, adhesion and strength, which largely depend on both the technological conditions of the bitumen production process. It is shown that the use of domestic bitumens in the creation of a modern technology for the production of composite bituminous materials, which should solve the

environmental and economic aspects of the industry, is of particular relevance in modern conditions

2. The structure of PRB 70/100 bitumen and the resulting bituminous lacquers was studied by IR spectroscopy and standard methods for the study of bituminous materials. The analysis of modern scientific and technological achievements and the results of developments that take into account the mechanism of action of various additives to bitumen materials allowed us to create an original classification of additives and components that allow us to effectively regulate the quality of raw materials, materials and products at each of the technological stages of the production and technological complex of bitumen production.3. In order to research of the physical and mechanical properties of petroleum bitumen the following methods were used: determination of the homogeneity and extensibility on DB-150 ductilometer, the depth of needle penetration on the PNB-02M penetrometer, softening temperature according to Ring and Ball, brittleness temperature. To study the structure of bitumen, bitumen varnishes IR-Fourier spectrometer Shimadzu IR Prestige-21 with an attachment of the disturbed total internal reflection Miracle from Pike Technologies was used.

3. New paint and varnish materials based on modified domestic bitumens were created and formulations of bituminous paint and varnish materials with improved performance properties were developed, the regularities of the influence of modifying additives of various nature on the performance properties of bituminous paint and varnish materials were determined and their optimal concentrations were found to ensure the spatial dispersed structure of the required quality. For the first time, a formulation of bitumen paint and varnish material with improved physical, chemical and operational characteristics based on modified bitumen, additives that combine structuring and plasticizing properties, has been developed. A patent for a utility model of the Republic of Kazakhstan "Bituminous composition with mineral filler" was obtained. No. 4530 dated 03.06.2019.

4. The influence of the modifier-Kulantau vermiculite on the rheological and physico-mechanical properties of bituminous paint and varnish materials was studied for the first time.The resulting effect of modification is established, which is determined by qualitative and quantitative regularities, a number of accompanying processes with the participation of other individual components. The use of Kulantau vermiculite as a part of anticorrosive bituminous varnish provides stable adhesion in a wide temperature range, preservation of high plasticity and protective properties during long-term operation, does not require a high degree of preparation of the metal surface before application

5. The physicomechanical and protective properties of coatings under various temperature conditions are studied. According to the results of the study of the physical and mechanical properties of various coating compositions, it is shown that bituminous coatings exceed unmodified coatings in impact

strength by 1.3 times (No. 1)-1.8 times (No. 3), while their water absorption capacity decreases from 2.5 times (No. 2) to 6.8 times (No. 1) lower. The study of the adhesive strength of coatings based on the adhesive nature of the separation showed that bituminous coatings with a vermiculite filler have the greatest adhesion (No. 4). It is shown that an increase in humidity contributes to a decrease in the adhesive strength of the coating, the more intense the lower the test temperature. Assessment of the resistance of bitumen coatings to atmospheric corrosion in laboratory conditions and at facilities (sections of the oil pipeline and oil storage facilities) showed that it is optimal to protect the outer surface of the structure with coatings containing expanded vermiculite of the Kulantau field (No. 4).6. The physical, mechanical and protective properties of coatings in different temperature conditions have been studied. The study of the physical and mechanical properties of various compositions of coatings showed that bituminous coatings surpass epoxy coatings in impact strength by 1,3 times (№1) -1,8 times (№3; №5) while their ability to absorb water decreases from 2,5 times (№ 2) to 6,8 times (№1). The study of the adhesion strength of coatings by the adhesion nature of breakdown showed that bitumen coatings with a vermiculite filler (№5) have the highest adhesion.

An increase in moisture content contributes to a decrease in the adhesive strength of the coating, and is more intense with the decrease of the test temperature.

The resistance of bituminous coatings to atmospheric corrosion in laboratory conditions and at facilities (oil pipeline and oil storage equipment) was evaluated and showed that it is optimal to protect the outer surface of a structure by coatings containing expanded vermiculite from the Kulantau field (No.4).

6. The technology of obtaining anticorrosive bituminous paint and varnish materials with high performance properties, which can be used to protect the external surfaces of main and oil and gas pipelines and pipelines for various purposes and tanks from corrosion, has been developed. The implementation of the results of the dissertation research allows for stable adhesion in a wide temperature range, maintaining high plasticity and protective properties during long-term operation. The effectiveness of the developed technology is confirmed by pilot tests conducted on the basis of the enterprise JSC "Kentau Transformer Plant" (the test report is attached to the dissertation).

Reliability rating and validation of results. The reliability of the obtained results is ensured by the use of modern means and research methods and is confirmed by the analysis of technical literature, previously conducted experimental studies based on the fundamental provisions of oil dispersed systems theory.

Work evaluation. The main results of the work were presented at the following international conferences, seminars and forums: at the International

Scientific and Practical Conference "Auezov Readings - 16:"The Fourth Industrial Revolution: New Opportunities for Kazakhstan Modernization in the Field of Science, Education and Culture, Shymkent, 2018; at 16 “Uluslararasi Türk Dünyasi Sosyal Bilimler Kongresi", Shymkent, 2018; at the international scientific and practical conference of the Russian Federation: XII International conference of young scientists on petrochemistry "Bulatov readings", Krasnodar, 2018; at the V-the International annual conference "Industrial technologies and engineering" dedicated to the 75th anniversary of M. Auezov South Kazakhstan State University and the 90th anniversary of Academician Sultan Tashirbaevich Suleimenov (ICITE-2018); at the international scientific and technical conference "Innovative developments in the field of chemistry and technology of fuels and lubricants", Tashkent (Uzbekistan), 2019; at the scientific and practical conference "Current problems of the petrochemical complex. Extraction and processing", Russian State University, Moscow, 2019; at the international scientific-practical conference "Auezov readings – 18, Shymkent: Auezov SKU, 2020.

Personal contribution of the doctoral student

The author analyzed scientific, technical and patent sources on the topic of the thesis; the experimental part of the work has been completed; analysis has been performed, processing and interpretation of practical data have been obtained; materials for publication in scientific journals and conferences have been prepared; the results of research were reported at scientific and practical conferences.

Publication of research results. The main results of the thesis research were published in 15 printed publications: 2 articles are published in international scientific journals which are included in the Scopus and Thomson Reuters Web of Science databases, the Egyptian Journal of Chemistry (Egypt), Rasayan Journal of Chemistry (India), 3 articles are published in journals recommended by the Control Committee in the Sphere of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan; 8 publications are in the materials and theses of international and republican scientific seminars and conferences, 3 of them are published in the materials of foreign conferences; 1 patent for a utility model of the Republic of Kazakhstan "Bituminous composition with a mineral filler".

The structure and scope of the doctoral dissertation. The dissertation work is presented on 106 pages of typewritten text, includes 37 figures and 18 tables. The thesis consists of an introduction, a review of the literature, a description of objects and research methods, results and results discussion, a conclusion and a list of used sources of 169 titles.