**Modified Polymer-Bitumen Compositions with Improved Properties**

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**Abstract.** This study presents the results of the development of the composition and technology for producing polymer-bitumen composite protective layers and coatings designed for use in severely continental weather conditions. Ingredients from secondary raw materials - rubber, waste from the chemical oil and gas processing industry - are recommended for composite protective layers and coatings based on bitumen, in accordance with the requirements for use in severely continental weather conditions. The composition and technology for producing multifunctional modifiers and organo-mineral modifiers were developed to improve the operational properties of bitumens based on selected ingredients. The content and process of bitumen modification with the created multifunctional modifiers and organo-mineral modifiers, their physicochemical properties and structure, the place and conditions of application are presented. The influence of physicochemical properties and the content of selected ingredients and modified bitumen on the technological, rheological, physico-mechanical, dynamic, and operational properties of the polymer-bitumen composite protective layer and coating obtained on their basis in substantiated.

**Keywords:** Bitumen, polymer-bitumen, composition, modifier, multifunctional, technology, ingredient, rheology, dynamics, layer, coatings

**INTRODUCTION**

Today, bitumen and composite coatings based on it are used as a protective layer in mechanical engineering and instrument engineering, on highways and railways, on bridges and tunnels, in the construction of residential and industrial buildings [1, 2, 3]. At the same time, in order to increase the resistance of bituminous composite coatings to external aggressive environments and mechanical stresses, physicochemical, technological, physico-mechanical, dynamic, operational properties, and service life, special attention is paid to the creation of modified ingredients that form their structure based on the requirements [4, 5].

Scientific research is being conducted on the creation of modified ingredients and high-molecular polymeric emissions based on bitumen and composite coatings based on it, used as a protective layer in mechanical engineering and instrument engineering, on highways and railways, on bridges and tunnels, in the construction of residential and industrial buildings, increasing their resistance to external and aggressive environments, creating ingredients based on modified and high-molecular polymeric waste to increase technological, rheological, operational properties and service life, modifiers that determine the structure of the composition, studying their physicochemical properties, structure, and sphere of action, creating the composition of composite coatings, technologies, and machines for their production [6, 7, 8].

Also, a number of studies have been conducted to improve the operational reliability of polymer-bitumen coatings, including: in the period of accelerated development of the bitumen industry, in order to obtain composite materials and coatings obtained from polymer-bitumen binders, a filling-binding interfacial structure, pre-set using surfactants, lead-bitumen coatings, and strengthening fillers, reducing the influence of aggressive components in the composition of products on metal structures, ensuring the reliability of technological equipment, highways, and railways, increasing productivity and energy conservation through the targeted use of effective polymer-bitumen coatings and coatings based on them on the working surfaces of technological machines and structures [9, 10].

The aim of the study is to develop the composition and technology for producing polymer-bitumen composite protective layers and coatings intended for use in severely continental weather conditions.

**OBJECTS AND METHODS OF RESEARCH**

Secondary raw material resources, the chemical and oil and gas processing industries, worn-out rubber, and bitumens produced at the Ferghana Oil Refinery were used.

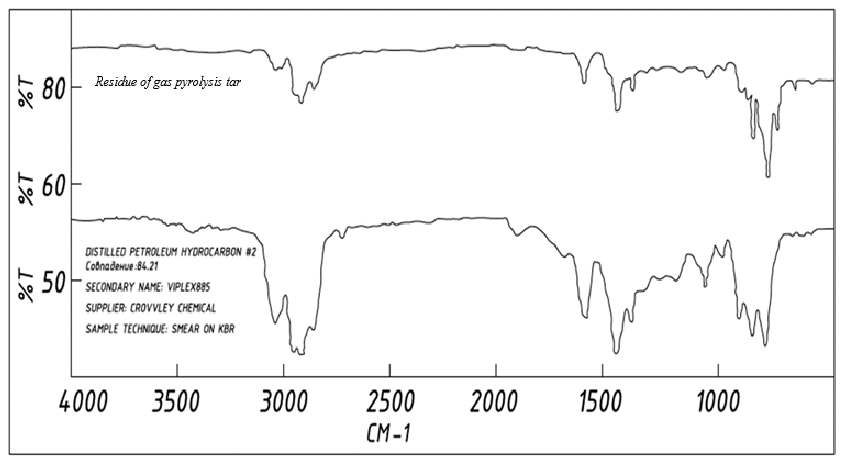
In this work, standardized physicochemical, physico-mechanical, kinematic, and dynamic properties for polymer-bitumen compositions and their modifying action concerning a set of indicators of bituminous binders were determined according to the standards PNST 86-2016 (GOST 58400.1-2019), PNST 88-2016 (GOST 58400.6-2019); a search for recipe and technological solutions for obtaining and applying hybrid bitumen modifiers, providing synergistic effects concerning indicators of bitumen materials, characterizing resistance to rut formation, plasticity (PNST 88-2016 (GOST 58400.6-2019)), fatigue failure at positive temperatures (PNST 81-2016 (GOST 58400.7-2019)) and negative temperatures (PNST 89-2016 (GOST 58400.9-2019)).

**MAIN PART**

The state of obtaining, properties, improving the properties of petroleum bitumens, and the production of protective layers and coatings based on them, the trends in changing the requirements for their properties. An analysis of this issue showed that, while maintaining the trend of increasing demand for these compositions, research work aimed at expanding the use of petroleum bitumens based on local and secondary raw materials that meet severely continental weather conditions remains relevant [11, 12].

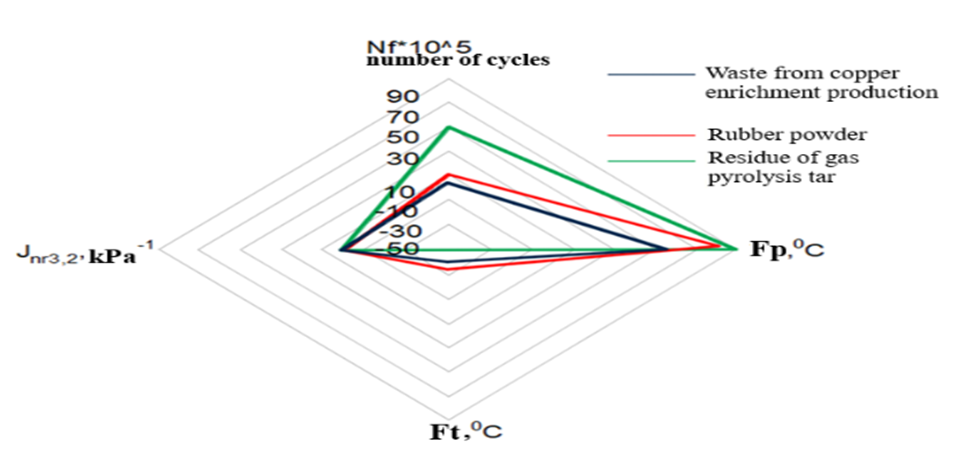
It is known that in severely continental climates, protective layers and coatings based on bitumen quickly fail. The main reason for this is that bitumens, which are the basis of the composition used in them, do not withstand severely continental weather conditions. To modify bitumens and increase the resistance of the protective layers and coatings obtained on their basis to severely continental weather conditions, technological, rheological, physicomechanical, and deformational shifts and destruction, ingredients based on local raw materials were selected, physicochemical properties were studied, and, based on them, the composition and technology for producing an organomineral modifier were created [13, 14].

At a polymer production enterprise, a tar-product, specifically gas pyrolysis resin, is generated as a waste product. This resin is a black, odorless solid. The gas pyrolysis resin primarily comprises alkanes, dienes, olefins, cycloalkanes, and arenes, which are formed during the pyrolysis of natural gas. Its molecular weight is approximately 1000-1200, with a softening point ranging from 120-180°C. It is well-established that the flash point of ingredients utilized in bituminous compositions should be no less than 184°C [15]. Therefore, we subjected the tar-product to thermal treatment at 200-240°C for 120 minutes. This process resulted in a reduction of the tar-product’s quantity to 45%, yielding a black liquid substance with a molecular weight of roughly 800-1000. The composition of the resulting substance was subsequently analyzed using FTIR spectroscopy (Figure 1).

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**FIGURE 1.** FTIR spectrum of the gas pyrolysis resin stillage

The figure reveals that its structure is similar to that of the plasticizer dibutyl phthalate; therefore, it can be used to modify bitumen compositions.



**FIGURE 2. Comparison of the modification of BND 60/90 bitumen with gas pyrolysis resin stillage, waste from a copper-concentrating enterprise, and rubber powder**

When studying the composition of waste from a copper-concentrating plant, it was found to contain the following elements (%): Cu – 0,527, S – 0,801, Mg – 0,802, Zn – 1,45, Ca – 1,69, K – 2,15, Al – 4,56, SI – 17,8, Cl – 0,122, Ti – 0,242, Cr – 0,0377, Mn – 0,204, As – 0,0126, Rb – 0,0226, Sr – 0,0131, Y – 0,0017, Zr – 0,214, Mo – 0,223, Ag – 0,0013, Sn – 0,0055, Sb – 0,0468, Ba – 0,123, Ir – 0,0145, Pb – 0,322. It was hypothesized that the group of these elements enhances the activity of the resulting organomineral modifier [16].

It is known that the problem of processing worn rubber products and tires is currently relevant. Studies have shown that the particle size is 50-140 μm, density is 1200-1.250 g/cm3, weight content is 4.30-4.50 g/cm3, specific surface area is 1100-2200 cm2/g, pH is 7-8, and oil adsorption is 90-100 ml/100 g. Therefore, their crushed powder was selected as the main ingredient in obtaining organomineral modifiers [17].

In obtaining an organomineral modifier for modifying bitumens, butadiene-styrene rubber was used as an ingredient to increase the elasticity, frost resistance, and corrosion resistance of the composition [18]. The influence of each of the selected ingredients on certain properties of the organomineral modifier was determined (Figure 2), and based on the results obtained, an optimal composition and production technology were created.

Based on the results obtained, the following compositions of the organomineral modifier were recommended (Table 1):

**TABLE 1.** Composition of developed organomineral modifiers

|  |  |  |  |
| --- | --- | --- | --- |
| Ingredient Names | М-1 | М-2 | М-3 |
| Ingredient content, parts by weight per 100 parts | | |
| Gas Pyrolysis  Resin Still Bottom | 82,0 | 77,0 | 65,0 |
| Waste from Copper-Concentrating Plant | 5,0 | 3,0 | 7,0 |
| Thermo-mechanically Ground Powder of Worn Rubber Products | 10,0 | 15,0 | 20,0 |
| Butadiene-Styrene Rubber | 3,0 | 5,0 | 8,0 |

It is proposed to use the samples of Table M-1 in desert zones, M-2 in general zones, and M-3 in mountainous zones when modifying bitumens used for producing protective layers and coatings.

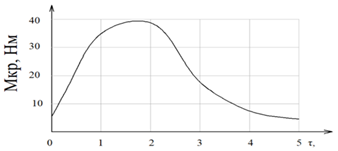
It is known [19] that the operational properties of bitumens currently used in road construction in the Republic of Uzbekistan do not meet the requirements of rapidly changing weather conditions. Considering this, the effect of the organomineral modifier, created on the basis of local raw materials, on the main indicators of the technological process of preparing bitumens BND 40/60, BND 50/70, BND 60/90 and compositions thereof, used in road construction, on the mixing temperature, was studied. Based on the results of scientific research, it was shown that the introduction of organomineral modifiers into road bitumen at 200°C gives good results (Table 2).

Based on the data in the table, it is evident that the recommended organomineral modifiers influence the operational properties of road bitumen 60/90. They increase the softening point, lower the freezing point, which is its main indicator, and enhance ductility and elasticity. This results in the possibility of obtaining modified road bitumen that meets the demands of rapidly changing, sharply continental weather conditions.

**TABLE 2.** Influence of modifier content on bitumen properties

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Bitumen Grade | Modifier Number | Modifier Amount, wt. % | Softening Point (Ring & Ball), °C | Fraass Breaking Point, °C | Needle Penetration, 0°C, 0.1 mm | Needle Penetration, 25°C, 0.1 mm | Ductility, 0°C, cm | Ductility, 25°C, cm | Elastic Recovery, 0°C, % | Elastic Recovery, 25°C, % |
| BND 60/90 | - | - | 47 | -15 | 8,9 | 80 | 3,5 | 55 | 4 | 13 |
| Modified BND 60/90 | 1 | 3 | 52,14 | -16,1 | 8,5 | 78 | 4,9 | 52 | 5 | 13 |
| Modified BND 60/90 | 1 | 6 | 55,28 | -16,6 | 7,0 | 75 | 6,1 | 56 | 7 | 15 |
| Modified BND 60/90 | 1 | 9 | 58,15 | -17,8 | 6,5 | 72 | 7,9 | 50 | 8 | 17 |
| Modified BND 60/90 | 2 | 3 | 53,14 | -16,9 | 7,9 | 76 | 5,8 | 51 | 6 | 15 |
| Modified BND 60/90 | 2 | 6 | 56,58 | -17,2 | 6,1 | 73 | 7,3 | 54 | 9 | 18 |
| Modified BND 60/90 | 2 | 9 | 59,14 | -18,3 | 5,8 | 70 | 9,0 | 48 | 10 | 20 |
| Modified BND 60/90 | 3 | 3 | 55,22 | -17,2 | 6,1 | 74 | 8,0 | 49 | 7 | 18 |
| Modified BND 60/90 | 3 | 6 | 58,28 | -17,8 | 5,5 | 70 | 9,5 | 46 | 11 | 22 |
| Modified BND 60/90 | 3 | 9 | 60,40 | -18,8 | 4,8 | 60 | 11,0 | 44 | 12 | 25 |

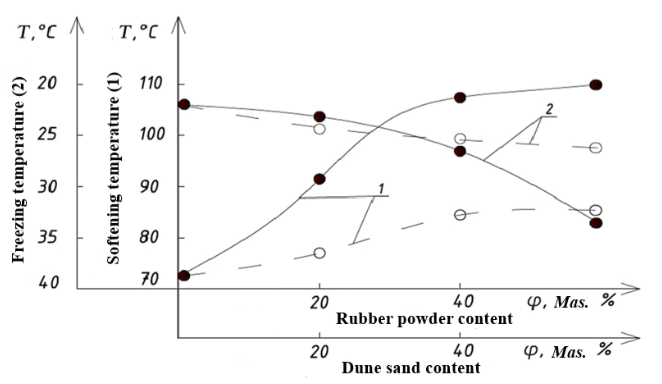
It is known that the bituminous composition used in road construction is multi-component, with each added ingredient playing its own role in its operational properties. Considering this, it is necessary to develop a composition based on the requirements for obtaining road pavements based on modified bitumen, taking into account the weather conditions of the regions. In the development of these compositions, we proposed to add to the composition of the modified bitumen thermomechanically ground powder of worn rubber products based on butadiene-styrene and isoprene rubbers to improve its resistance to destruction, cold, heat, and wear, and studied their properties. As a result, the addition of thermomechanically ground powder of worn rubber products based on butadiene-styrene and isoprene rubbers to the composition led to technological problems in obtaining a homogeneous mixture. To achieve the goal, the process of swelling the thermomechanically ground powder of worn rubber products based on butadiene-styrene and isoprene rubbers at a certain temperature in the modified bitumen was introduced into the technological process (Figure 3).

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**FIGURE 3.** Influence of thermomechanically ground worn rubber products based on butadiene-styrene and isoprene rubbers on the preparation time of a composition based on modified bitumen

As can be seen from the figure, the temperature of the technological process for loosening the thermomechanically ground powder of worn rubber products based on butadiene-styrene and isoprene rubbers is 200°C, the loosening time is 4-5 hours, and its optimal amount in the composition is 40 wt.%. In this case, based on the active organic compounds contained in the modified bitumen, the thermomechanically ground powder of worn rubber products based on butadiene-styrene and isoprene rubbers swells at high temperatures, and additional active centers are formed as a result of the rupture of vulcanization networks remaining in their composition. This leads to an increase in the operational properties of the composition.

The influence of organomineral modifiers and ingredients used in the development of polymer-bitumen compositions for protective layers and coatings on the technological and physico-mechanical properties of the composition has been studied. As a result, the dependence of the softening and freezing temperatures of the composition on the content of organomineral modifiers and ingredients was established (Figure 4). From the curves, it can be seen that the temperature at which the polymer-bitumen composition softens increases with increasing content of organomineral modifier, thermomechanically ground powder of worn rubber products, and barchan sand.

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**FIGURE 4.** Influence of softening temperature (1) and freezing temperature (2) of the polymer-bitumen composition on the content of thermomechanically ground powder of worn rubber products (\_\_\_\_) and Ferghana barchan sand (—-)

Thus, the studies have shown that the softening temperature of the polymer-bitumen composition can increase the thermomechanically ground powder of worn rubber products by 1.5-2 times, the reason for which is that the vulcanization network, mainly torn under the influence of thermomechanical forces, begins to revulcanize under the influence of heat in the technological process, in which -C-S-C-, -C-Sn-C- are formed, this is justified by the increase in the physico-mechanical properties of the polymer-bitumen composition. The adhesion strength, penetration, and expansion at 25°C of polymer-bitumen compositions with mineral raw materials increase with an increase in the amount of the proposed ingredients, which made it possible to select a composition suitable for the climatic conditions of our republic. Similar results were observed in the three proposed organomineral modifiers.

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