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# THE MODIFICATION OF ROAD PETROLEUM BITUMEN WITH PETROCHEMICAL WASTES AND POLYMERS

Elena Emelyanycheva, Ayaz Abdullin

*Chemical Technology of Petroleum and Gas Processing Department*
*Kazan National Research Technological University*
*65 Karl Marx Str., Kazan, Russia*
*E-mail: eemelyanycheva@gmail.com*

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## ABSTRACT

*Petroleum bitumen is widely used as an organic binder in road construction. To meet the increasing quality requirements bituminous binders are modified with various additives, mostly with polymers. However, because of high cost of these polymers, other additives are considered, including various wastes from petroleum and petrochemical industries. Oil sludge, crumbed rubber and carbon black obtained from utilized car tires can be considered the largest-tonnage among them. The research considers the possibility of oil sludge, crumbed rubber and carbon black usage as modifiers of bituminous binders. Softening point, low-temperature properties, penetration and plastic-elastic properties were evaluated for all samples of modified binders. It has been found that the oil sludge affects bituminous binder characteristics in the best way. However, the bituminous binder modified with the oil sludge does not meet all the requirements for modified bituminous binder brands according to current standards. That is why the possibility of the complex modification of bitumen with the oil sludge and polymers was studied. A copolymer of ethylene with vinyl acetate and block copolymer of styrene and butadiene, have been studied. As the result of the study it has been revealed, that the complex modification of bitumen with the oil sludge and SBS block copolymer affects bituminous binder characteristics in the best way and the obtained samples meet all the requirements for modified bitumen.*

*Keywords: bitumen, modification, oil sludge, crumbed rubber, carbon black, polymers, bituminous binder.*

## INRTODUCTION

Petroleum bitumen is widely used as an organic binder in road construction. The annual increase in the load on motor roads leads to an increase in requirements for the quality of bituminous binder. In this regard, petroleum bitumen used as a binder in a road construction is modified with various additives [1]. In most cases, polymers are used as bitumen modifiers. However because of high cost of these polymers, other additives are considered, including various wastes mostly from petroleum and petrochemical industries [2]. The amount of this wastes that negatively affect the environment is annually increasing. A significant part of the wastes can be converted into secondary raw materials. The recycling of industrial wastes allows solving not only ecological, but also economic tasks. As modifiers for the production of bituminous binders different kinds of wastes and by-products from oil refining and petrochemistry have been studied, such as acid tars, alkaline wastes, resins of pyrolysis, oil fractions, synthetic rubber production by-products, secondary polymers and polymers production wastes [3 - 9].

Oil sludge, crumbed rubber and carbon black can be considered the largest-tonnage among industrial wastes from oil refining and petrochemistry [10]. Crumbed rubber and carbon black are usually obtained from utilized car tires [4, 7, 8]. Oil sludge is formed in large quantities during the production, processing and transportation of oil. Due to the fact that the existing methods for its disposal are not sufficiently effective, enterprises are forced to accumulate oil sludge and constantly increase the volumes of sludge collectors, which leads to intensive pollution of soils, air, and groundwater. The main methods of neutralization of oily waste, including oil sludge, are: thermal [10 - 12], biological [11 - 15],

chemical [11, 12, 16, 17], physicochemical [18, 19]. Each of these methods has its drawbacks, while it should be taken into consideration that hydrocarbon part of oil sludge is a valuable organic raw material [10]. With all the variety of known methods of oily waste storage and disposal, the problem of its processing and using remains one of the most pressing. Therefor the estimation of the possibility of oil sludge introduction into bituminous compositions for road construction may be considered scientifically interesting issue as a possible way for their rational utilization.

## EXPERIMENTAL

### Materials

To prepare modified bitumen samples, three road petroleum bitumens with penetration grade 40/60, 50/70, 90/130 were used. Their characteristics are presented in Table 1.

As modifiers for bitumen, oil sludge, crumbed rubber and carbon black were studied.

The oil sludge is a complex mixture of petroleum products with traces of mechanical impurities and water combined with polyethylene wastes. Its softening point according to R&B method is 111ºC, Fraass breaking point is -46ºC, sulfur content is 2.6 wt. %, the ratio of oil sludge: polyethylene wastes is 8:2.

Crumb rubber is crushed rubber, obtained by the destruction of used car tires, with a particle size of 0.1 - 0.5 mm, its bulk weight is 470 kg $m^{-3}$, nominal tensile strength is 20.0 MPa.

Carbon black is a highly dispersed amorphous carbon powder, the product of used car tires recycling. Its particles diameter is 9 - 320.0 μm, specific surface is 114.0 $m^2$ $g^{-1}$, ash content is 0.4 wt. %, bulk weight is 320 kg $m^{-3}$.

Sevilen is a copolymer of ethylene and vinyl acetate with mass fraction of vinyl acetate – 26 - 30 wt. % and elongation at break - not less than 600 %. Its density is 0.950 g $cm^{-3}$ and breaking strength is 12.5 MPa.

Kraton is a block copolymer of styrene and butadiene with mass fraction of styrene 30 - 32 wt. % and elongation at break - not less than 880 %. Its density is 0.940 g $cm^{-3}$ and breaking strength is 33.0 MPa.

### Methods

Modified bituminous binders were prepared according to the following procedure. Petroleum road bitumen was loaded to a metal container equipped with a stirrer, an electric heater and a thermometer. The container was heated up to 160°C, as a result, bitumen became melted. After 10 minutes of stirring at this temperature studied additives were added. The mixture was stirred at this temperature for 2 hours.

Laboratory tests of the quality of the prepared modified bitumen samples were conducted one day after the preparation, in accordance with the standard of Russian Federation 52056-2003. The prepared samples of modified bitumen were tested according to standard methods, the main malacometric properties, such as softening point, Fraas breaking point, penetration at 25ºC and 0ºC, ductility, elasticity at 25ºC and 0ºC of the samples were studied.

Before testing the homogeneity of modified bitumen samples is determined. A glass stick is immersed into a prepared sample for 3 - 4 sec, then it is removed and visually the state of the binder film on its surface is

Table 1. Main performance properties of bitumen.

| Performance property | Road petroleum bitumen | | |
|---|---|---|---|
| | 40/60 | 50/70 | 90/130 |
| R&B test, ºC | 59,4 | 58,5 | 46,5 |
| Fraass breaking point, ºC | -22,4 | -24,8 | -20,8 |
| Penetration at 0ºC, x 0,1 mm | 12,5 | 31,0 | 36,0 |
| Penetration at 25ºC, x 0,1 mm | 40,0 | 50,0 | 96,2 |
| Ductility at 0ºC, cm | 7,6 | 10,4 | 56,7 |
| Ductility at 25ºC, cm | 24,0 | 30,7 | 100,0 |
| Elasticity at 0ºC, % | 21,1 | 5,7 | 17,1 |
| Elasticity at 25ºC, % | 33,3 | 18,6 | 22,6 |

estimated. The bituminous binder should drain from the stick evenly and there should be no clots or grains on its surface. The homogeneity is determined by comparing the results of the three determinations.

To characterize the softening point of modified bitumen samples Ring and Ball method is used, which is determined in accordance with the standard of Russian Federation 32054-2013, the main regulations of which correspond to the standard EN 1427 test method for softening point of bitumen. The softening point is defined as the average of the temperatures at which each of the two bitumen discs softens so that a standard ball pushes the bitumen downward by 25 mm (1 inch).

The test method of determining Fraass breaking point consists of cooling and periodic bending of a thin bitumen sample and determining the temperature at which thirst cracks appears on its surface. It is determined in accordance with the standard of Russian Federation 33143-2014, the main regulations of which correspond to the standard EN 12593.

The penetration of modified bitumen samples is characterized by the depth to which the standard needle is immersed into a test sample of bitumen under specified conditions (temperature, load and duration of the load application), which is expressed in units corresponding to tenths fractions of a millimeter (0.1 mm). Penetration value of a bitumen sample is determined at 25°C (the load is 100 g, the test time is 5 sec) and at 0°C (the load is 200 g, the test time is 60 sec). It is determined in accordance with the standard of Russian Federation 33136-2014, the main regulations of which correspond to the standard EN 1426.

To characterize tensile properties of bitumen samples ductility is used, which is determined in accordance with standard of Russian Federation 33138-2014. The method includes stretching of a bitumen sample at a constant rate and temperature to determine the extensibility of bitumen. Ductility value of a bitumen sample is determined at 25°C and at 0°C.

The method for determining the elasticity of modified bitumen samples includes the evaluation of the proportion of elastic (fully reversible) deformation in the ultimate deformation of samples. It is determined at 25°C and at 0°C in accordance with the standard of Russian Federation 52056-2003.

## RESULTS AND DISCUSSION

The research considers the possibility of oil sludges, crumbed rubber and carbon black usage as modifiers of bituminous binders. The following tasks have been solved in order to achieve this goal: the samples of bituminous binder based on road petroleum bitumen of penetration grades 40/60, 50/70, 90/130, modified with oil sludge, rubber crumb, carbon black, have been obtained; analysis of the main quality indexes of the bituminous binders with the studied additives has been carried out;

Table 2. Characteristics of bitumen 40/60 modified with oil sludge.

| Performance property of the sample | Additive content in the sample, wt. % | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0 | 0.5 | 1.0 | 2.0 | 2.5 | 3.0 | 5.0 |
| R&B test, ºC | 59.4 | 60.5 | 61.1 | 61.1 | 64.1 | 65.1 | 64.1 |
| Fraass breaking point, ºC | –22.4 | –22.8 | –24.5 | –22.5 | –17.8 | –15.9 | –20.2 |
| Penetration at 0ºC, x 0.1 mm | 12.5 | 12.5 | 11.8 | 6.8 | 13.2 | 10.0 | 7.2 |
| Penetration at 25 ºC, x0.1 mm | 40.0 | 39.3 | 22.0 | 21.6 | 19.8 | 16.8 | 21.3 |
| Ductility at 0ºC, cm | 7.6 | 4.8 | 6.8 | 6.2 | 6.1 | 5.2 | 5.8 |
| Ductility at 25ºC, cm | 24.0 | 14.0 | 17.0 | 16.0 | 14.0 | 8.0 | 8.5 |
| Elasticity at 0ºC, % | 21.6 | 16.6 | 11.8 | 19.4 | 18.1 | 23.1 | 22.4 |
| Elasticity at 25ºC, % | 33.3 | 45.0 | 41.2 | 37.5 | 39.3 | 25.0 | 23.5 |

Table 3. Characteristics of bitumen 50/70 modified with crumbed rubber.

| Performance property of the sample | Additive content in the sample, wt. % | | | |
|---|---|---|---|---|
| | 0 | 3.0 | 5.0 | 7.0 |
| R&B test, ºC | 58.5 | 60.9 | 62.5 | 64.0 |
| Fraass breaking point, ºC | –24.8 | –17.6 | –19.2 | –20.5 |
| Penetration at 0ºC, x 0.1 mm | 31.0 | 24.0 | 22.3 | 20.0 |
| Penetration at 25ºC, x 0.1 mm | 50.0 | 38.0 | 31.3 | 39.0 |
| Ductility at 0ºC, cm | 10.4 | 6.6 | 6.2 | 6.8 |
| Ductility at 25ºC, cm | 30.7 | 13.5 | 11.5 | 14.8 |
| Elasticity at 0ºC, % | 5.7 | 10.6 | 1.6 | 4.4 |
| Elasticity at 25ºC, % | 18.6 | 20.7 | 20.4 | 20.9 |

the optimal compositions of the bituminous binders have been selected; the technology for the production of the modified bituminous binder has been developed.

The main characteristics of bitumen modified with oil sludge inerted with polyethylene wastes are presented in Table 2. The additive has been studied in the range of concentrations from 0.5 wt. % to 5.0 wt. %. Softening point, low-temperature properties, penetration and plastic-elastic properties were evaluated for all samples of the modified binders.

The introduction of oil sludge leads to an increase in the heat resistance of the binder. This can be explained by the influence of asphaltenes in oil sludge. The framework of asphaltenes swollen in aromatic hydrocarbons becomes more clearly expressed when their content in bitumen increases, for this reason the softening point increases. The breaking point increases with an increase of the additive content in bitumen, which can be explained by even the little presence of mechanical impurities in the oil sludge. The introduction of the oil sludge practically does not affect the elasticity of bitumen, but at the same time reduces the penetration and ductility indexes. The decrease of ductility of bitumen can be explained by the presence of asphaltenes and mechanical impurities in the additive, which reduce the plasticity under tensile stresses. The optimal additive content is 1.0 wt. % and 2.5 wt. %.

The main characteristics of bitumen modified with crumbed rubber are presented in Table 3. A more developed surface of the crumbed rubber will contribute

Table 4. Characteristics of bitumen 50/70 modified with carbon black.

| Performance property of the sample | Additive content in the sample, wt. % | | | |
|---|---|---|---|---|
| | 0 | 1.0 | 2.0 | 3.0 |
| R&B test, ºC | 58.5 | 59.7 | 60.1 | 60.2 |
| Fraass breaking point, ºC | –24.8 | –21.8 | –20.1 | –23.4 |
| Penetration at 0ºC, x 0.1 mm | 31.0 | 28.0 | 28.3 | 28.0 |
| Penetration at 25ºC, x 0.1 mm | 50.0 | 38.3 | 37.6 | 39.3 |
| Ductility at 0ºC, cm | 10.4 | 6.6 | 6.2 | 6.0 |
| Ductility at 25ºC, cm | 30.7 | 15.0 | 13.0 | 11.0 |
| Elasticity at 0ºC, % | 5.7 | 5.1 | 5.5 | 5.3 |
| Elasticity at 25ºC, % | 18.6 | 18.0 | 18.5 | 18.0 |

to its more effective swelling in the molten part of the bitumen. The additive has been studied in the range of concentrations from 3.0 wt. % to 7.0 wt. %.

The introduction of crumbed rubber leads to an increase of the heat resistance of bitumen. This is due to an increase in the amount of dispersed phase in bitumen

Table 5. Characteristics of bitumen 50/70 and 90/130 modified with oil sludge and polymers.

| Sample of bitumen binder | R&B test, ºC | Penetration at 0ºC, 0.1 mm | Penetration at 25ºC, 0.1 mm | Ductility at 0ºC, cm | Ductility at 25ºC, cm | Elasticity at 0ºC, % | Elasticity at 25ºC, % |
|---|---|---|---|---|---|---|---|
| Original 50/70 | 59.4 | 12.5 | 40.0 | 7.6 | 24.0 | 21.1 | 33.3 |
| 1.0 wt. % oil sludge + 1.0 wt. % Sevilen | 65.1 | 22.4 | 35.4 | 9.7 | 23.0 | 11.3 | 30.0 |
| 1.0 wt. % oil sludge + 2.0 wt. % Sevilen | 66.9 | 30.8 | 33.4 | 6.0 | 11.0 | 10.4 | 18.2 |
| 2.5 wt. % oil sludge + 1.0 wt. % Sevilen | 65.6 | 31.0 | 34.0 | 5.9 | 12.0 | 13.5 | 20.8 |
| 1.0 wt. % oil sludge + 1.0 wt. % Kraton | 66.8 | 22.0 | 31.4 | 9.5 | 27.5 | 24.5 | 48.4 |
| 1.0 wt. % oil sludge + 2.0 wt. % Kraton | 69.8 | 22.5 | 26.0 | 9.5 | 19.0 | 38.9 | 62.6 |
| Original 90/130 | 46.5 | 36.0 | 96.2 | 56.7 | 100.0 | 17.1 | 22.6 |
| 1.0 wt. % oil sludge + 1.0 wt. % Kraton | 49.8 | 51.2 | 68.0 | 22.3 | 41.5 | 33.6 | 32.5 |
| 2.5 wt. % oil sludge + 1.0 wt%. Kraton | 51.4 | 41.6 | 60.6 | 28.3 | 86.0 | 31.8 | 39.5 |
| 2.5 wt. % oil sludge + 2.0 wt. % Kraton (PMB 60) | 56.2 | 33.3 | 61.8 | 40.0 | 100.0 | 70.5 | 80.5 |
| 1.0 % wt. oil sludge + 3.0 % wt. Kraton (PMB 60) | 61.5 | 35.6 | 61.3 | 85.8 | 100.0 | 71.5 | 81.1 |
| 2.0 wt. % oil sludge + 3.0 wt. % Kraton (PMB 40) | 62.3 | 25.0 | 57.0 | 48.0 | 100.0 | 74.3 | 82.1 |

structure. The breaking point value increases, which can be explained by the adsorption of a part of oil fractions of bitumen by the crumbed rubber, because it is the oil fraction responsible for low temperature properties of bitumen. The introduction of crumbed rubber reduces the ductility and penetration indexes. The optimal modifier content is 3.0 wt. % and 7.0 wt. %.

The main characteristics of bitumen modified with carbon black are presented in Table 4. The influence of this additive on bitumen properties is similar to the previous modifiers, expressed in an increase in heat resistance and a slight decrease in the breaking point. The additive does not improve elasticity, but reduces the penetration and ductility of bitumen.

Based on the analysis of the studied additives influence on the bituminous binder properties, it was found that the oil sludge in the concentrations of 1.0 wt. % and 2.5 wt. % affects bituminous binder characteristics in the best way. However, the bituminous binder modified with the oil sludge does not meet all the requirements for modified bitumen brands according to the standard of Russian Federation 52056-2003. That is why the possibility of the complex modification of bitumen with the oil sludge and polymers was studied. Sevilen, a copolymer of ethylene and vinyl acetate, related to the class of thermoplastics, and Kraton, a thermoelastoplastic, being a block copolymer of styrene and butadiene, were studied.

The main characteristics of the bitumen samples modified simultaneously with the oil sludge and the polymers are presented in Table 5.

As the result of the study it was revealed, that the complex modification of bitumen with the oil sludge and Sevilen does not lead to an improvement of elastic properties of the binder. On the other hand all samples of the bituminous binder modified with the polymer Kraton together with oil sludge show an improvement in the heat resistance index due to both the content of asphaltenes in oil sludge and the influence of polymer and also show an improvement of elastic properties of the binder. They have a lower penetration than that of the original bitumen due to an increase in the viscosity of the bitumen binder. Three samples meet all the requirements for two brands of modified bitumen PMB 40 and PMB 60.

The technology for the industrial production of the modified bituminous binder has been developed. The technology for the industrial production of modified bituminous binder will include a pre-mixing stage, the stage of homogenization in a colloid mill, and ripening stage of a modified product. According to the technology bitumen is pumped from the raw container to the pre-mixing vessel. The process temperature is 160°C - 185°C. The polymer Kraton and oil sludge are fed into the pre-mixing vessel, where the distribution of the modifiers in the bitumen takes place. Then the flow is fed to the colloid mill, where the total homogenization occurs. After that, it enters the ripening tank, where for 3 hours, with constant stirring and maintaining the temperature, the modifiers are completely dissolved.

## CONCLUSIONS

The research considers the possibility of oil sludges, crumbed rubber and carbon black usage as modifiers for bituminous binders. The research has revealed that the modification of petroleum bitumen with the studied additives can improve softening point of the binder, but the introduction of additives leads to a decrease in ductility and an increase in the breaking point of the binder. The modification of bitumen with the studied additives reduces the penetration, which leads to the change in the bitumen grade to a more viscous one. It should be taken into the consideration in order to obtain a certain penetration grade of bituminous binder. Oil sludge and crumbed rubber affect the improvement of the elasticity index at certain ratios of bitumen and modifier. Based on the analysis of the studied additives influence on bituminous binder properties, it has been found that the oil sludge in the concentrations of 1.0 wt. % and 2.5 wt. % affects bituminous binder characteristics in the best way. However, the bituminous binder modified with the oil sludge does not meet all the requirements for modified bituminous binder brands according to current standards. The complex modification of bitumen with the oil sludge and copolymer of ethylene and vinyl acetate does not lead to an improvement of the elastic properties of the binder. However, the samples of modified bitumen with oil sludge and SBS block copolymer Kraton in the following ratios of the components: 1.0 wt. % of the oil sludge and 3.0 wt. % of Kraton; 2.5 wt. % of the oil sludge and 2.0 wt. % of Kraton; 2.0 wt. % of the oil sludge and 3.0 wt. % of Kraton, meet all the requirements for PBB 40 and PBB 60 according to the Standard of Russian Federation 52056-2003. As a result,

the technology for the industrial production of the modified bituminous binder has been proposed.

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