УДК 665.637.8

A. O. Shrubok, PhD student (BSTU); **E. I. Grushova**, PhD, professor (BSTU);
T. N. Pasko, student (BSTU)

MODIFICATION OF OIL SLUDGE BY HIGHLY DISPERSED CARBONACEOUS ADDITIVE

The effect of modification of tar by highly carbonaceous additives on the rate of the oxidation process and the quality of oxidized bitumen has been studied. The dependences of the softening temperature of bitumen from the oxidation time have been obtained. Penetration, penetration index of oxidized bitumen modified with highly carbonaceous additives tar fractions have been determined. The relaxation characteristics of oxidized bitumen: dependences of the relaxation time and the width of the temperature range of the duration of the process of oxidation have been obtained. It has been established that the rate of the process of obtaining oxidized bitumen increases with the number entered modifier by reducing the induction period.

Introduction. The most acute problem in the production of oxidized bitumen in the post-Soviet space is the issue of compliance of finished products to customer requirements, associated primarily with the poor quality of the raw materials used in the production of bitumen. In the last decade the development of world science and technology is characterized by the development of effective ways to influence the macroproperties of the system by changing the properties of the micro-level [1]. This principle is applied to oil systems and implemented, mainly through the use of modifiers that affect the structural and colloidal properties of petroleum systems [2]. Furthermore, the use of modifiers can reduce the material costs of producing high quality product without substantial and costly changes in the manufacturing technology.

As it is known [3], on the physico-chemical properties of the oil dispersed system can be influenced by changing the ratio of the structural components of the constituent. The easiest way to change the ratio of "dispersion medium: the dispersed phase" is to introduce in the oil dispersed system the components that make up one of these phases. From the literature it is known [4] that the introduction of solids in the system contributes to the formation of additional own phase, characterized by the presence of a clear interface with the other components of the system, which are inert with respect to these components. However, despite the background for research in this field, currently the matter of use of solid carbonaceous additives into the oil systems remains open. In this regard, the purpose of our study was to investigate the influence of highly dispersed carbon containing additive as a modifier of oil sludge used as raw material in the preparation of oxidized bitumen on oxidation process and structural and colloidal properties of derived from it oxidized bitumen.

Main part. The raw materials of the oxidation process used tar production "Naftan" (Novopolotsk) (Table 1). As a modifier was investigated the diamond charge of NPO "Cynthia" (Minsk). It is known that diamond charge react with oxidants in a liquid phase at elevated temperatures 150–300 °C [5] that may be used as modifiers in oxidation of sludge at 210–280 °C.

Table 1

Properties of raw materials - oil tar ("Naftan")

Indicator	Value
Relative density, ρ_{20}^{20}	1.007
Temperature $_{b.b.}$,°C	>450
Penetration at 2525°C, 0,1 мм	>290
Softening point, °C	34.3
Group composition, wt %:	
– asphaltenes	7.5
– oil	68.4
– resin	24.1

The diamond charge is a black powder with a bulk density of 0.04–0.15 kg/m^3 (pycnometric density 2.6–2.7 kg/m^3) and specific surface area of 350–450 m^2/g. The structure of the diamond charge except nanodiamonds includes graphite structures, amorphous carbon, admixtures of metals and their compounds. The elemental composition of the investigated diamond sharge is submitted in Table 2. Micrograph of the investigated diamond charge is shown in Fig. 1.

Table 2

The elemental composition of the diamond charge

Item	Contents cell, wt %
carbon	89.99
oxygen	7.92
silicon	0.02
chlorine	0.13
calcium	0.11
iron	0.09
copper	1.74

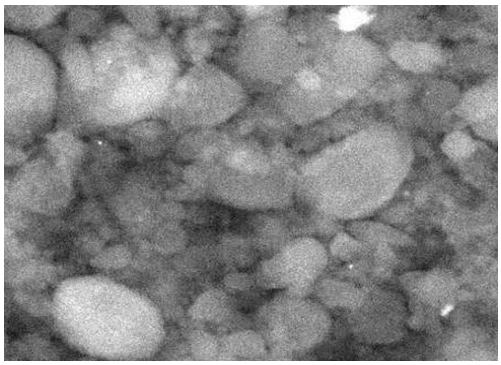

Fig. 1. Microphotograph of the diamond-charge

A 10% suspension of diamond charge in the diesel fraction was previously prepared to improve the distribution of the nano-additive in the raw material. It was introduced into a preheated to 60 °C oil sludge with stirring. Distribution efficiency of oil modifier in the volume of sludge was achieved by bubbling air in the oxidation process [2]. Oxidation of the obtained raw material mixture was performed in a laboratory reactor at a temperature of 245 °C, air flow 1400 ml/min and oxidation during 8 hrs.

Depending softening temperature of oxidized bitumen from oxidation time using unmodified raw materials and modified by diamond-charge in the amount of 0.06, 0.15 and 0.22 wt % are shown in Fig. 2.

To establish the contribution of diesel fuel in the oxidation process was carried out the oxidation of oil sludge containing the equivalence of input slurry, the amount of diesel fuel (Fig. 2, curve 2). The experimental data show that the introduction of the diesel fuel in the raw material mixture in small amounts do not affect the flow rate of the oxidation process.

As can be seen, the introduction of finely carbonaceous additives as a modifier in the sludge allows to intensify the process of oxidation. The obtained dependences are complex and ambiguous character. Apparently, this is due to different effect of the ultrafine carbon containing additives on the one hand, due to the formation of an additional phase, which does not react with the components of the oil dispersed system, and on the other hand, due to the interaction of the incoming charge of diamond transition metals which are known to act as catalysts for liquid phase of oxidation [2].

When introducing the modifier to 0.15 wt %, a change in the type and slope of the kinetic curve, which indicates a change in the direction of the process of oxidation compared with the oxidation of the unmodified material. In the case where the amount of modifier in the feed mixture is greater than 0.15 wt %, the nature of the curve changes, due, apparently to the prevailing image of the new action over the action of ultrafine phase of metals of transition valence.

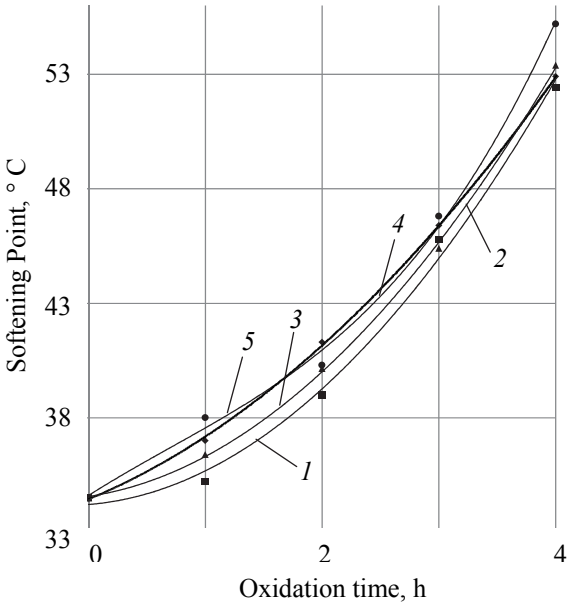

Fig. 2. Dependence of the softening temperature oxidized bitumen from oxidation time:
1 – oxidized bitumen from oil sludge without modifier;
2 – oxidized bitumen petroleum sludge with diesel fuel;
3, *4*, *5* – oxidized bitumen from tar modified the charge of diamond in an amount of 0.06, 0.15 and 0.22 wt % calculated on the charge accordingly

One of the most important indicators of ductility and hardness of oil road bitumen, which measures the resistance of road binder shear by periodic action of compression, and the temperature difference is penetration, and to characterize the degree of structurizing of bitumen indicators such as penetration index Ip are used characterize resistance of bitumen to temperature depression and it is calculated by an empirical relationship [2]:

$$I_p = \frac{20 \cdot t_{RaB} + 500 \cdot \log P - 1952}{t_{RaB} - 50 \cdot \log P + 120},$$

where t_{RaB} – softening point, °C, log P - penetration logarithm (base 10) at 25 °C (in units of 0.1 mm).

Fig. 3 shows the dependence of penetration and penetration index of oxidized bitumens in the amount of injected oil tar modifier.

According to Fig. 3, the introduction of diamond charge of up to 0.15 wt % in oil sludge yields oxidized bitumens with low values of penetration and penetration index . Decrease in penetration index indicates an increase in thermal sensitivity of obtained bitumen, which is typical for the type of bitumen sol [3]. Consequently, the introduction of the ultrodispersed modifier in the feed of oxidation process leads to the formation of an

ordered structure of bitumen and hence a more stable oil dispersion system. Bitumens having a stable colloidal system are characterized by greater durability and resistance to the effects of heavy loads.

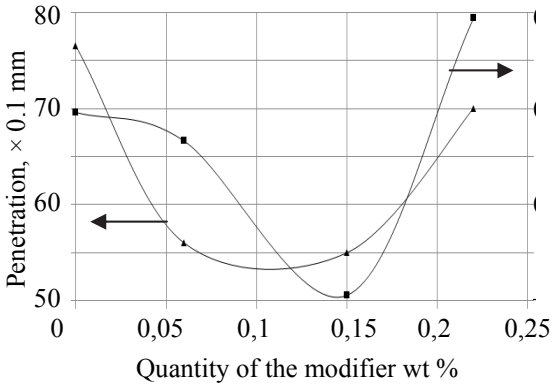

Fig. 3. Dependence penetration and penetration index oxidized bitumens penetration of the amount of introduced modifier

Increased penetration and penetration index in an amount of modifier 0.22 wt % is due to the formation of a large amount of fine particles, which increases the mobility of this bitumen. These results can be explained by the growing influence of the developed surface of modifier input on the structure of petroleum bitumen, as well as by changes in the ratio of reaction rates of primary and secondary oxidation that affects the component composition and structural organization of oxidized bitumen .It is worth noting that the results obtained from the modified raw bitumen by physicochemical properties comply with EN 12591 STB "Road bitumen. Technical requirements and methods of determination".

To assess the structural colloidal organization of received oxidized bitumen characteristics of phase transition were defined. It is believe [6], that in the kinetic phase transitions (softening processes - glass) and the field of viscous flow changes in the properties of high-viscosity oil systems have relaxation nature and are associated with the restructuring of the supramolecular structure and the change of intermolecular interaction energy with the composition . Change evaluation of relaxation time and temperature interval of softening of oil dispersion system under the influence of a constant load was carried out on the base of a standard method for determining the softening point of bitumen by the method of "Ring and Ball" (STB EN 1427). For the relaxation time, according to [2, 6], was taken the time from the beginning of the formation of a visible meniscus on the bottom edge of the ring until it passes a certain distance in the standard unit for measuring the softening temperature. The interval of the softening temperature determined by from the temperature of formation of a visible meniscus on the bottom face of the ring to a temperature corresponding to the time to drop the ball. Width of the interval and the relaxation time of the phase transition of the 2nd kind are determined by the nature of intermolecular interactions between the components of the bitumen. Fig. 4 shows the dependence of the relaxation time on the duration of oxidation time.

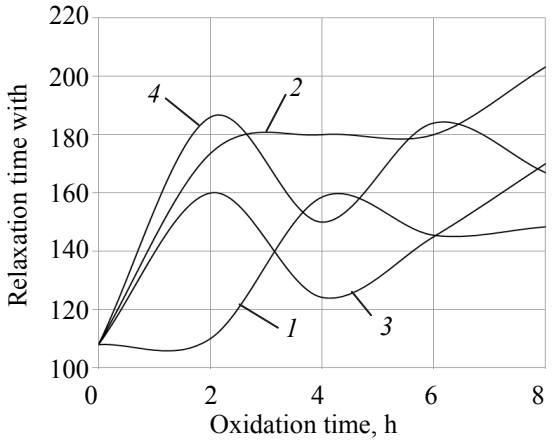

Fig. 4. The relaxation time the duration of oxidation: *1* – oxidized bitumen from oil sludge without modifier, and *2*, *3*, *4* – oxidized bitumen of the sludge modified in the charge of diamond 0.06, 0.15, and 0.22 wt % based on the batch respectively

Relaxation time in the plastic region has no clear correlation with temperature characteristics, but has a similar character to the studied systems [3, 6]. Bitumen obtained from unmodified raw induction period is observed (up to 2 hr of oxidation), the relaxation time is constant, then there is a peak corresponding to the most ductile state. Bitumens, obtained from the modified materials are characterized by a reduction of the induction period and the time of maximum displacement. Dependences on the width of the temperature range of the phase transition of the 2nd kind are shown in Fig. 5 and are similar in nature to the relaxation time of the duration of oxidation.

From the literature [3, 6] it is known that the oil disperse systems, various processes are possible restructuring of the molecular structure with energies from 30 to 1338 J/mol for the second order phase transition. Having multiple points on the extreme dependence of the relaxation processes indicates adjustment of structural formations in the oxidation process petroleum feedstock, while the number of extreme points and the nature of the curve is the same for all the dependences obtained, indicating that a similar flow of the oxidation process in all systems studied and is not contrary to

existing ideas about relaxation dependence oil disperse systems [2, 3, 6]

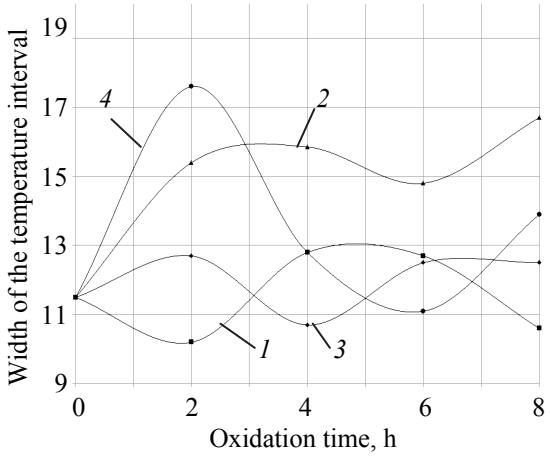

Fig. 5. Temperature dependence of the width an interval of the duration of oxidation: *1* – oxidized bitumen from oil sludge without modifier, and *2*, *3*, *4* – oxidized bitumen of the sludge modified in the batch of diamond 0.06, 0.15, and 0.22 wt % based on the batch respectively

Conclusion. Thus, studies made it possible to establish that the use of diamond as a charge modifier provides raw a catalytic effect on the oxidation process increases with increasing amounts of the modifier introduced. At the same time received blown bitumens are characterized by lower values of penetration (55–68×0,1 mm) and penetration index (–0.28–0.48) compared with bitumen produced by the conventional method (77×0,1 mm and 0.88 corresponditively), which is probably indicative of a hundred metastable colloidal system. On the basis of experimental data on the relaxation characteristics of oxidized bitumen shows that the oxidation of petroleum sludge, modified in the charge of diamond, there is a reduction of the induction period (up to 2 hours), and the oxidation process is characterized by the variety processes restructuring supramolecular structures. The resulting bitumen meet all existing standards and can be used as a road trafficion, building and roofing material.

This work was financially supported by BRFFR (grant number X12M-051).

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Received 27.02.2013