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THE OXIDIZED BITUMENS FROM THE MODIFIED RAW MATERIALS

The effect of modification of tar by iron (III) stearate on the rate of the oxidation process and the quality of oxidized bitumen has been studied. The dependences of the softening temperature of bitumen upon the oxidation time, the dynamic viscosity of bitumen on the temperature have been obtained. Penetration, penetration index, group composition and thermal-oxidative stability of oxidized bitumen modified by iron (III) stearate have been determined. It was determined that small quantities of a modifier (up to 1.5 wt %) in the raw material don't influence the rate of oxidation, and with increasing content of the modifier in the raw material the rate of the process is increased by 1.6–4.0 times.

Introduction. Modern technologies of obtaining oxidized bitumen are characterized by the use of different effective ways to affect the colloidal structure of crude oil and product oxidized bitumen [1]. To reduce material costs for the production of quality products, technologies of the oxidation process through the use of modified raw materials are widely distributed [2]. In addition to intensifying the process of oxidation, obtaining high-quality bitumen corresponding modern standards remains an important task. It was suggested to use materials that either positively affect the quality of the product, or can reduce the cost of production of oxidized bitumen as modifiers of raw materials by reducing the time of oxidation The first group of modifiers include such modifiers as extract of selective refining of oils, industrial or anthracene oil, fractions C_{21}–C_{25} of synthetic fatty acids [2]. Irone (III) chloride [2] salts of the metals of variable valence [3] may be used as second oxidation catalysts. These modifiers intensify the process of oxidation. As a result, the time and energy consumption for the production of oxidized bitumen are reduced. However, the use of ferric chloride (III) can cause corrosion of equipment due to the formation of HCl as follows:

$$FeCl_3 + RH \leftrightarrow [FeCl_2 \cdot R^{\cdot} \cdot HCl] \leftrightarrow FeCl_2 + HCl + R^{\cdot}$$

It was interesting to find such a modifier that, on the one hand, would intensify the oxidation process, and on the other – would enable us to obtain high quality marketable bitumen. Analysis of the references [1–3] showed that salt metals of variable valence of various carboxylic acids can be used as such modifiers.

In view of the above, the purpose of the study was to investigate the influence of a modifier which is an iron salt of stearic acid, on the process of obtaining the oxidized bitumen and the qualitative characteristics of finished bitumen.

Main part. Tar produced by JSC Naftan (Belarus) was used as a raw material of the oxidation process (Table 1). Iron (III) stearate synthesized according to the following scheme being a modifier of the raw material:

$$3CH_3(CH_2)_{16}COONa + FeCl_3 \cdot 6H_2O =$$
$$= [CH_3(CH_2)_{16}COO]_3Fe\downarrow + 3NaCl + 6H_2O$$

Table 1

The properties of raw materials – oil tar (JSC Naftan)

Index	Value
Relative density, ρ_{20}^{20}	1.007
Temperature н. к., °C	>450
Penetration at 25°C, 0.1 mm	>290
Softening point, °C	34.3
Group composition, wt %:	
asphaltenes	7.5
oils	68.4
resins	24.1

Iron (III) chloride hexahydrate (125 g) dissolved in water was slowly poured by heating and stirring to multipurpose soap (587 g), containing 72 wt % of sodium stearate, dissolved in hot water and. The resulting gummy residue, consisting, according to IR spectroscopy (Fig. 1), of the target product and impurities of stearic acid and its sodium salt was filtered, washed with hot water. After drying and grinding fine-grained powder was obtained.

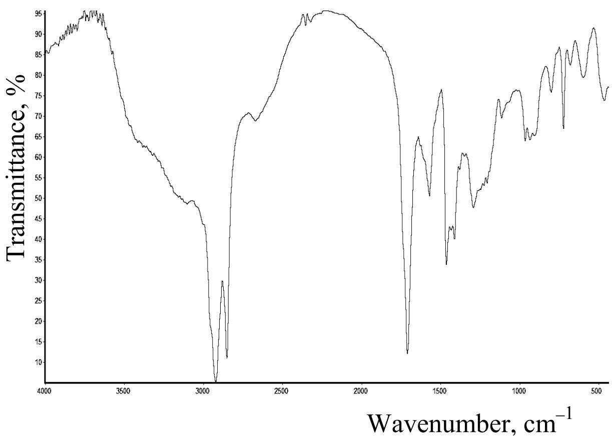

Fig. 1. IR spectrum of the synthesized iron (III) stearate

Modifier of 0.5, 1.5, 3.0 and 5.0 wt % was added to the pre-heated to 60°C oil tar while stirring. The oxidation of the obtained raw mixture was conducted in a laboratory batch reactor at 245°C, air flow rate 1400 ml/min, the oxidation time 8 hours.

Dependencies of the softening temperature of the oxidized bitumen on oxidation time using unmodified raw material and raw material modified by iron stearate at 0.5, 1.5, 3.0 and 5.0 wt % are shown in Fig. 2.

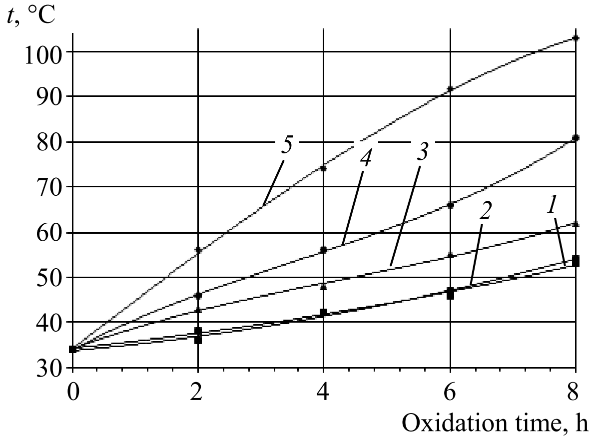

Fig. 2. Dependence of the softening temperature of oxidized bitumen upon the duration of oxidation:
1 – oxidized bitumen from non-modified tar;
2, *3*, *4*, *5* – oxidized bitumen from tar modified by iron (III) stearate at 0.5, 1.5, 3.0 and 5.0 wt %, respectively

According to the presented dependencies, the introduction of iron (III) stearate as a modifier to the tar has a catalytic effect on the oxidation process increasing with the concentration of the modifier in the raw material. Thus, when iron (III) stearate in the amount of 5.0 wt % is used as a modifier of raw material, oxidation time can be reduced by 4 times. In addition, at low concentrations of modifying additive the oxidation rate does not change, but at a concentration of 5.0 wt % the type and slope of the line that characterizes the rate of change of the softening temperature in the oxidation process change. This indicates a change in the nature of the reactions of degradation and polymerization.

According to [1], the introduction of 2.0 wt % iron chloride to the tar, catalyzes the oxidation process and reduces the time of this process by 1.74 times. As can be seen from Fig. 2, with the introduction of iron (III) stearate into the raw material in a quantity 3.0 wt % the oxidation time decreases by 1.7 times, indicating a higher efficiency of ferric chloride.

In conditions of severe exploitation of road bitumen, i.e., periodic impact of shear stress, compression, and the temperature drops, there is a destruction of pavement, and the resistance of the roadway to such pressures depends on the ductility and elasticity of bitumen. One of the most important indicators of ductility and hardness of oil road bitumen is penetration, and to characterize the degree of structure of bitumen we use such an indicator as the penetration index Ip, which characterizes the resistance of bitumen to temperature depression and is calculated by the empirical relation [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).

Table 2 shows the penetration and penetration index for the resulting oxidized bitumen.

Table 2

Penetration and penetration index

Raw material for obtaining oxidized bitumen	Penetration	Penetration index
Oil tar	57.1	0.6
Oil tar + iron (III) stearate (0.5 wt %)	74.2	0.5
Oil tar + iron (III) stearate (1.5 wt %)	43.8	1.8
Oil tar + iron (III) stearate (3.0 wt %)	35.6	3.6
Oil tar + iron (III) stearate (5.0 wt %)	29.2	5.6

According to Table 2, introduction of iron (III) stearate to the oil tar results in oxidized bitumen with low values of penetration and a high index of penetration. The increase in penetration index indicates a lower thermal sensitivity of obtained bitumen, which is typical of the bitumen of gel type [1]. Therefore, the introduction of iron (III) stearate as a modifier of the raw material leads to the structuring of the dispersed system and the formation of solid bitumen frame of aggregated particles of a dispersed phase with an immobilized inside the framework dispersion medium. These bitumen can be used in the manufacture of roofing and building materials.

Besides, the penetration index for oxidized bitumen obtained from modified raw materials containing iron (III) stearate of more than 1.5 wt % with the oxidation time more than 8 hours, meet the requirements for roofing and construction bitumen (State Standard 9548 and State Standard 6617).

The quality of road surface depends not only on the properties of the individual materials used, but also on the conditions and quality of mixing, laying and compaction, which largely depend on the viscosity of the binder. The measurement of the dynamic viscosity of the samples was carried out on bitumen rotary viscometer Brookfield DV-II + + IV Pro (spindle SC4-21/13R, sample volume 7.1 ml) for the spindle speed 0.5 vol. / min in the temperature interval 50–120°C. The dependence of the dynamic viscosity of the obtained oxidized bitumen on the temperature is shown in Fig. 3. As seen from the dependencies, with the increasing of concentration of iron (III) stearate in raw bitumen dynamic viscosity increases, which seems to be due to the formation of the grid frame of asphaltene complexes.

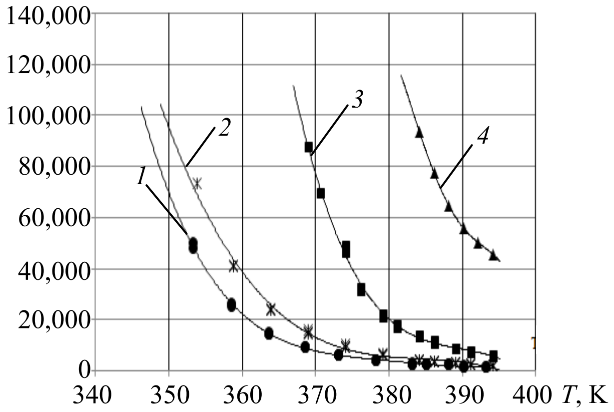

Fig. 2. Dependence of the dynamic viscosity of oxidized bitumen upon the temperature: *1* – oxidized bitumen from non-modified tar; *2*, *3*, *4* – oxidized bitumen from tar modified by iron (III) stearate at 0.5, 1.5 and 3.0 wt %, respectively

Colloidal structure and rheological properties of oxidized bitumen largely depend on the chemical composition of their group.

Depending on the structure and chemical properties of the components of the bitumen, the building blocks that will predetermine the behavior of bituminous material in the operation may be formed. The change in group composition in the oxidation process characterizes the rate of oxidation and the conversion of substances by polymerization reactions and destruction.

Table. 3 shows the experimental data obtained by determining the group composition of oxidized bitumen according to Markusson method [4].

Table 3

Group chemical composition

Raw material for obtaining oxidized bitumen	The composition of oxidized bitumen		
	Asphaltenes	Oils	Resins
Oil tar	18.8	61.5	19.7
Oil tar + iron (III) stearate (0.5 wt %)	19.6	59.0	21.4
Oil tar + iron (III) stearate (1.5 wt %)	25.7	54.9	19.4
Oil tar + iron (III) stearate (3.0 wt %)	27.7	53.4	18.9
Oil tar + iron (III) stearate (5.0 wt %)	33.7	52.7	13.6

The presented experimental data show that the increase of iron (III) stearate in the original tar, seems to intensify the rate of polymerization reactions, policondecsation, since there is an increase in the asphaltene content of the final product due to the transformation of oils and resins.

At the same time of oxidation, bitumen obtained from modified raw materials, contain a larger amount of asphaltenes, but by the content of oils and resins are inferior to bitumen produced in the traditional way. It is known that the increase of the amount of asphaltenes in the oxidized bitumen indicates the formation of the structural grid of asphaltenes and the resulting decrease in thermal sensitivity of bitumen, which proves our assumption of the formation of bitumen of “gel” type in the oxidation of the modified raw materials. These bitumens have a rigid structure, low thermal sensitivity and can be used as building and heat insulation materials.

Table 4

Thermal stability of oxidized bitumen

Object	Thermal stability		
	The change in mass, wt %	Change of softening, *T*, ° C	Residual penetration, %
Bitumen produced by oxidation of the oil tar	0.13	4.6	76.5
Bitumen produced by oxidation of the oil tar containing 0.5 wt % of iron (III) stearate	0.05	3.5	82.5
Bitumen produced by oxidation of the oil tar containing 1.5 wt % of iron (III) stearate	0.05	4.1	81.1
Bitumen produced by oxidation of the oil tar containing 3.0 wt % of iron (III) stearate	0.06	5.1	74.8
Bitumen produced by oxidation of the oil tar containing 5.0 wt % of iron (III) stearate	0.1	5.7	74.5

Service life of a bitumen binder depends on its resistance to thermal oxidative aging. Aging resistance test method is defined by heating in a thin layer at 163°C for 5 h [2]. The results of determining the resistance of oxidized bitumen to thermal oxidative aging are presented in Table 4. The study of thermal oxidation stability of obtained bitumen showed that the introduction of the iron (III) stearate into the oil tar leads to a decrease in such indicators as weight and residual penetration, and to the increase of the softening point compared with oxidized bitumen obtained by traditional technology. The bitumen obtained by the oxidation of tar modified by iron (III) stearate in the amount of 0.5 wt % is the most stable. With increasing content of iron (III) stearate in the raw material thermal stability decreases slightly and is within the requirements for thermal and oxidative stability of bitumen (STB EN 12591, State Standard 9548 and State Standard 6617).

Conclusion. Thus, the results of research revealed that the use of iron (III) stearate as a modifier of raw material has a catalytic effect on the oxidation process and helps reduce oxidation time by 1,6-4,0 times and, therefore, reduce the time, material and energy costs of production. It is shown that during the process of oxidation of oil tar, modified by iron (III) stearate the appearance of a complex structural grid of asphaltenes takes place, resulting in formation of bitumen of "gel" type. The resulting bitumen meet all existing standards and can be used as a road, building and roofing material.

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