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FEATURES OF LIQUID PHASE OXIDATION OF TAR IN THE PRESENCE OF MODIFIERS-CATALYSTS

Modifiers that provide catalytic effect in the tar oxidation were considered. The use of iron stearate, cobalt salts as modifiers was studied. The modifier concentration in the tar amounted to 5.0% by weight. The tar modification effect on the oxidation kinetics was defined. The relationships between oxidation rate constants and oxidation time were analyzed for the modifiers-catalysts. It was demonstrated that modifiers which contained salts of metals with variable valence had the catalytic or inhibitory effect on the oxidation, depending on the modifier concentration in the tar.

It was shown that the addition of modifiers-catalysts effects on the quality characteristics of the oxidized bitumen. The relationships between softening point and penetration were determined for oxidized bitumen from the modified or unmodified tar. The article presents a comparison of oxidized bitumen derived from modified tar by modifiers-catalysts in the optimal concentration. modifier nature was the main factor determining the effectiveness of modifiers, which affected the structure of the oil system. Inhibitory and catalytic effects on the oxidation were executed by the addition of brown coal pyrolysis resins and oil shale pyrolysis resins, respectively.

Analysis of the kinetic curves allowed establishing the following: iron stearate had the greatest effect on the oxidation process, the effect allowed to increase rate constant to 8.7 times. It has been established that the addition of cobalt modifier can improve the thermal-oxidative stability of the oxidized bitumen.

Key words: tar, modifiers, oxidation, kinetics, the rate constant.

Introduction. In the manufacture of oxidized bitumen for road surfaces, the main challenge facing the manufacturer is the production of inexpensive and quality products. Industrial technology of production of oxidized bitumen in view of the deteriorating quality of crude oil for the process of oxidation allows to obtain bitumen of the required quality. Modern trends in the development of science and technology link the solution to this problem with the development of effective methods of influence of changing its microproperties on macroproperties of the system. In the production of oxidized bitumen the effective and least costly way of such effect is the regulation of the properties of bitumen binders through the use of modifiers at different stages of the production process [1]. Since the main factors influencing the quality data of oxidized bitumen, are the group composition of the initial raw material and technological parameters of oxidation, the greatest interest is the way of changes in quality characteristics of oxidized bitumen through modification of the feedstock.

Despite the presence of many works on modifying the oil system, the mechanism and kinetics of liquid-phase oxidation of modified petroleum base, remains poorly understood [1–3]. In this regard, the aim of this work was to study peculiarities of liquid-phase oxidation of the modified oil.

Main part. As the raw materials of the oxidation process the tar of JSC "Naftan" (Belarus) were used (Table 1).

The intensification of the oxidation process and the transformation of the obtained oxidized bitumen was carried out by introducing into the oil tar modifying additives of different chemical nature. The analysis of literature data showed that the greatest interest is represented by the modifier containing catalyst of the oxidation process. Such catalysts include various metals (Zn, Sn, Al, Fe, Co), salt, mineral and organic acids or compositions based on them. The catalytic action of salts of metals of variable valency is due to their ability to react with the hydrocarbons with the formation of free radicals [2].

Table 1

Properties of raw materials – oil sludge (JSC "Naftan")

Indicators	Values
Relative density, ρ_{20}^{20}	1.007
Temperature b.k.,°C	>450
Penetration at 25°C, 0.1 mm	>290
Softening temperature, °C	34.3
Group composition, wt %:	
– asphaltenes	7.5
– oils	68.4
– resins	24.1

The oxidation process of the modified petroleum residue was carried out at the laboratory unit at a temperature of (245 ± 2)°C, specific air flow rate of 1.0 $dm^3/(min \cdot kg)$ and duration of oxidation to 8 h as modifiers of catalysts of the oxidation process iron stearate, cobalt salts [4, 5] were studied.

To establish process kinetics the oxidation rate constant was determined according to the following formula [6]:

$$K = \frac{1}{\tau} \ln \frac{t_r^\tau}{t_r^0},$$

where K is the oxidation rate constant, h^{-1}; τ – duration of oxidation, h; t_r^τ – softening temperature of oxidized bitumen upon the oxidation time τ, °C; t_r^0 – softening temperature of feedstock, °C.

Earlier it was studied the dependence of softening temperature on the duration of oxidation of the oil tar modified by iron stearate (III) [4], and shown that the introduction of tar as a modifier stearate iron (III) has a catalytic effect on the oxidation process, increasing with increasing concentration of the modifier in the raw material. The introduction of stearate iron (III) in an amount of 5.0 wt % in the raw material of the oxidation process allows you to get oxidized bitumen with a softening temperature of 46°C is 4 times faster than the unmodified material.

Based on the formula calculated the rate constants of the oxidation of tar in the presence of stearate iron (III) depending on the duration of oxidation (Fig. 1).

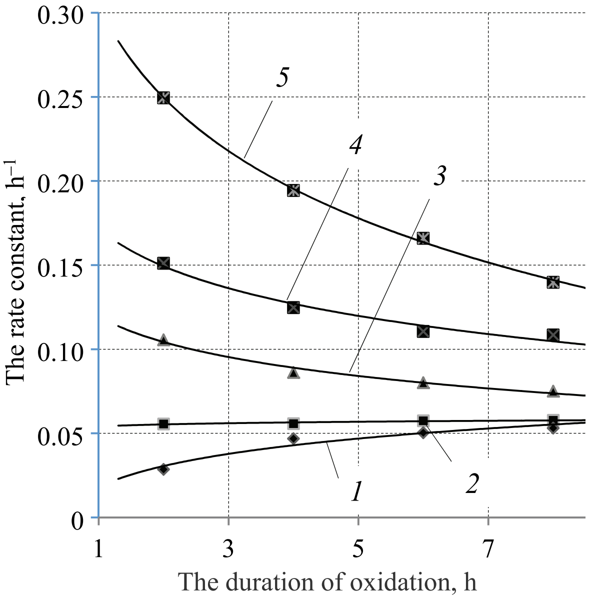

Fig. 1. The dependence of the rate constant of oxidation of tar modified by iron stearate (III), of the duration of oxidation: *1*, *2*, *3*, *4*, *5* – the oxidation of tar modified by iron stearate (III) the number 0; 0.5; 1.5; 3.0 and 5.0 wt % , respectively

Analysis of the dependence of the rate constant of the oxidation duration, showed that the introduction of stearate iron (III) leads to a sharp increase in the rate of the process in the initial time, then the speed is reduced with increasing duration of oxidation.

Speed reduction is due to adverse reactions of metals of variable valence in the lower oxidation number and the spatial difficulties in the conversion of organic compounds because of their increasing molecular weight. The increase in the concentration of stearate iron (III) in tar leads to an increase of the rate constant to 8.7 times the initial time and to 3.1 times the duration of oxidation of 8 h.

In addition to iron salts, as it is well known [2], the oxidation process of hydrocarbons is strongly influenced by cobalt salts. In the processes of liquid-phase oxidation of hydrocarbons, as catalysts in an amount of 0.05–2.00 wt % mainly manganese and cobalt salts of carboxylic acids are used, due to their synergistic effect, so it is advisable to investigate the effect of industrial catalysts for oxidation processes (cobalt naphthenate), and other cobalt salts (octoate). Besides in the production process cyclohexanone catalyst sludge which contains more than 4 wt % cobalt is formed, and it can also be used as an oxidation catalyst.

Study of cobalt salts as modifiers of the oil feed showed that the introduction of oil raw material of cobalt naphthenate – an industrial catalyst for the oxidation of cyclohexane in an amount of 0.1 to 1.8 wt % (0.005–0.090 wt % in terms of cobalt) and cobalt octoate in the amount of 1.8–3.6 wt % (0.038–0.075 wt % in terms of cobalt) leads to reduction of duration of oxidation 1.1–1.3 times (increase of the rate constant in the initial time up to 2.1 times), and at high concentrations of cobalt naphthenate, inhibition of the oxidation process (reduction of the rate constant at the initial moment of oxidation 1.3 times) [5] (Fig. 2).

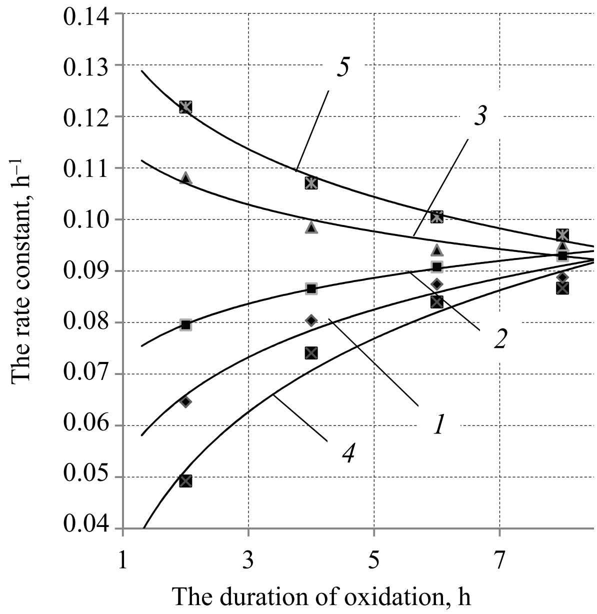

Fig. 2. The dependence of the rate constant of oxidation of the sludge, modified with salts of cobalt, of the duration of oxidation: *1* – oxidation of petroleum tar; *2*, *3*, *4* – oxidation of the sludge, modified with cobalt naphthenate in the amount of 0.1; 1.8 and 2.8 wt % , respectively; *5* – oxidation tar, modified octoate cobalt in the amount of 3.6 wt %

This is due to the increasing role of reactions of chain termination in the process of liquid-phase oxidation with increasing amount of introduced modifier.

Because the catalytic action of cobalt salts was observed at low concentrations, then a similar effect manifests itself in the presence of cobalt catalyst slurry [5]. The nature of cobalt-containing sludge on the process kinetics is shown in Fig. 3.

With the introduction of the catalyst slurry in the amount of 0.11 wt % into the oil raw materials, an increase in the rate constants of 1.7 times the initial time and 1.2 times at the duration of oxidation of 8 h occurs. In the case of using a modifier in high concentrations (5 wt % for raw materials), the rate constant decreases in 2 times at the initial time and 1.5 times at the duration of oxidation of 8 h.

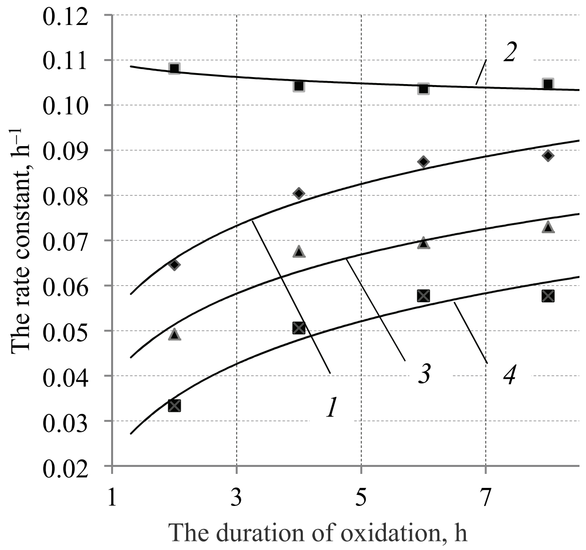

Fig. 3. The dependence of the rate constant of oxidation of the sludge, modified with salts of cobalt, the duration of oxidation:
1, *2*, *3*, *4* – oxidation of the sludge is modified by the catalyst slurry in an amount of 0; 0.11; 1.1 and 5.0 wt % (0.005, 0.01 and 0.05 wt % in terms of cobalt), respectively

The most important quality indicators of oxidized bitumen, which characterize their qualitative properties are softening point and penetration.

In Fig. 4 the dependence of the softening temperature of the penetration of oxidized bitumen obtained from modified and unmodified oil of tar is presented.

The analysis of the presented dependences showed that for the same softening point of bitumen obtained from tar modified with cobalt naphthenate and cobalt-containing sludge, have greater penetration than the oxidized bitumen from unmodified tar. For the same penetration bitumen obtained from tar modified by iron stearate, have a lower softening temperature.

The obtained experimental values of the softening temperature, penetration, penetration index and the temperature of the fragility characterize the performance properties of the oxidized bitumen.

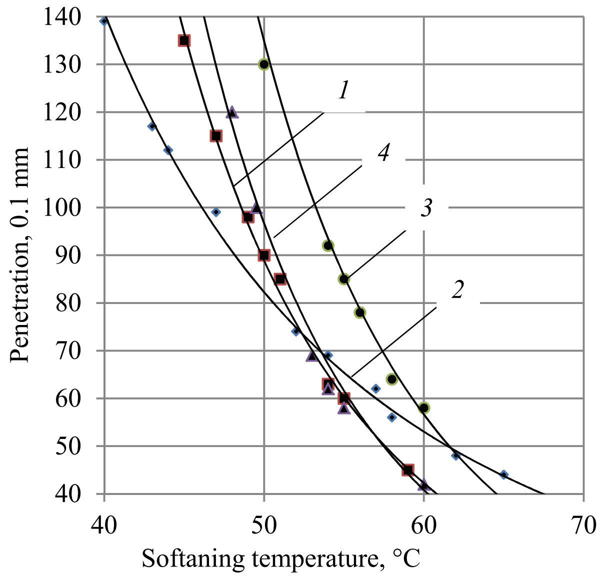

Fig. 4. The dependence of the softening temperature oxidized bitumen of penetration:
1 – oxidized bitumen from unmodified tar;
2 – oxidized bitumen from tar modified by iron stearate;
3 – oxidized bitumen from tar modified by cobalt naphthenate; *4* – oxidized bitumen from tar modified cobalt-containing sludge

Analysis of these values showed that the oxidation of bitumen are formed of the "Sol-gel" and "Gel" (in the case of use of high concentrations of oxidation catalysts). Bitumen of type "Sol-gel" have a high softening temperature and elasticity. The bitumen of the type "Gel" are characterized by a high softening temperature and low ductility, which leads to increased brittleness of the material.

Introduction to higher concentrations of the modifier, intensifying the process of oxidation (iron stearate, cobalt naphthenate), leads to a decrease of plastic properties and brittle fracture temperature, which has a negative influence on operational properties of binders based on such binders, therefore, the optimal concentrations of these modifiers should be determined depending on the requirements to the finished product.

Earlier studies allowed to establish the optimal concentrations of the studied modifiers for production of oxidized bitumen [4, 5]. For a more complete characterization of the effects of modifiers on the physicochemical properties of the resulting bitumen for bitumen obtained from modified raw materials, have also been identified such factors as ductility, adhesion to mineral fillers (marble) and flash.

Comparison of oxidized bitumen obtained from modified raw materials of the studied modifiers, catalysts in optimal concentrations, are given in Table 2.

Table 2

Comparative characteristics of the bitumen obtained from tar with the use of modifiers, exhibiting the properties of catalysts

Parametres	Modifiers				
	Stearate iron (III)		Catalyst sludge		
Amount of modifier, wt %	0	1.5	0	0.11	5.0
Kinetics of the process					
Time of oxidation to achieve the softening temperature of 46°C , h	6.0	3.1	5.2	4.2	7.6
Rate constant K, $h^{-1} \cdot 10^2$	5.340	8.230	7.320	7.770	6.557
Prosess effect, K / K_0	–	1.54	–	1.06	0.90
Quality index					
Softening temperature, °C	52.1	65.7	52.1	54.0	49.0
Penetration at 25°C, 0.1 mm	75.1	43.8	75.1	62.0	98.0
Penetration index	0.6	1.8	0.6	0.3	0.3
Brittleness temperature, °C	–13.7	8.3	–13.7	–14.0	–18.6
Ductility at 25°C, cm	100	65	100	100	100
Adhesion to mineral fillers, the number of the pattern	1	1	1	1	1
Flash point, °C	240	245	240	240	238
Solubility, %	99	99	99	99	99
The content of asphaltenes, wt %	18.8	25.7	18.8	–	–
The content of oil, wt %	61.5	54.9	61.5	–	–
The content of resin, wt %	19.7	19.4	19.7	–	–
Dispersion	0.23	0.35	0.23	–	–
Resistance to hardening:					
Weight change, g	–0.13	–0.05	–0.13	–0.09	–0.07
Change of softening point, °C	4.6	4.1	4.6	4.1	4.0
Residual penetration, %	76.5	81.1	76.5	75.2	78.0

To assess the effect of modifiers on the rate of oxidation the effect of process (E) according to the following formula was calculated [7]:

$$E = \frac{K}{K_0},$$

where K is the rate constant of oxidation of the modified residue, h^{-1}; K_0 – the rate constant of oxidation of unmodified tar, h^{-1}.

Physical and chemical properties of oxidized bitumen obtained from unmodified and modified materials under the same process conditions, may differ materially.

The introduction of 1.5 wt % of stearate of iron (III) in tar provides a reduction in the duration of oxidation is almost 2-fold increase in the effect of the process of 1.54 times. Thus quality characteristics of oxidized bitumen comply with the requirements of EN 12591.

It is established that the introduction of cobalt-containing modifiers allows to improve thermal and oxidation stability of the resulting oxidized bitumen, to reduce the temperature of brittleness. Softening point and penetration of bitumen containing catalyst sludge, change after warm-up in less than bitumen obtained from modified raw materials, indicating the protective effect of cobalt-containing sludge.

Inhibition of oxidative processes by the use of cobalt-containing modifiers at high concentrations (cobalt-containing sludge is more than 5 wt % for raw materials) increases the durability of oxidized bitumen while minimizing the effect of process 10%.

Analysis of the kinetic curves allowed to establish the following: the greatest impact on the oxidation process has a stearate of iron, allowing to increase the rate constant of the process to 8.7 times; the variation of the concentration of cobalt-containing modifier in the oil sludge allows to intensify and to inhibit the oxidation process.

Conclusion. It is established that the modifiers containing salts of metals of variable valency, may have on the process of catalytic oxidation and the inhibitory effect depending on their concentration in the oil feedstock. Stearate iron (III) intensifies oxidation process, at the content of 5.0 wt % tar stearate iron (III), the rate constant for oxidation increases 8.7 times.

Effect on the oxidation process of cobalt modifiers (industrial oxidation catalyst (cobalt naphthenate), cobalt octoate and production wastes containing more than 4 wt % cobalt) is twofold: at low concentrations of cobalt salts catalyze the oxidation process, and higher – inhibit.

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