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High-Melting Point Asphalt on the basis of High-Paraffin Oil Tar

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Abstract

Objectives: A special place among oil bitumen is occupied by refractory bitumen - bitumen of solid marks or, as they are called, solid bitumen. **Methods:** They differ from the liquid bitumen with high softening point and some other physical and chemical properties, conditioned by the technological mode of production. Bitumen of solid brands find their application in various sectors of the economy both in pure form, as the basic raw material, or as a mixture with various organic products and minerals as part of the production of a number of technical materials. **Results:** The positive qualities of refractory bitumen and asphaltites, making them indispensable for heat and water proofing of underground channel-free heat conductors are: high softening point; thermo plasticity, which excludes the appearance of cracks; watertight; low water absorption (up to 30 times less than bitumen perlite). The possibility of obtaining high-melting grades of bitumen from high-paraffin tar in the presence of a catalytic complex by "conventional oxidation" that is the raw material purge air, and without purging air using potassium permanganate as a source of molecular oxygen. It is shown that in "conventional oxidation" (sparing of oxygen of air) in the presence of a catalyst complex it is possible to achieve a high softening temperature - over 100^0C - almost four times faster than using air purging without purging catalyst. **Applications:** Using the catalyst of atomic oxidation of petroleum residues showed that it took about 7 hours to reach the softening temperature of almost 130^0C

Keywords: Refractory Bitumen, High-Paraffin Tar, Oxidation, Catalytic Complex

1. Introduction

One of the most important areas in the field of oil refining is a rational use of petroleum residues by involving them in processes such as Vis breaking, coking, deasphalting, bitumen production, and others[1-4]. Petroleum asphalts are one of the most large-tonnage oil products in Russia and abroad. They are widely used in road construction, repair of roads, airfields, industrial and civil engineering[5,6]. A special place among bitumen occupied by refractory bitumen[7-9]. They differ from the liquid bitumen with high softening point and some other physical and chemical properties, conditioned by technological mode of production. Bitumen of solid brands find their application in various sectors of the economy both in pure form, as the basic raw material, or as a mixture with various organic products and minerals as part of the production of a number of technical materials. Solid grade bitumen is widely used as the main raw material in the manufacture of roofing materials as a cover coat applied to the surface of the board. Bitumen of solid brands is successfully used as coloring material for the renovation of old roof felt and larboard roofs; it is an excellent material for the production of protective and insulating coatings of pipelines. There are many moisture-proof materials that are known to be composed of a mixture of refractory grade bitumen with various additives (asbestos, ground stone material, cement, diatomaceous earth, sand and etc.). In the electrical industry solid bitumen is used for production of electrically insulating materials such as coatings,

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composites and sealing compounds, adhesives mass for insulation tapes and electrode paste. Plastics industry is a big consumer of refractory bitumen. The bitumen is introduced into plastic masses as the main component part of binders, which are then compounded with fillers (asbestos, kaolin, petroleum black and etc.). This brand of refractory bitumen rubrax consumed by rubber industry. The rubber rubrax is introduced as a softener and an amplifier, as well as to impart greater smoothness when processed. Rubrax stands out in comparison with other liquid emollients derived from petroleum because it can be introduced into the rubber in a large amount without lowering its mechanical properties, thereby significantly saving expensive rubber. During production of plastic skin and leather substitute's rubrax is used as part of the rubber-resin adhesive and promotes better mixing of rubber with a fibrous material. From mentioned not complete list of applications of solid bitumen becomes clear that the need to pay the most serious attention to the production of refractory bitumen is urgent. The oxidation of heavy oil residues (HOR) with the air is the main process of bitumen production. Modern technology of production of oxidized bitumen is the oxidation of petroleum residues by atmospheric oxygen without a catalyst. The temperature range in industrial applications is 230 ÷ 270 ° C; air consumption - 2,8 ÷ 5,5 m3 / (m2 • min); duration - up to 12 hours at a column diameter of 3,2 ÷ 3,4 m and a height of 14 ÷ 15 m. The main factors of the oxidation process (more precisely, the oxidative dehydration) are temperature, flow rate and pressure. The higher the oxidation temperature, the faster the process. However, at too high temperatures the reaction of formation of carbenes and carboides is accelerated, which is unacceptable. The air flow rate, the degree of its dispersion across the cross section of the oxidative column significantly affects the intensity of the process and the properties of bitumen. Traditionally fine dispersion of oxygen in the tar is achieved by using specially designed uterine devices. Increasing the air flow to a certain limit, other things being equal leads to a proportional increase in the rate of oxidation (ie, oxygen is the initiator of the process). If too much air is supplied temperature in the reaction zone can rise above allowable as an exothermic oxidation reaction. Considering the methods and principles of the intensification of the process of production of oxidized bitumen, there are two approaches. The first is to intensify the process of achieving bitumen production through the use of mechanization and automation, while maintaining the traditional manufacturing equipment. They increase productivity of oxidizers, increase the temperature or increase the load on air, use catalysts or apparatus for more effective contact of air with raw material. The second way to intensify the process of production of oxidized bitumen based on the theory of controlled external effects of intermolecular forces and effects of phase transitions. Various adjuvants are added, influence tar with mechanical and energy fields, which are able to change the structure of the dispersed oil residues and thereby change the intensity of the oxidation process and the properties of received bitumen[10]. The duration of the oxidation process depends on the air flow in relation to contact specific surface. To reduce the time of oxidation it is expedient to increase the specific surface area. Increased airflow is economically feasible until an excessive increase in size of the bubbles at a sufficiently high specific surface area of contact between the phases. Recently the most effective ways of dispersing the tar by the way of introducing in it of dispersants and application of physical fields of various intensities and frequencies have been used. A high degree of dispersion of oxygen in the tar is provided by introducing into it the optimum amounts of the various flavors of petroleum origin, causing reduction of surface tension measured at a temperature of oxidation. In order to improve quality, lower energy intensity, oxidation reactor is often equipped with vibration sprayer and gas-dynamic transducer mounted respectively at the outlet connection of the original product and air supply. Finding ways to optimize the process of oxidation in the manufacture of refractory bitumen is a very urgent task. Solutions are necessary, which will focus on the intensification of oxidation to reduce the process time. Thus, it is necessary also that the resulting product meets the quality requirements. The aim was to study the effect of the catalyst complex developed by us on the intensity of the oxidation of tar in the preparation of refractory bitumen, as well as its impact on the quality characteristics of the commodity product.

2. Materials and Methods

As a raw material for refractory bitumen tar of paraffin-naphthenic base of Elkhovskoye oil refinery Management (ENPU) was used, this is a mixture of high-vacuum distillation residues of petroleum of Mordovo-Karmalskiy and Kuakbashskiy deposits of the Republic of Tatarstan. Physical and chemical properties of tar from ENPU PJSC "Tatneft" (ENPU) presented in Table 1. In the first series of experiments tars oxidation conducted at a batch laboratory machine at a temperature 250^{0}C and air flow of 3 l/min*kg of raw material. The laboratory setup is an oxidative cube of 100 mm in diameter and 200 mm in height, the load of which on average is up to 1000 cm^3. Oxidation was used on both the initial tar, and activated tar (together with the catalyst complex). In a second series of experiments to produce refractory bitumen as an oxygen source potassium permanganate was used in an amount of 1% for raw materials. The process was conducted in a stirred tank reactor at a temperature 250^{0}C with vigorous stirring (stirrer speed 600 rev / min). The process also conducted in the presence of a catalytic complex. To monitor the kinetics of both the first and second case, a periodic sampling to determine the softening temperature was carried out. The softening point determined by the method of "ring and ball" according to GOST 11506, the point of which is to determine the temperature at which a bitumen located in a ring of specified sizes, softens under the test conditions, moving under the action of the steel ball touches the lower plate. These refractory bitumen samples were analyzed for the main quality indicators stipulated in regulatory requirements for the product. Thus, the depth of needle penetration determined according to the method described in GOST 11501; the mass fraction of substances insoluble in toluene determined according to GOST 20739; flashpoint - according to GOST 4333; solubility of bitumen in linseed oil and its mix with white spirit, as well as an acid number of bitumen - GOST 21822-87; conditional viscosity determined according to GOST 6258; the mass fraction of water and ash - according to GOST 2477 and GOST 11512, respectively; the change in mass after heating - according to GOST 18180; the mass fraction of sulfur determined according to GOST 1437; the mass fraction of paraffin wax - according to GOST 17789; bitumen solubility in carbon disulfide determined according to GOST 20739. Group bitumen chemical composition determined by the following method: maltenes content (amount of oils and resins) and asphaltenes determined by a method based on the use of n-hexane as a solvent on the stages of asphaltenes settlement and adsorption removal of tarry substances in a Soxhlet apparatus. Asphaltenes recovered from bitumen using n-hexane as a solvent which taken in a 40 fold excess in relation to the raw material. The solution kept in the dark at room temperature for 24 hours. The precipitate separated by filtration on a Buchner funnel through filter paper of average density. Adsorbed on the filter solids (asphaltenes) washed with n-hexane in a Soxhlet apparatus to cease solvent dyeing, then asphaltenes extracted with chloroform. After distillation of chloroform on rotary evaporator, asphaltenes dried to constant weight in vacuum. Resins and oils isolated by standard adsorption method on silica gel.

3. Results

In Figure 1 the kinetics of the oxidation of the original tar ENPU is shown. It reveals that the dependence of softening temperature changes on the length of oxidation. The kinetics of tar oxidation ENPU with catalytic complex is shown in Figure 2. In the presence of a catalyst complex intensification of TNO oxidation process happens, which expressed in the reduction of raw material presence in the reaction zone in approximately

Table 1. Physical and chemical properties of ENPU tar

Indicators	Value
Density, kg/m^3	0,9878
Relative viscosity, RV_{80}	51,76
	28,23
Content, %mass: – CAB – Sulphur – Paraffins	0,887
	15
Asphaltens/resins	0,45

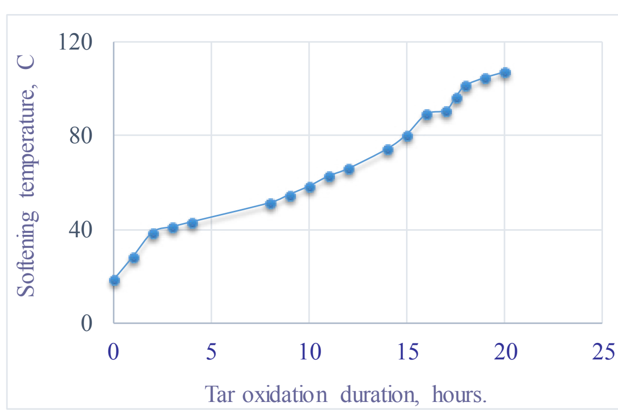

Figure 1. Dependence of T_{size} bitumen on the duration of oxidation.

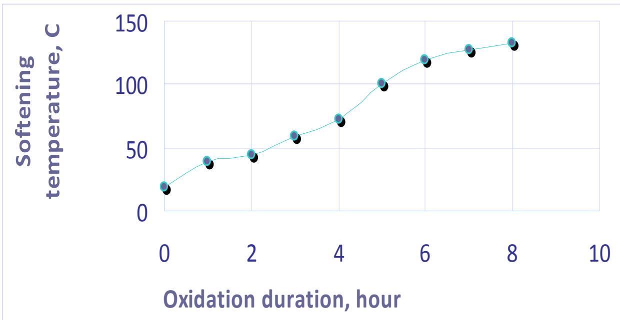

Figure 2. The dependence of the softening temperature of the oxidized TNO on the duration of the oxidation.

Table 2. Component composition of refractory bitumen

Component content	Content, % mass.
– malthenes	58,44
– asphaltenes	40,96
– carbenes and carboides	0,6

Table 3. Comparative characteristics of bitumen according to GOST 21822-87 with a sample of refractory bitumen

Indicators	B	V	G	Refractory bitumen
	GOST 21822-87			
Exterior	Solid black material			
Relative viscosity, VU50, not more	18			
Needle penetration depth at 25^{0}C, cm not more, cm	11,0	8,0	5	4
Softening temperature, ^{0}C	100-110	110-125	125-135	100
Flash temperature, not lower	240	250	260	250
Ash content, % not more	0,2	0,2	0,2	>0,2
Bitumen solubility in linseed oil (1:1, 270-280^{0}C)	Full			
-alloy of bitumen with linseed oil in white spirit (2:1)	Full			
Content of substances not soluble in hot benzol % mass.	0,15			0,6
Acid number, mg KOH/for 1 g of bitumen, not more	2,0			0,36

3.8 times. The Table 2 shows the results of analysis of group chemical composition, received in the presence of catalyst complex of refractory bitumen sample with softening temperature of 100^{0}C. The Table 3 presents the qualitative characteristics of the 100-degree sample of refractory bitumen. From Table 3 it is clear that, in accordance with GOST 21822-87 on "Special Bitumen for paint products" the received sample of refractory bitumen is of grade "B". Table 3 shows kinetics of the synthesis process of refractory bitumen from tar ENPU in the presence of potassium permanganate and a catalytic complex, expressed in dependence of softening temperature change on the length of the process. From the data presented in Figure 3 we can see that it is possible to obtain refractory bitumen with a softening point 126^{0}C in 7 hours. Table 4 shows the results of analysis of group chemical composition of the obtained sample of refractory bitumen with softening temperature of 126^{0}C. The Table 5 shows the characteristics of the obtained sample of bitumen. Analysis of the data in Table 4 shows that the obtained sample of refractory bitumen corresponds to A-30 first grade according to GOST 781.

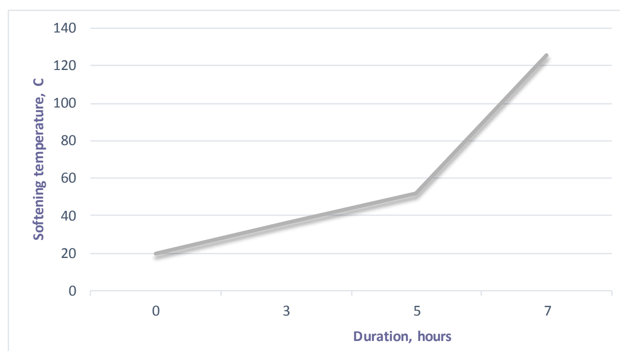

Figure 3. Dependence of TNO softening temperature change on time.

Table 4. Group chemical composition ща refractory bitumen

Component content	Content, % mass.
Oils	43,8 %
Benzol resins	18,6 %
Benzol spirit resins	9,8 %
Asphaltens	27,7 %

Table 5. Comparative characteristics of the bitumen according to GOST 781 with a sample of refractory bitumen

Indicator name	Norm for mark				Refractory bitumen
	A-30		A-10		
	OKP highest grade 02 5651 0201	OKP first grade 02 5651 0200	OKP highest grade 02 5631 0101	OKP first grade 02 5651 0100	
1. Softening temperature, ^{0}C	125-135	125-135	125-130	125-135	126
2. Depth of needle penetration at 25^{0}C, мм*10^{-1}	30-40	26-40	8-13	5-19	27
3. Change of mass during heating during two hours at 150^{0}C, %, not more	0,1	0,1	0,1	0,1	0,1
4. Mass part of ash, %, not more	0,5	0,5	0,3	0,5	0,5
5. Mass part of water, %, not more	Absence	Traces	Absence	Absence	Absence
6. Mass part of sulphur, %, not more	1	-	2	-	-
7. Mass part of solid paraffins, %, not more	2	5	3	5	5,9
8. Solubility in carbon sulphur, chloroform, benzol and trichloroethylene, %, not less	99	99	99	99	99

4. Conclusions

Kinetics of the oxidation of the original tar ENPU is shown, which represented with the dependence of the changes of softening temperature from the length of oxidation. In the presence of the catalyst complex intensification of oxidation of TNO happens, which expressed in the reduction of raw material presence time in reaction zone of approximately about 3.8 times. In accordance with GOST 21822-87 the obtained sample of refractory bitumen related to grade "B".

5. Summary

The results of these studies confirm the possibility of a significant intensification of the process of oxidation in the presence of a catalyst complex. The use of potassium permanganate as an oxygen source generally allows avoiding flow of oxygen from the outside, which greatly simplifies the hardware formation of the process. At the same time, the received samples of refractory bitumen comply with quality requirements for marketable product. Comparison of changes in the group chemical composition, in particular, asphaltenes, shows that the bitumen sample with T_{size} 126^{0}C their content is 1.5 times smaller than in the sample with T_{size} 100^{0}C.

5.1 Conflict of Interest

The author confirms that the data do not contain any conflict of interest.

6. Acknowledgements

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