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Development of the Technology of Black Oil Macromolecular Structuring in the Process of its Oxidation for Obtaining the Bituminous Insulating Materials

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Abstract: One of the effective ways to improve the properties of special bitumens are their chemical and physical modification. When considering a chemical approach, we assumed that a process of oxidative polymerization is connected with radical-chain reactions. That is why when carrying out an oxidizing process of residual oil stock, it is necessary to use the modifiers, which are able to take part in this process, subjecting the segments of paraffin chains to chemical structuring with further formation of polycyclic naphthene-aromatic fragments, promoting the intense resin formation and preventing from the formation of the asphaltene crystalline phase. The analysis of physical-mechanical properties of bituminous insulating materials (BIM), based on acidified flux oil, showed the ambiguity of their assessment, i.e. at identical speeds of fuel-oil residues oxidation processes, there are differences in strength properties of coverings (C). The properties of air-blown asphaltic bitumen are regulated by resizing of the core and solvation shell of the complex structural unit (CSU) by injection of multicomponent bifunctional modifier (MBM), promoting the reduction of oxidation duration and the improvement of physical-mechanical and insulation properties of BIM.

Key words: Residual oil stock · Paraffin-asphaltene associates · Physical-chemical modification · Oxidative polymerization · Complex structural units · NMR-relaxometry · Infrared spectroscopy

INTRODUCTION

When selecting the source raw material, the results of the earlier studies were taken into consideration [1-19], proving that the oxypolymerization ends at the stage of bitumen obtaining. Therefore, the raw material for special bitumen production is the flux oil of naphthene-aromatic sub-structure - Karabashsky NBZ (KNBZ) and paraffin-naphthene substructure - Elkhovsky NPU (ENPU) OJSC "Tatneft" (Table 1).

The investigations of structural-dynamical properties of flux oil by impulse NMR show high inhomogeneity of chemical group composition of resinous-asphalthene materials (RAM) in the flux oil of ENPU (Fig. 1) due to high content of paraffin HC (Table 1), corresponding to high content of phase A – 75%mass. and low frequency of core precessions of the phases under study. Formerly it was found out, that the structural dynamical analysis (SDA) of oil disperse systems has the phases A, B and C, which are conventionally classified as oil, resins and asphaltenes respectively, due to their different content and molecular mobility.

Based on naphthene-aromatic composition and low content of paraffin HC, flux oil of KNBZ is the most appropriate raw material for BIM production; it is proved by the investigations of structural-dynamical (Fig. 1) and physical-mechanical properties of end products.

The selection of wood processing byproduct (WPB) as a bitumen modifying agent is connected with high convergence of interconversion of their components at high-temperature oxidation. WPB contains unsaturated acids, which react in oxypolymerization with petroleum acids and promote reduction of asphaltene discharge. A selection of multicomponent bifunctional modifier (MBM) - a component of synthetic oil production (CSOP) as a main raw material is explained by high capability to chemical structuring due to formation of ethers, having the better film-forming property. It was found out that at temperature of 240°C and more manganese dioxide (MD) with organic acids forms salts, soluble in bitumen and as a consequence, has a catalyzing effect in oxidizing process. It was revealed that raw material stay period in reaction zone maximally reduces at injection of three-component modifier and at simultaneous yield

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Table 1: Physical-chemical properties of flux oil

Indices	Flux oil		
	Karabashsky NBZ	Elkhovsky NPU	Mordovo-Karmalsky PB
Density, kg/m^3	0,9686	0,9878	0,9985
Relative viscosity, RV_{80},	22,96	51,76	80,0
Content, %mass.:			
- CAB	18,25	28,23	55,8
- Sulphur	0,492	0,887	5,2
- Paraffins	< 2,0	15,0	15,0
Asphaltenes/resin	0,64	0,45	0,47

Table 2: Component composition of special bitumens

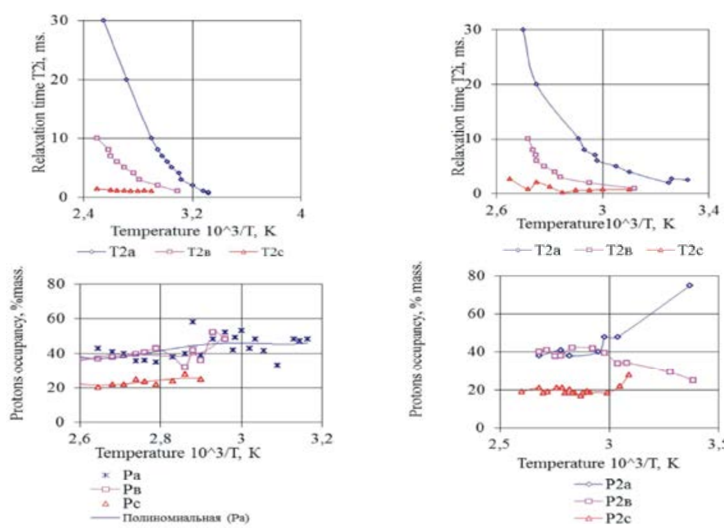
Components	The content of components in special bituments, oxidized with MBM (T_{flux} = 100°C), % mass	
	ENPU	KNBZ
-Malthenes	58,44	61,31
-Asphaltenes	40,96	38,09
-Carbenes and carboids	0,60	0,81

Table 3: Structural-group composition of asphaltenes

T_{soft} of bituments, where the asphaltenes were extracted, °C	Condensity, $D_{1600}/(D_{820}+D_{880})$	Oxidation, D_{1700}/D_{1600}
85	3,04	0,49
100	3,60	0,67
103	1,26	0,71
124	2,62	0,64

Table 4: Infrared spectroscopic studies of high-melting point bitumens

T_{soft} of bitumen, °C	Content of structural groups*, rel. unit						
	CH_2, 720sm^{-1}	CH_3, 1380sm^{-1}	CH_2+CH_3	Branching, CH_3/CH_2	$C{=}C_{arom}$	SO, 1030 sm^{-1}	CO, 1700 sm^{-1}
85	0.12	0.66	0.78	5.50	0.47	0.23	0.38
100	0.13	0.62	0.75	4.77	0.35	0.21	0.24
103	0.22	0.68	0.90	3.09	0.44	0.21	0.31
124	0.20	0.79	0.99	3.90	0.59	0.33	0.49



a - flux oil of KNBZ b - flux oil of ENPU

Fig. 1: The dependencies of spin-spin relaxation time and hydrogen proton occupations of phases a, b, c on temperature

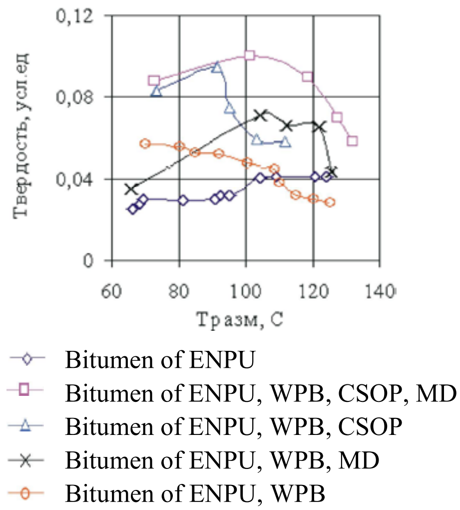
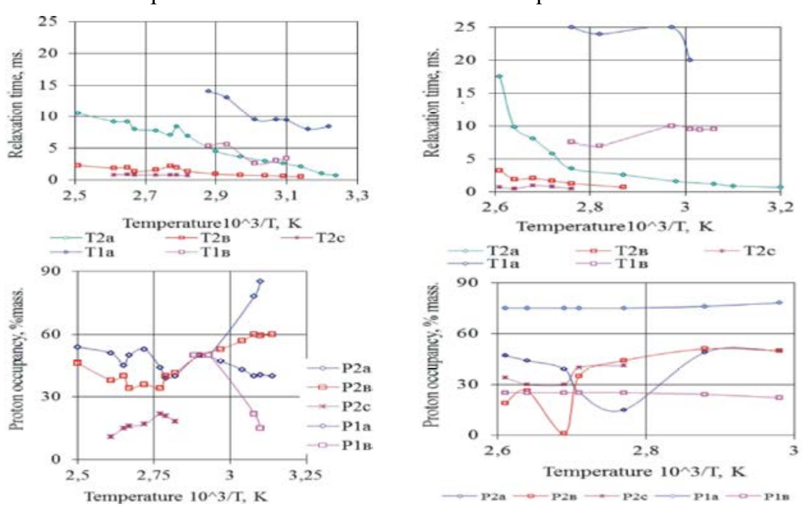


Fig. 2: The impact of MBM components on shardness of bitumen lacquers



a - bitumen-1 b - bitumen-2

Fig. 3: The results of the analysis of structural-dynamical states of special bitumens of Elkhovsky NPU

increase of bitumen-1 (special bitumen of ENPU, modified MBM, Tflux. = 100°C) by 17 % and the formation of decomposition products reduces by 15 to 17%. It is known, that at temperature of 250°C CSOP and MD promote the destruction of oil inhibitors, able to speed down its polymerization. Low physical-mechanical properties of BIM based on bitumen-3 (special bitumen of KNBZ, modified MBM, Tflux. = 100°C), are explained by high content of carbenes and carboids 0,81 (Table 3) and structural peculiarities of phases A and B, where the content of phase A is 90%mass. and it has a negative impact on BIM film-formation feature.

In the course of investigations of BIM, based on special bitumens of ENPU (both with MBM and without it - bitumens 1 and 2), it was determined an inverse proportion of covering strength on rheological characteristics of BIM. Therefore, MBM usage in oxidation of ENPU flux oil significantly increases the hardness (Fig. 3) and it is characterized by multiply less values of dynamic viscosity and shearing stress of BIM, what proves the existence of BIM structural net, formed by their micelle structure. It was revealed, that the dissolution rate of bitumen-1 in aromatic solvent is higher than the one of bitumen-2.

Abnormality of BIM high physical-mechanical (Fig. 2) and low rheological properties, obtained based on bitumen-1, containing up to 41% of asphaltenes (Table 2) as compared to the requirements of GOST 5631-79 with asphaltene content up to 39%, is explained by the chemical structure of disperse system components (Fig. 3a), high chemical homogeneity of phases B and C,core precession frequency and content of the phase B.

This phenomenon is proved by a comparative analysis of structural-group composition of bitumens and extracted asphaltenes as per the data of infrared spectroscopy (Table 3, 4). In this case the bitumens with Tsoft equal to 85, 100 and 124°C refer to one type of oxidized raw material, i.e. flux oil of ENPU together with additives with different oxidation rate.

The studied samples shall be divided into two groups in the content and composition of paraffin structures. So, the bitumes with Tsoft equal to 85 and 100°C the total content of methylene and methyl groups is lower and the branching of paraffin structures is higher, than in the bitumes with Tsoft equal to 103 (bitumen-2) and 124°C. Alongside with that, bitumen-1 has low content of aromatic structures; its asphaltenes are more condensed and less oxidized, than the ones of bitumen-2.

The change of asphaltene structure in special bitumens promotes their high chemical homogeneity with resin components due to the mutual diffusion of phases B and C (Fig. 3).

CONCLUSIONS

The results of the investigations, taking into consideration the data, obtained by impulse NMR, infrared spectroscopy and physical-mechanical analysis show that the BIM are plastified due to the asphaltenes, which have the properties of "heavy" resins, because of oxidative polymerization of MBM and flux oil components of ENPU.

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