

Development of the Technology of Macromolecular Structuring of Naphtha Crude Residues During Their Oxidation to Produce Bitumen Insulation Materials

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Abstract: One of effective methods to improve the properties of special bitumen is their chemical and physical modification. The chemical approach suggests the oxidative polymerization is related to chain-radical reactions. Therefore, the modifiers which able to participate in the oxidation of crude naphtha residues, by chemical structuring of the segments of paraffinic chains followed by the formation of polycyclic naphtho-aromatic fragments that contribute to gumming and preventing the crystalline phase of asphaltene formation are required. Analysis of physical-mechanical properties of the bituminous insulating material (BIM) obtained from oxidized tars showed the ambiguity of their assessment, i.e. the differences in the strength properties of the coatings (C) were observed at similar velocities of naphtha residue oxidation. Modification of the properties of oxidized bitumen occurs by alteration of the nucleus size and the solvate shell of a structurally complex unit (CSU), the introduction of a multi-component bifunctional modifier (MBM) that reduces the oxidation duration and improves the physical, mechanical and insulating properties of BIM.

Key words: Naphtha crude residues • Paraffin-asphalt associates • Physical-chemical modification • Oxidative polymerization • Structurally complex units • Nuclear magnetic resonance relaxation (NMR-relaxation) • IR-spectroscopy

INTRODUCTION

The results of our previous studies [1-19] evidencing that oxidative polymerization is accomplished at the stage of construction bitumen synthesis were taken into account during selection of raw material sources. As the result, tars of naphthene-aromatic (Karabash Oil-Bitumen Plant (KOBP)) and paraffin-naphthene bases (Elkhovskiy Petroleum Refining Plant (EPRP) OAO “Tatneft”) served as the raw material for production of special bitumen (Table 1).

Studies of structural and dynamic properties of tars by impulse NMR are showed a high degree of heterogeneity of the group chemical composition of resin-asphaltene substances (RAS) in EPRP tar (Fig. 1) due to the high content of paraffinic hydrocarbons (Table 1) corresponding to the high content of phase A-75 % wt and low frequency of precession of the nuclei of studied phases.

Previously, the structural-dynamic analysis (SDA) has showed that oil dispersed systems contain the phases *A*, *B* and *C*, which due to their different

Table 1: Physical-chemical properties of tars

Parameters	Tars		
	Karabash OBP	Elkhovskiy PRP	Mordovo-Karmalskiy natural bitumen
Density, kg/m ³	0,9686	0,9878	0,9985
Relative viscosity, RV ₈₀ ,	22,96	51,76	80,0
Content, % wt.:			
- resinous-asphaltenic substances	18,25	28,23	55,8
- scrape	0,492	0,887	5,2
- paraffins	< 2,0	15,0	15,0
Asphaltene / resins	0,64	0,45	0,47

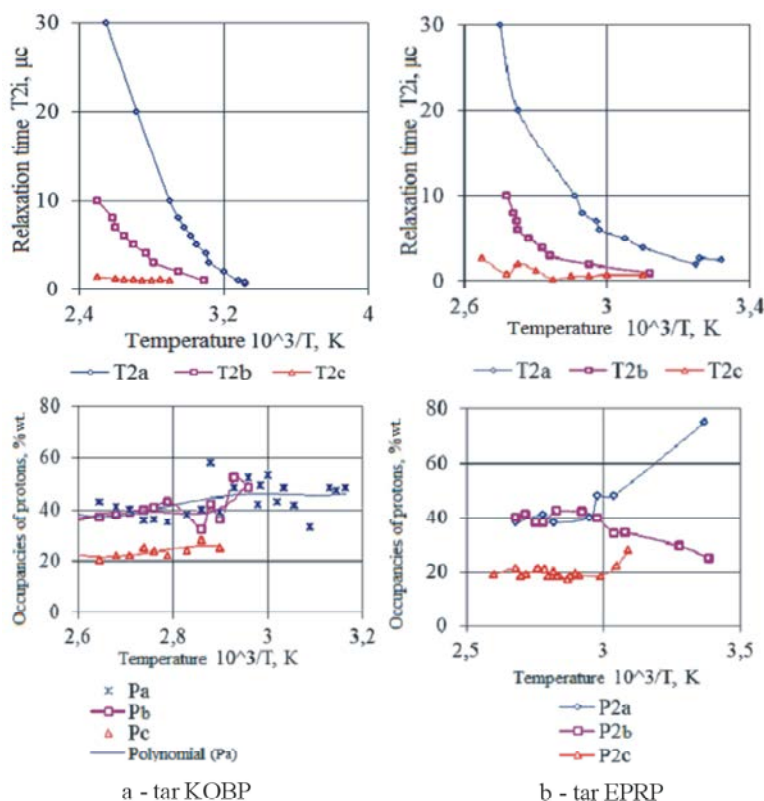


Fig. 1: Dependences of the spin-spin relaxation time and hydrogen proton occupancies in phases a, b and c on temperature.

concentration and molecular mobility are conventionally referred to oils, resins and asphaltenes, respectively.

Based on the naphthene-aromatic composition and small content of paraffinic hydrocarbons, KOBP tar is the most convenient raw material for the production of BIM, what is confirmed by studies of structural-dynamic (Fig. 1) and physical-mechanical properties of the final products.

A choice of a co-product of wood processing (CWP) as a modifying agent of bitumen is related with high convergence mechanism of reciprocal transformations of their components in high-temperature oxidation. CWP contains unsaturated acids, which reduce the release of asphaltenes in oxidative polymerization together with petroleum acids. The choice of the multicomponent bifunctional modifier (MBM)-a component of polymer oils production (CPOP) as the main raw material is stipulated by its high capacity to chemical structuring due to the formation of esters with better film-forming ability. It was found that manganese dioxide (MD) at 240°C and above forms salts with the organic acid which are soluble in bitumen medium and as a result catalyzing the oxidation. It was identified that

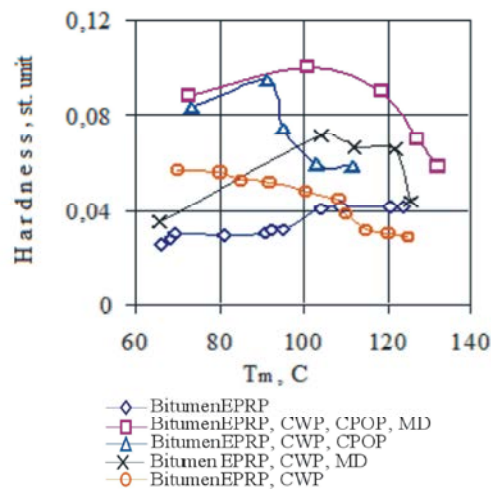


Fig. 2: Influence of MBM components on bituminous varnish

the maximum reduction in the time of material presence in the reaction zone reveals at the introduction of the three-component modifier with simultaneous increase of bitumen-1 output (special bitumen EPRP, modified MBM, $T_m = 100^\circ\text{C}$) by 17% and the formation of degradation

Table 2: Composition of special bitumen

Components	Content of components in special bitumen oxidized with MBM ($T_m = 100^\circ\text{C}$), % wt.	
	EPRP	KOBP
- malthenes	58,44	61,31
- asphaltenes	40,96	38,09
- carbenes è carboides	0,60	0,81

Table 3: Structural-group composition of asphaltenes.

T_m of bitumens, used for asphaltenes extraction, $^\circ\text{C}$	Condensing, $D_{1600}/(D_{820}+D_{880})$	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: IR spectroscopic studies of high-melting point of asphalts

T_m of bitumen, $^\circ\text{C}$	Content of structural groups *, in rel. units						
	CH_2 , 720cm^{-1}	CH_3 , 1380cm^{-1}	CH_2+CH_3	Branching, CH_3/CH_2	$\text{C}=\text{C}_{\text{aromatic}}$	SO , 1030 cm^{-1}	CO , 1700 cm^{-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

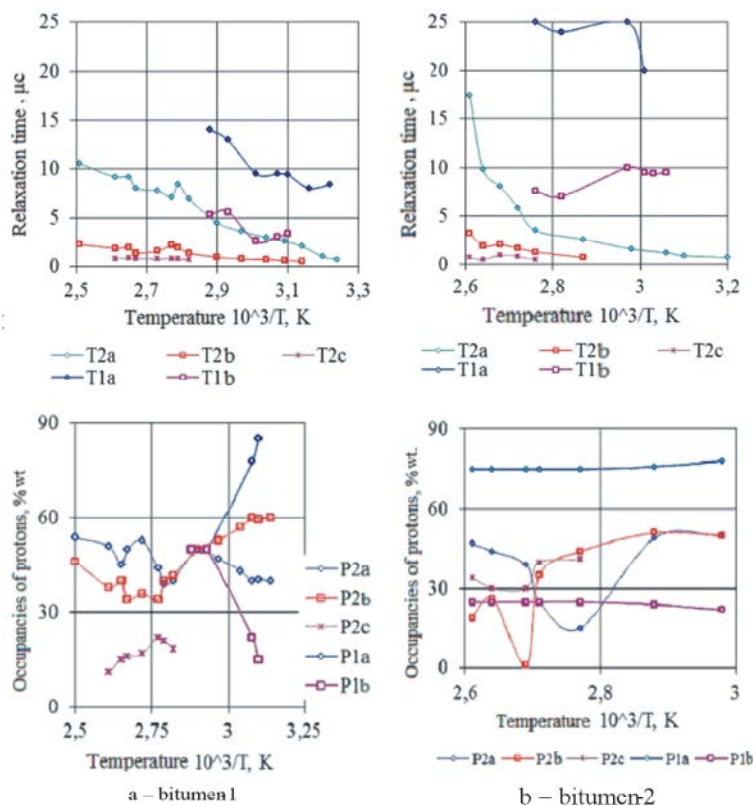


Fig. 3: The results of the analysis of the structural and dynamical states special bitumen Elkhovskiy EPRP.

products reduces by 15-17%. It is known that the inhibitors capable to slowing of polymerization are destroyed at 250°C and the presence of MD and CPOP. Low physical and mechanical properties of BIM based on bitumen-3 (special bitumen KOBP, modified MBM, $T_m = 100^\circ\text{C}$) can be explained by the high content of carbenes and carboids 0.81% (Table 3) and structural features of

phases A and B, in which the content of phase A is 90% wt. and has a negative impact on the film-forming ability of BIM.

Our studies of BIM based on special bitumen EPRP (both with MBM and without-bitumen-1 and -2) have identified inverse proportional dependence between hardness of C and the rheological characteristics of BIM.

Thus, the implementation of MBM in the oxidation of tar EPRP promotes a significant increase in the hardness (Fig. 3) and characterizes by lower dynamic viscosity and shear tension of BIM, what is an evidence of a spatial lattice structure in BIM formed by their micelle structure. It was found that the resolution rate of bitumen-1 in an aromatic solvent is higher than for bitumen-2.

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

This phenomenon according to IR spectroscopy is confirmed by a comparative analysis of the structural-group composition of bitumens and separated asphaltenes (Tables 3 and 4). In this case, bitumen with T_m equal to 85, 100 and 124°C belong to the same type of oxidizing material, i.e. tar EPRP together with additives of different oxidation.

The studied samples should be divided into two groups according to content and structure of the paraffin structures. Thus, total content of methyl and methylene groups of less paraffinic and branching structures higher in bitumen T_m 85 and 100°C than in bitumens with T_m 103 (bitumen-2) and 124°C. Moreover, bitumen-1 characterizes by low content of aromatic structures and its asphaltenes are more condensed and less oxidized than bitumen-2.

Changes of the structure of asphaltenes in special bitumens promote their high chemical homogeneity with the components of resins due to reciprocal diffusion of phases B and C (Fig. 3).

CONCLUSIONS

In our studies, we have determined using impulse NMR, IR spectroscopy and physical-mechanical analysis that BIM are plasticized due to asphaltenes possess the properties of the “heavy” resins as a result of oxidative polymerization of MBM components and tar EPRP that BIM the fact that.

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