



Scientific and Practical Aspects of Bitumen Emulsion Mastic Creation

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Abstract

It is interesting to consider the possible application as an alternative raw material in the manufacture of bituminous emulsion material residual bitumen grade BNN 80/120, production technology which implies a significant reduction in the proportion of paraffinic hydrocarbons by allocating them in the oil fractions in the evacuation of heavy petroleum residues. As a raw material in the production of BEM they should use the bitumen obtained from the heavy oils of naphthenic aromatic base with a minimum content (up to 2% by weight) [1] of high-molecular straight-chain paraffinic hydrocarbons (P-HC), whose reserves are largely limited and difficult to access. In this regard, the expansion of the raw material base of bitumen production due to the involvement of HOR resinous paraffin base confirms the relevance of the studies. The difficulties in the production of insulating BEMs, that meet the requirements of GOST 30693-2000 on the basis of oxidized HOR paraffin base, are explained by the fact that protective coatings (P_K) from such materials with the decrease in the glass transition temperature (point) are characterized by an increased intensity of internal stress (δv) in the volume of BEM, in which the increase of the strength growth intensity (δp) occurs, so premature spontaneous destruction occurs in the process of oxidative destruction, i.e. in the conditions of their operation. This is explained by the fact that at the temperatures above T_{st} , highly elastic and plastic deformations develop in bitumen, and internal stresses relax easily. With decreasing T_{st} , the rigidity of bitumen increases sharply, the relaxation processes decelerate, and internal stresses increase substantially.

Keywords: bitumen-emulsion materials, residual bitumens, oxidized bitumens, adhesion-strength properties, solvents, IR- Fourier spectroscopy, NMR spectroscopy, deformability.

1. Introduction

In Russia, cationic water-bitumen emulsions (WBE) remain a relatively new type of organic binder [1-3]. First of all, this is due to the peculiarities of the chemical composition, the structure and the nature of raw materials - heavy oil residues (HOR), the technological conditions of their processing processes, aimed mainly at the production of oxidized (mainly up to 80% by weight), residual, and compounded bitumen. It should be noted that the main advantages of bitumen as the basis of waterproofing material, in particular bitumen emulsion mastics (BEM), include their high insulating properties with respect to aqueous media. It has been established [2,3] that water absorption of bitumens depends on their hardness, which, when the bitumen is kept in water for a long time, does not exceed 1-3% by weight. Besides, BEM have a lower viscosity in the temperature range from (+5) to 80 °C and a higher degree of adhesion to mineral and metal surfaces. The most important indicator of BEM quality is the rate of decay, according to which WBE are classified as fast-, medium- and slow-disintegrating, EBC-1,2,3, respectively. It is known [2,3] that the rate of BEM decomposition is regulated not only by the use of emulsifiers, but also by the introduction of stabilizers, polymers with different chemical structures and molecular weight distributions (MWDs).

Thus, it is of interest to consider as residual raw materials in the production of BEM residual bitumen of BNN grade 80/120. This, in its turn, will make it possible to approach the issue of elastic-

deformation and adhesive strength increase of composite bituminous materials more effectively [3,4], which can also be provided by the modification of bitumens with the help of polymers [3,4,5,6] by the reduction of the internal stresses in the first place and the increase of BEM relaxation ability to external influences.

2. Methods

The physico-chemical combination of high-molecular compounds (HMCs) with bitumen for BEM production is limited in connection with the low emulsifying ability of bitumen-polymer materials (BPM) [2]. This is due to the fact that the KBM is based on highly oxidized bitumen of BN 70/30 grade with T times in the range of 70-80 °C, corresponding to GOST 6617-76. Thus, the influence of the polymer component on KBM properties is directly proportional to the content of the maltene fraction in bitumen. From this point of view, it is advisable to use the BEM bitumen with a lower T times in production. In this regard, the paper studies the possibilities of bitumen use: BND 90/130, produced in accordance with GOST 22245-90, obtained from HOR mixture of Romashkino and Kama oil [2] and unoxidized BNN 80/120, produced according to TC 0256-097-00151807-97. BEM fillers were represented by such products as quicklime and asbestos, which serve as a filler. Asbestos, in addition to high strength, has a low thermal conductivity (0.35-0.41 W/(m · K), the resistance to high temperatures, a high friction coefficient, for example, steel - 0.8. The indicator that determines the qualitative

characteristics of BEM is the length of asbestos fibers, which serves as the main feature by which asbestos is classified.

In order to determine the difference in the structure of the considered bitumens [2,4], the IR spectroscopy (IRS) method was used. The spectral coefficients are determined in the work for their characterization. The spectra were recorded by film on IR Fourier spectrometer of Perkin-Elmer Ltd. The band of 1460 cm^{-1} is considered as the main (reference) band. It relates to the deformation vibrations of CH_2 groups in open paraffin chains and naphthenes, which are considered a kind of organic matter measure. The spectral coefficients reflecting the relative characteristics of bitumen component composition and structure were determined as the ratio of the optical band characterizing a functional group to the optical density of the reference strip. The condensation of asphaltenes was determined by the ratio of the optical densities $D_{1600}/(D_{820} + D_{880})$, proceeding from the fact that, the more unsubstituted C-H bonds, the less aromatic structures are condensed, and vice versa. The oxidation of asphaltenes was determined by the ratio of the optical densities of D_{1700}/D_{1600} . The condensation of asphaltenes was determined by the ratio of the optical densities $D_{1600}/(D_{820} + D_{880})$, on this basis, the more unsubstituted CH bonds, the less aromatic structures are condensed and vice versa.

Using the data of pulsed NMR of the initial states of oil systems [2,8,9,10], they allow us to put forward the prerequisites for the physicochemical and thermodynamic activity of the oil dispersed system (ODS) with the change in their dispersed composition [2,4,6,12] i.e. in the case of HOR processing, by the activation of maltenes with polymer additives or various fillers. During the description of bitumen analysis results bitumens using the pulsed NMR, the model was used in which the magnetic moments or the spins of individual nuclei constitute the spin system of a given substance in their totality [2]. The spin system has the temperature

generally different from the temperature of its environment (lattice) or the temperature of this substance. This model allows us to consider two processes independent of each other: energy exchange inside the spin system (spin-spin relaxation) and energy exchange between the spin system and the lattice (spin-lattice relaxation). Each of these processes proceeds in time with a certain definite velocity and is characterized by its constant - the spin-spin relaxation time T_2 and the spin-lattice relaxation time T_1 [2]. The reciprocals of these times are the measure of the corresponding relaxation rate, and $T_2 > T_1$ always [2,8,9,10,13]. The structural-dynamic states of HOR under various temperature regimes were studied as an original raw material of the oxidation process. The following measurement modes were used for the analysis of bitumen: the start-up period $T = 500\text{ msec} - 2\text{ s}$, the interval between 900 and 1800 pulses $N = 5 - 1000$, the number of accumulations $n = 3-50$. The analysis time did not exceed 3 min. The measurements of the spin-spin relaxation times T_{2i} were performed using the Carr-Parsell-Meibum-Gill technique [2,8]. In all samples, the polyexponentiality of the envelope spin-echo signals was found, which is mainly divided into three spin-spin relaxation times. In the process of research, bitumen samples were divided into the phases "a", "b" and "c", as was mentioned above, with spin-spin relaxation times T_{2a} , T_{2b} and T_{2c} and the proton population of P_a , P_b and P_c , depending on the mobility of hydrogen protons in them, while the error of the amplitude measurements did not exceed 2%.

3. Results

Physicochemical properties and group hydrocarbon composition of the studied bitumens, determined by the VNIINP technique and by the adsorption method [2,4,6] are presented in Table 1.

Table 1: Characteristics of bitumen road viscous, taken for research

| Indicator Name | GOST 22245-90 BND 90/130 | The sample of BND 90/130 | TC 0256-097-00151807- 97 BNN 80/120 | The sample of BNN 80/120 |
|--|---------------------------------------|-----------------------------|---|-----------------------------|
| Needle penetration depth*0,1 mm -at 250C -at 0 0C | 91-130 28 | 119,6 50,4 | 80-120 | 81,0 40,5 |
| Softening point, 0C | No less than 43 | 43,3 | No less than 43 | 43,0 |
| Extensibility, cm - at 250C - at 0 0C | No less than 65 No less than 4 | 91,7 11,0 | 100,0 | 100,0 20,5 |
| Temperature, 0C - brittleness - flash | No more than - 17 No less than 230 | - 23,2 234 | - No less than 220 | - 12,9 240,0 |
| Cohesion with sand withstands according to control sample | - | №3 | №2 | №3 |
| Group chemical composition, % wt. | | | | |
| Oils | - | 39,46 | - | 36,71 |
| benzene resins | - | 31,96 | - | 37,71 |
| alcohol-benzene resins | - | 13,19 | - | 14,82 |
| asphaltenes | - | 15,39 | - | 10,76 |
| C + A/M | - | 1,53 | - | 1,72 |
| C/A | - | 2,93 | - | 4,88 |

Based on the absorption bands by IRS method, the content of the groups was determined: 720 cm^{-1} - methylene groups (CH_2), 1380 cm^{-1} - methyl groups (CH_3), the branching as the ratio CH_3/CH_2 ,

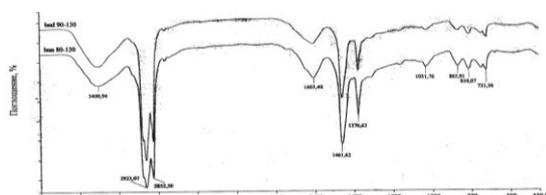


Fig. 1: IRS analysis of BND 90/130 and BNN 80/120 bitumens

the double bonds of the aromatic ring ($C = S_{arom}$), 1030 cm^{-1} sulfoxide groups (SO) and 1700 cm^{-1} - carbonyl groups (CO). The results are shown on Fig. 1-5, Table 2.

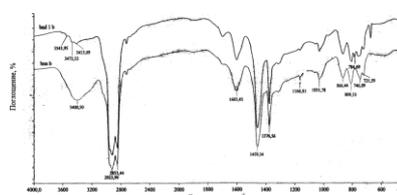


Fig. 2: IRS analysis of benzene resins in BND 90/130 and BNN 80/120 bitumens

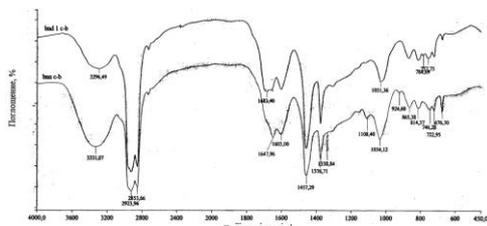


Fig. 3: X-ray analysis of alcohol-benzene resins in BND 90/130 and BNN 80/120 bitumens

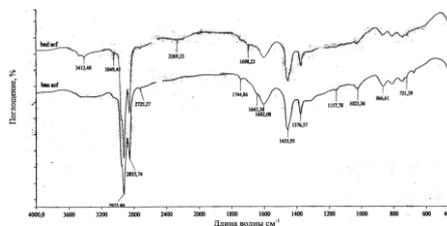


Fig. 4: IRS analysis of asphaltenes in BND 90/130 and BNN 80/120 bitumens

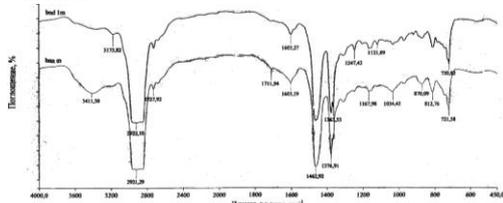
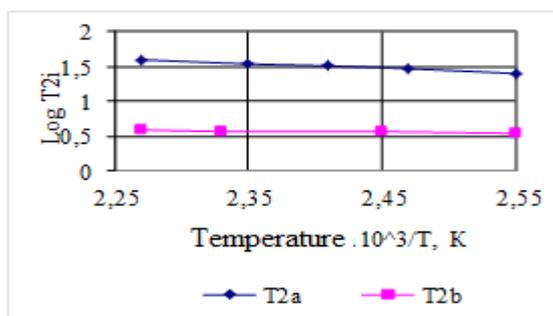
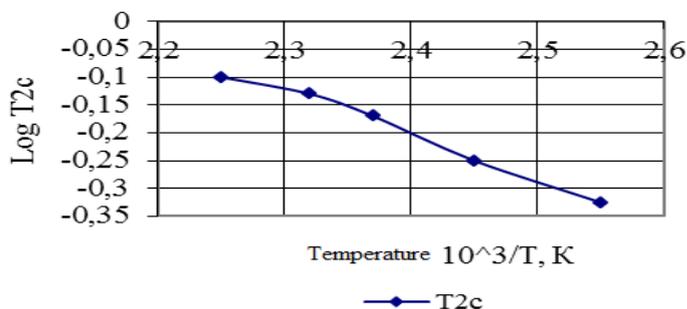


Fig. 5 X-ray analysis of oils in BND 90/130 and BNN 80/120 bitumens

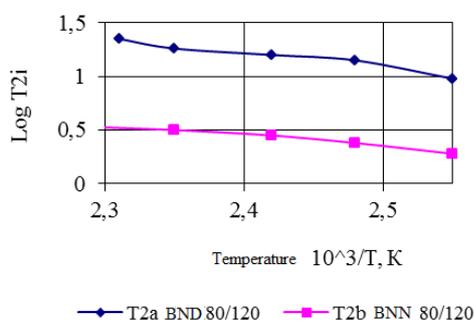


(a)

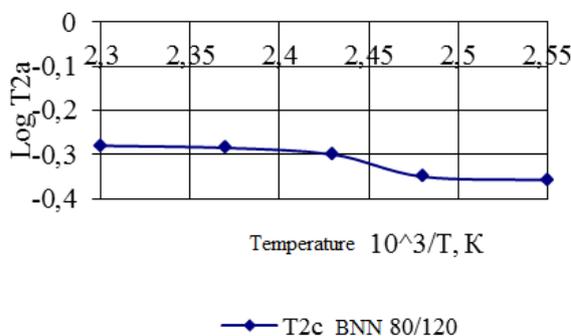


(b)

Figure 6: The dependence thermograms of spin-lattice relaxation times (T2) of the phases a, b (a) and c (b) for the bitumen of BND 90/130 grade



(c)



(e)

Figure 7: The dependence thermograms of spin-lattice relaxation times (T2) of the phases a, b (a) and c (b) for the bitumen of BNN 80/120 grade

The obtained data of the studies of spin-lattice relaxation times (T2) of the phases a, b (a) and c (b) for the bitumen of BND 90/130 grade represent the characteristic cooperative behavior

of the group chemical composition of bitumens: oils, resins and asphaltenes [8].

Table 2: Structural group composition of oil bitumens of BND 90/130 and BNN 80/120 grades

| Bitumen brand | Structural group content ^a , a.u. | | | | | | | |
|------------------------|--|-----------------|--------------------|----------------------------------|-----|-----------------|-----------------|------------------|
| | CH ₂ | CH ₃ | CH+CH ₃ | CH ₂ /CH ₃ | SO | CO ₂ | CO ₃ | Condensate level |
| Bitumens | | | | | | | | |
| BND 90/130 | 0,6 | 2,4 | 3,0 | 4,0 | 0,3 | - | - | 1,4 |
| BNN 80/120 | 0,5 | 2,5 | 3,0 | 5,0 | 0,5 | - | - | 1,0 |
| Oils | | | | | | | | |
| BND 90/130 | 2,9 | 11,6 | 14,5 | 4,0 | 1,5 | 0,4 | - | 0,38 |
| BNN 80/120 | 2,2 | 8,8 | 11,0 | 4,0 | 1,2 | 0,4 | - | 0,55 |
| Benzene resins | | | | | | | | |
| BND 90/130 | 0,6 | 2,6 | 3,2 | 4,3 | 0,7 | 0,3 | - | 0,56 |
| BNN 80/120 | 0,5 | 2,3 | 2,8 | 4,6 | 0,7 | 0,3 | - | 0,75 |
| Alcohol-benzene resins | | | | | | | | |

| | | | | | | | | |
|-------------|-----|-----|-----|-----|-----|---|-----|-----|
| BND 90/130 | 0,4 | 1,9 | 2,3 | 4,8 | 0,8 | - | - | 2,0 |
| BNN 80/120 | 0,3 | 1,6 | 1,8 | 5,3 | 1,0 | - | - | 2,0 |
| Asphaltenes | | | | | | | | |
| BND 90/130 | 0,3 | 1,5 | 1,8 | 5,0 | 0,5 | | 0,3 | 2,0 |
| BNN 80/120 | 0,2 | 1,5 | 1,7 | 7,5 | 0,5 | | 0,2 | 2,0 |

Relative to C=C_{apom} 1600 cm⁻¹

Table 3: Physicochemical properties of rubbers

| Properties | Rubber name | |
|---|-------------|------------------|
| | EPDM | Butadiene rubber |
| Relative elongation at break %, no more than | 400 | 400-450 |
| Weight loss on drying %, no more than | 0,5 | 0,3 |
| Conditional tensile strength MPa (kgf/cm ²) at 100 °C | 18,6 | 21,3 |
| Frost resistance coefficient at -45 °C | 0,8 | 0,75 |

Then they performed the studies in the field of bitumen modification by various copolymers [1,2,3,4,6,7,11], namely synthetic ethylene-propylene triple and butadiene rubber, the physico-chemical properties of which are presented in Table 3.

The results of the conducted studies of BEM samples prepared in various ratios are presented in Table 4.

Table 4: Physical and chemical properties of solvents

| Indicators | Name of solvent | |
|---|------------------------------|-------------------|
| | solvent -1 | solvent -2 |
| Mass fraction of water, % | 0,01 | 0,1 |
| Appearance | Colorless transparent liquid | Dark brown liquid |
| Freezing point, °C, not higher | -45 | -60 |
| Flash point in a closed crucible, not less than | 100 | 90 |
| Kinematic viscosity at 20 °C, sSt, no more | 8,0 | 6,0 |

The analysis of some BEMs with its participation is shown in Table 5.

Table 5: The analysis of some BEM samples

| Operational characteristics | 7 Samples of prepared mastic | | | |
|--|------------------------------|------|------|------|
| | 1 | 2 | 3 | 4 |
| Heat resistance for 5 hours, 0C | 55 | 60 | 64 | 56 |
| Water resistant | Absolute | | | |
| Water absorption for 24 hours, % | 0,03 | 0,02 | 0,03 | 0,04 |
| Flexibility at temperature (-15)-(-20) 0C on a rod with a diameter 25 mm | Withstand | | | |
| The brittleness of the initial BPS, 0C | -25 | | | |
| Softening temperature of the coating composition, 0C | 64 | 68 | 63 | 65 |
| Adhesion (adhesion to the surface of the base used) | 1 | 1 | 1 | 1 |

4. Discussion

It is established [1,2,3,4,6,7,11] that polymer additives allow to lower T_{xp} and increase the heat resistance of bitumens simultaneously. At present, there are many years of observations of various types of Пк with the participation of polymers with different MMPs. A long period of operation is their common trait. Along with these properties, they improve deformation ability in the entire range of operating temperatures, water resistance, and a complex of adhesive strength properties.

Based on presented data (Table 1), it can be concluded that the group chemical composition of bitumen BNN 80/120 is structured. This is confirmed by the fact that the penetration values are much lower and the extensibility values are higher, at that T_{xp} is lower and the flash point (T_{vsp}) is higher than with BND 90/130 analogue. This indicates that the bitumen BNN 80/120 has an elastic-deformation capacity higher than that of the bitumen 90/130. However, it should be taken into account that the presented samples do not meet the specifications by bitumen adhesion index, since BND 90/130 is characterized by a high content of NP-HC (according to ENPU data - more than 4% by weight), and BNN 80/120 is characterized by a high degree of intermolecular interaction (IMI), leading to the decrease of its adhesion. In this regard, it is necessary to study the relationship between the physico-chemical nature of raw materials, the methods of its modification and the properties of oxidation products and BEM samples. Thus, in the spectra of asphaltenes (Fig. 4), 1600 cm⁻¹ band refers to the deformation vibrations of C = C bonds of the aromatic ring and is an analytical feature of the substituted aromatics. Their spectra contain three absorption bands C-H bond valent vibrations in substituted aromatic rings in

different positions: 880-870, 820-810, and 750 cm⁻¹. The last band is covered by a 720 cm⁻¹ band of CH₂-groups, so it was not taken into account. It follows from the data of Table 2 that the content of structural groups in BND 90/130 and BNN 80/120 is different. So BND 90/130 is more condensed, and contains more methylene CH₂ groups than BNN 80/120, which is confirmed by the ratio of CH₂/CH₃ groups. At the same time, oils and benzene resins are more condensed in BNN 80/120 with the same condensation of asphaltenes in both bitumens.

The measured temperature range, at which the studies were performed, was not chosen randomly. In the temperature range of 120-160 °C the main technological operations with bitumens are carried out (Fig. 6,7). It is characteristic that the phase relaxation times in oxidized bitumen are higher than in unoxidized bitumen. With a temperature change in the interval of 120-160 °C, the population of "c" phase protons remains almost unchanged both for BND 90/130 and for BNN 80/120. With temperature increase, the population of phase "c" protons decreases, and the population of phase "a" protons increases.

Table 3 shows that the polymers are similar to each other by properties and have an increased elasticity, flexibility, waterproofing properties and the resistance to weathering. When bitumen is modified with polymeric additives, the main task is an effective homogenization of bitumen with a polymer involving solvents, the promoters of the dissolution process, and physicochemical diffusion of bitumen and polymer dispersions [2]. The heterogeneity of the composition causes the lack of elasticity [4]. Solvents are the components that have acceptable T_{vsp} values, which can ensure the preparation of BPM at the temperatures of 120-140 °C [3]. The developed petrochemical solvents, introduced in stoichiometric ratios, are used as dissolving media for rubbers. The developed compositions of adhesive polymer dispersions for road mastics can be used directly in their composition and independently as the part of oil bitumen as adhesion additives.

5. Conclusions

With the temperature increase from 120 to 160 °C, the mobility of the high-molecular components of the "c" phase increases, which is characterized by the increase of T2C time. Apparently, this is not enough to release asphaltenes from the "cage", "out of setu", i.e. the structure of the asphaltene bitumen part has deformative stability. A higher diffusion factor is observed between the molecules of oils and resins, characterized by the phase "a" and "c". From the data given, it follows that the phase equilibrium of BNN 80/120 bitumen components is more sensitive to temperature changes than that of BND 90/130 bitumen.

6. Summary

In order to increase the service life of the roofing material, it is necessary to proceed with the processes of polymer molecule structuring in the bitumen matrix, since otherwise, when HMC is combined with the bitumen, the processes of oxidative degradation or aging take place in the dynamics.

During the development of scientific and practical approaches to the production of high-quality BEMs conforming to GOST 30693-2000, it is necessary to take into account that after the BEM decomposition on the surface of the substrate into the aqueous and bitumen-containing part, the adjustment of the adhesion-strength and elastic-deformation characteristics by high-molecular compounds becomes an important measure.

By their properties, the developed composite materials, as a rule, exceed the average or total properties of individual components, i.e. a synergistic effect is revealed. The result of the studies is the development of universal BEMs for road and civil construction, including those exceeding the requirements of GOST 30693-2000.

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