Dynamic characteristics of modified bitumen systems

L V Fedorova¹, Z O Tretyakova², M V Voronina²

¹Bauman Moscow State Technical University, 5/1, ul. Baumanskaya 2-ya, Moscow, 105005, Russia.

²Saint-Petersburg Mining University, 2, 21st Line, St Petersburg, 199106, Russia

E-mail: momd@yandex.ru

Abstract. Thiokol-modified bitumens are investigated. Based on the measurements of time-dependent viscosity parameters (melting point, penetration, and spin-spin relaxation time T2), it is established that at a content of thiokol more than 25%, formation of a continuous phase is possible, which shows up as a sudden change in the bitumen properties and is associated with the phase inversion. The method of bitumen modification suggested can be recommended for obtaining roofing materials.

Keywords: bitumen, thiokol, modification, rheology

1. Introduction

Bitumen is produced by distillation of crude oil and is a complex mixture of high molecular weight petroleum hydrocarbons and their hetero derivatives containing oxygen, sulfur, nitrogen and metals [1]. The properties of petroleum bitumen depend mainly on their chemical composition. Oil bitumen due to a valuable set of technical properties are widely used in building materials [2]. Bitumen is a thermoviscoelastic material in which the temperature and speed of application of the load have a great influence on their behavior [3-5].

It is well known that bitumens in the conditions of their storage and operation are subject to aging.

The durability of bituminous materials is limited mainly by their unsatisfactory deformation stability-stiffness and brittleness at low and fluidity at elevated temperatures. The leading direction in the modification of bitumen in order to eliminate these shortcomings is their compatibility with polymers [6, 7].

There is a steady trend of increasing consumption of polymer composite materials used in atmospheric conditions, primarily in construction. The most common among them as sealing, waterproofing and roofing materials that can long-term and effectively resist the effects of aggressive factors such as ultraviolet (UV), ozone, radiation, water, in a wide temperature range from -60 to +100°C, are bitumen compositions based on elastomers [8]. A special place among them is occupied by compositions based on polysulfide oligomers, the main representative of which is liquid thiocol. This is due to their properties—high resistance to climatic influences (ultraviolet, ozone, water), in the case of liquid thiols – unique oil and gas resistance and the ability to provide reliable sealing and operation under the influence of these aggressive factors in conditions of significant alternating deformations in a wide temperature range: from-60 to +100°C [9].
The analysis of modern publications suggests that not enough attention is paid to the problem. Most of the works (from a huge number of publications) devoted to the modification of bitumen polymers, is empirical in nature. The theory of compatibility of polymers with bitumen has not yet been created. Meanwhile, knowledge of the structure of bitumen and polymers in combination with the accumulated empirical data, allows you to get a General idea of the processes occurring during their combination, and explain in accordance with these ideas, the observed changes in the properties of composites [10].

The rheological properties of bitumen essentially depend on their composition and primarily on the content of the main structure-forming components, which include the most high-molecular components, resinous-asphaltene substances, as well as paraffins at temperatures below their crystallization temperature, which can significantly influence on the properties of bitumen [11–15].

Viscosity increases in proportion to the volume of particles of the dispersed phase and the degree of their aggregation. Aggregation of particles leads to an increase in apparent viscosity, since aggregates reduce the effective cross-section of the flow channel and create additional inhibition of the displacement of the fluid layers. Destruction of the structure or deformation of solvate shells causes an anomaly of viscosity [16].

One of the indispensable conditions for improving the properties of bitumen when modified by polymers is their compatibility, estimated by such an indicator as the solubility parameter.

In connection with the above, the modification of bitumen thiocols, characterized by high heat resistance and frost resistance.

2. Methods and materials
We used oil bitumen of trademark BN-70/30 with the following characteristics: softening point 69°C, penetration 13x0.1 mm at 25°C and 8 x 0.1 mm at 0°C, ductility 3 cm at 25°C and 0 cm at 0°C, brittleness temperature -80°C, and flash point 220°C. As a modifier, we used thiokol of trademark II: content of end SH-groups 2,15%, viscosity of 38 Pa·s, and glass transition temperature -59°C. The thiokol-based compounds are resistant to the action of corrosive media, atmospheric action, and ultraviolet (UV) radiation; they are moisture- and gas-impermeable, and ozone and frost resistant.

Thiokol was introduced into bitumen in the form of a sealing paste containing, besides the thiokol, 30 weight parts of P-803 technical carbon. The thiokol was cured in the bitumen medium by two curing agents of oxidizing type, namely by zinc oxide or manganese dioxide in the form of a curing paste (10 wt.% of the sealing paste). The thiokol content in bitumen varied from 5 to 50%. The properties of modified bitumens were estimated after holding the compounds at 23±2°C for one day to one year.

The dynamic viscosity and other rheological characteristics of bitumens and modified compounds were determined on a Polymer RPE-1m.2 rotational viscometer with a measuring cell of «cylinder—cylinder» type at 95°C.

3. Results and discussion
The modification of bitumen by thiocols, characterized by resistance to swelling in various solvents and oils, as well as a sufficiently high frost resistance, is investigated.

However, studies have shown that thiocols alone in bitumen systems do not give the desired result. Therefore, we proposed another method of such modification, namely the introduction of thiocol into bitumen together with a curing paste and a vulcanization accelerator (diphenylguanidine), which allowed to improve the complex properties of bitumen systems. However, as in other cases, the elasticity of bitumen, it is possible to significantly increase the viscosity of bitumen systems [17, 18].

As can be seen from figure 1, the softening temperature of bitumen increases both with increasing thiocol content in the composition and with aging of bitumen-thiocol systems in time (1 day, 20 days, 40 days). The obtained result testifies to the dynamic nature of the process of modification of bitumen thiocols together with curing paste, since the process of vulcanization of thiocols in time in the
medium of bitumen at a temperature of 20±20°C proceeds slowly and does not end, probably, even for 40 days.

Figure 1. Concentration dependences of bitumen softening temperature on thiocol content during its vulcanization during different number of days: I-1 day, II-20 days, III-40 days

Flow curves of the initial bitumen grade bn-70/30 and its modifications by thiocols depending on the exposure time of the systems are presented in figure 2 for the most optimal composition with 40% modifier content. At low values of shear rates (γ) for initial bitumen it is possible to allocate area γ in which the current close to Newtonian is realized, and area of sharp decrease in viscosity at the expense of destruction of coagulation structure of bitumen (non-Newtonian current) [19, 20].

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Figure 2. Flow curves of bitumen-thiocol systems with 40% content of vulcanizing thiocol depending on the time of vulcanization (I-IV) and 40% content of non-vulcanized thiocol (V); bitumen with 4% content of vulcanizing paste (VI).

When modified by thiocol, the character of the bitumen flow in the comparable region \( \gamma \) changes to non-Newtonian, while the values of \( \sigma \) are higher than that of the original bitumen. With increasing exposure time systems increases, and the degree of deviation from the Newtonian flow increases, indicating the destruction of structural formations of bitumen-thiocol systems with increasing \( \gamma \).

The introduction of unvulcanized thiocol (40%) leads to a significant decrease in the content of bitumen, while the nature of the flow is practically unchanged. Similarly, the action of hardening of the paste (4%). Therefore, in pure form, both thiocol and its modifier have a plasticizing effect on bitumen, more precisely, its Malten fraction.

The change in the content of vulcanizing thiocol in bitumen from 5 to 50% (figure 3) leads to both an increase in \( \sigma \) and a greater dependence of \( \gamma \) on \( \gamma \) in the studied range of shear rates. Even at small values of \( \gamma \), the flow of bitumen-thiocol systems is carried out due to the destruction of structural formations in this system. Thus, bitumen-thiocol systems are characterized by significant kinetic instability, and to the greater extent, the higher the content of vulcanizing thiocol and the longer the holding time of these systems.

4. Conclusions

Thus, the data indicate an increase in the hardness of the systems, from which it can be concluded that thiocol vulcanization occurs in the systems and the greater the concentration of thiocol in bitumen.

We also studied the change in the main performance indicators of bitumen-thiocol systems from the concentration of thiocol in them and from the time of their formation. However, it should be borne in mind that in the summer in natural conditions, when the roof surface is heated to 80-900C, the vulcanization time of thiocol in bitumen can be significantly reduced.

As a result of the conducted researches it is established that at modification of bitumen by thiocol, the continuous phase of thiocol sealant defining, eventually, the basic properties of the modified bitumen is formed.
Figure 3. Liquid curves of bitumen modified by different contents of vulcanizing thiocol after 30 days of vulcanization at a temperature of 200°C.
I-initial bitumen, II-bitumen+5% thiocol, III-bitumen+15% thiocol, IV-bitumen+25% thiocol, V-bitumen+40 thiocol, VI-bitumen+50% thiocol

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