Effect of the Viscogel Additive on the Rheological Parameters of Bitumen

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Abstract. Bitumen is a complex multicomponent colloidal dispersed system based on the interaction of asphaltenes (phase) and maltenes (medium). In the absence of external influence, this system is in a relatively stable state. Any external action shifts the equilibrium state of the colloid and initiates phase aggregation with a general transition of the binder from the state of gel or sol-gel to sol, with a qualitative change in properties. Thus, a quantitative change of the colloid phase entails a qualitative change in its state. Rheological additives are some of the promising ways to control the structure formation and characteristics of bitumen. This paper considers road bitumen modified by Viscogel additive in a concentration range of 1–5%. The influence of the additive on the rheological characteristics of bitumen was determined. The optimal amount of additive which positively affects the properties of bitumen was established. This was confirmed by the determined contact angles for bitumen samples with different concentrations of additives subjected to the aging process. Test data indicated system stability over 48 h of exposure to high temperatures. A model of interaction of a rheological additive within the asphaltenes-maltenes system is proposed based on the available data on the structure and dispersion of bitumen.

Keywords: Rheology · Bitumen · Viscosity · Aging

1 Introduction

Bitumen is a complex colloidal system comprised of paraffinic and naphthenic hydrocarbons, cyclic systems, and aromatic hydrocarbons connected by aliphatic chains. In this colloid, the maltenic medium acts as a dispersant for asphaltenes, which are contained in bitumen as a dispersed phase in the form of micelles [1]. The uniqueness of the bitumen structure determines its features, including an imbalance in the colloidal stability of the system under the influence of external factors. The most aggressive of them are high temperatures and pressure. They give rise to the process of aggregation of asphaltene complexes and contribute to a change in the properties of bituminous binder and its aging during the technological cycle of the binder existence and the entire life cycle of the composite based on it.

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From the point of view of colloidal chemistry, aging process of bituminous binder manifests itself unevenly, by changing its dispersed structure, rheological, and physical characteristics.

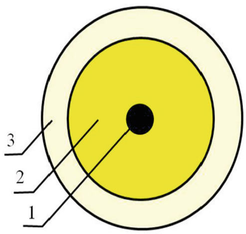
Asphaltenes are the most condensed polar centers of this system, which accumulate the maltenic part around the nuclei. Maltenes consist of oils and resins, the main difference of which is the ratio of hydrogen and carbon [2]. Thus, the maltenic part of bitumen is a kind of buffer that protects polar asphalt-resinous components (ARC) from premature aggregation. As a rule, asphaltenes are high-molecular, condensed hetero-organic compounds, consisting of carbon (80–84%), hydrogen (7.5–8.3%), sulfur (4.6–8.3%), oxygen (up to 6%), and nitrogen (0.4–1%). Resins are hydrocarbons composed of aromatic, naphthenic, and heterocyclic rings connected by short aliphatic bridges. Oils are composed of carbon (79–87%), hydrogen (8.5–9.5%), oxygen (1–10%), sulfur (up to 2%). Oils are paraffinic, paraffinic-naphthenic, and aromatic hydrocarbons, consisting of several polycyclic groups [3, 4].

Nowadays the following theories of bitumen structure are considered [5–8]:

- Bitumen as an oil dispersed system (ODS) [9]
- Bitumen as a colloidal system with a dispersed phase (asphaltenes) and a dispersed medium (maltenes) [10].

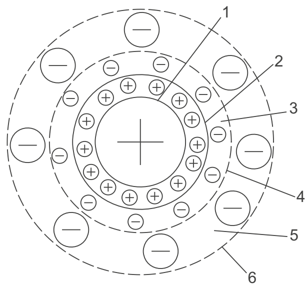
Within the framework of ODS [9, 11], conglomerates of asphaltenes and maltenes are usually called a complex structural unit (CSU), consisting of a core and a solvate shell (Fig. 1).

Within the framework of the colloidal theory [10, 12, 13], bitumen particles are called a micelle, which consists of a core, a layer of counterions, a colloidal particle and a diffuse layer (Fig. 2).



1-Core, 2-Solvate shell, 3- Intermediate layer;

Fig. 1. A complex structural unit [9]



1-Aggregate, 2-Core, 3- Layer of counterions,
4-Colloidal particle, 5- Diffuse layer, 6-Micelle

Fig. 2. Micelle structure [12]

By analysing the particle structure, and the nature of resins and asphaltenes [5–14], we state the following:

- Asphaltenes act as the aggregate core possessing the system charge.
- Resins, adsorbed on the surface of asphaltenes, form a layer of counterions and enter the diffuse layer of the system environment.
- Oils are a dispersed medium in which interactions between particles take place.

Based on these models, Unger [14] proposed a description of the molecules' interaction in a dispersed system according to the principle of charge and spin (Fig. 3).

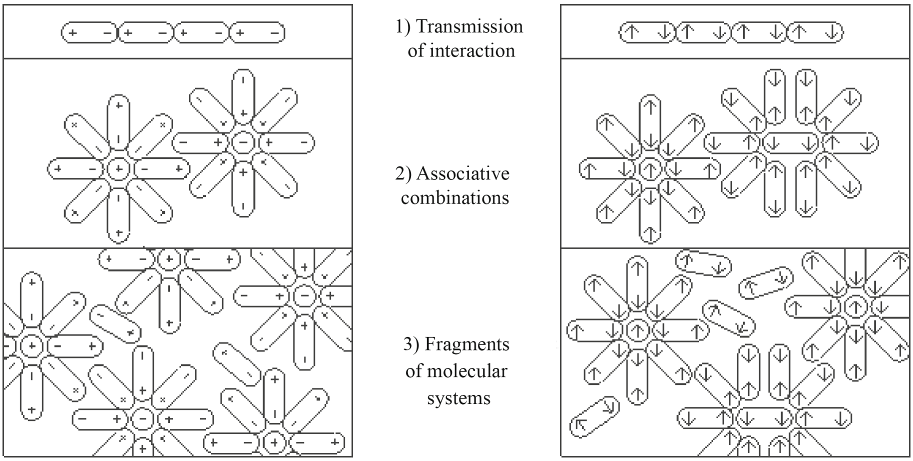


Fig. 3. Charge and spin models of molecular systems interactions [14]

According to the theory [14], the systems of charge principle can transfer charge over a long distance, and an associative combination model can be built based on the excess or missing charge. The uniform distribution of micelles in the system can be explained by the presence of a similar charge at the outer ends of molecules, as shown in Fig. 2. Based on the magnetic properties, the system comes to equilibrium.

In the absence of external influence, the spin model of interaction works according to the same principle as the charge one: a molecule is capable of transmitting an exchange effect, thus spreading it to the entire system. The concentration of the exchange action in a large volume leads to a multiplicity of spin-polarized layers, just as charge polarization leads to multiple electric layers. Since the tails of spin-polarized molecules are parallel, mutual repulsion occurs, which makes the system rather strong and stable [14].

Thus, it can be assumed that the charge interaction affects all processes occurring in the ODS, however, the influence of high temperatures or pressure affects the magnetic properties of the system, provoking a shift in equilibrium with a change in the properties of the system. Depending on the intensity of external factors, one can observe an increase in magnetic particles as a result of their agglomeration (an increase in the number and size of asphaltene aggregates) [15].

The most detrimental effect on the dispersed system of bitumen is exerted by the aging process, which occurs during both the mixture preparation and the road surface operation [16]. In the process of mixture preparation at the asphalt-concrete mixing plant, bitumen is distributed on the surface of the stone material in a thin film, which increases the negative effect of temperature and pressure, and leads to irreversible changes in the dispersed structure of bitumen by depleting the maltenic part of bitumen. As a result, the binder in the mixture has unpredictable properties [17].

To improve the rheological characteristics, the bitumen structure can be treated by magnetic field [18], sonication [19], or the introduction of rheological additives [5, 20–22].

The influence of magnetic field on the dispersed system of bitumen contributes to an increase in saturated and aromatic compounds and a decrease in the content of resins and asphaltenes. However, the system, which is under the influence of only a magnetic field, eventually partially or completely restores its original properties [18, 23].

Ultrasonic treatment of bitumen affects the temperature of the crystallization start, slowing down the phase transitions of the maltenic part into asphaltenes [19, 24, 25]. However, these changes cannot maintain their stability for a long time, and the relaxation process of the system is 2–7 days [19].

In this regard, the introduction of additives is the most rational way to regulate the rheological parameters of bitumen. A small amount of additive can improve the performance characteristics (softening temperature, brittleness, plasticity) of both bitumen and asphalt concrete mixture [26, 27].

At present, organoclay-based additives are used in various fields of technology [28–31], for example to increase the durability of paints. Concrete with organoclay has increased strength. However, the influence of organoclays on bitumen is practically not studied, which makes rheological additives a promising object of research.

This work aims at studying the influence of the rheological additive Viscogel on the rheological, physical and structural characteristics of bitumen.

2 Materials and Methods

The rheological additive Viscogel is a finely dispersed white powder. Its general chemical analysis showed a significant presence of carbon and oxygen, and a smaller amount of various impurities (Table 1). It also contains a small amount of Na, P, S, Cl, K, Ca.

Table1. Chemical content of the modifying additive

Chemical element	C	O	Al	Mg	Si	Fe
Mass,%	33.3	34.52	7.59	1.36	20.13	1.50

The powder structure was studied using the scanning electron microscope. It showed that the additive consists of microdispersed grains with an average size of 20–40 microns (Fig. 4).

The additive influence on the bitumen structure was studied by assessing the dynamic viscosity, which was chosen as the fundamental rheological factor. If the additive has some influence on the dispersed structure of bitumen, this will primarily affect the change

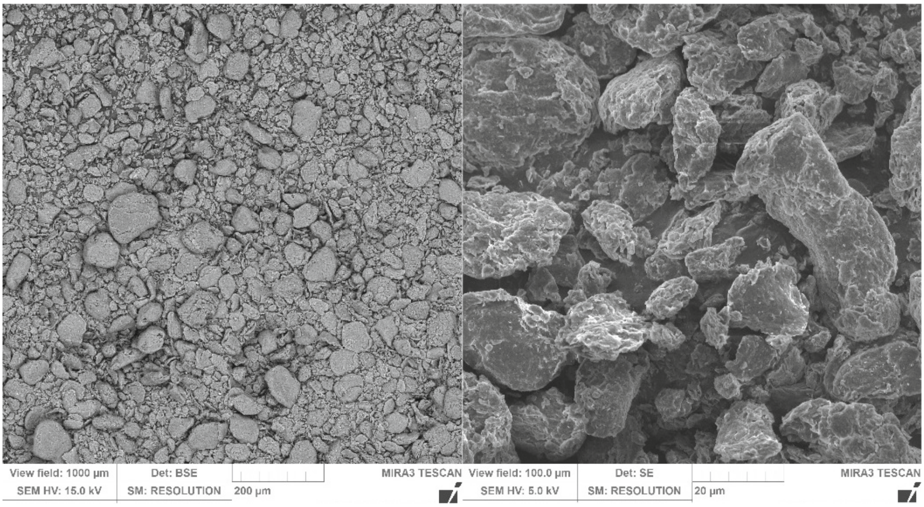


Fig. 4. Microphotographs of the viscogel additive

in the sample viscosity [32, 33]. The BND 50/70 road bitumen from the Moscow Oil Refinery was studied (Table 2).

Table 2. Main characteristics of bitumen

Depth of needle penetration, mm		Softening temperature, °C
0 °C	25 °C	53
25	55	

An additive in the amount of 1–5% was introduced into the prepared samples of bitumen. Further, the material was mixed using the laboratory mixer Silverson L5T for 30–40 min. Immediately after mixing, the samples were placed in cuvettes for further testing using the viscometer.

The dynamic viscosity was measured using the Brookfield DV2T rotational viscometer. The test temperature was varied from 120 to 200 °C with a step of 20 °C. The spindle rotation speed was selected individually for each test temperature, based on the testing instructions "Broorfield DV2T. Operating Instructions. Manual No. M13–167".

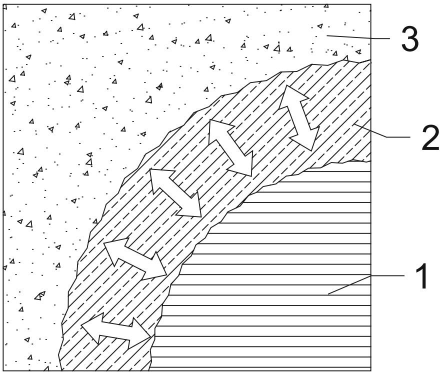
Also, the contact angle was determined. It is an important characteristic of the adhesion properties of bitumen and stone material, which is important for the major bitumen purpose, which consists in gluing the framework of the mixture [34, 35].

For this, the bitumen samples were modified with an additive in the amount of 0.5%, 1%, 2.5% of the bitumen mass and mixed according to the same principle as when determining the viscosity. The samples obtained were subjected to the aging process in a drying oven for 24 and 48 h at a temperature of 165 °C, having a bitumen contact with the air. The droplet was deposited on a prepared glass at a bitumen temperature of

120 °C. At this temperature the samples have the largest discrepancies in the viscosity and, as a consequence, their rheological properties are more pronounced.

3 Results and Discussion

Taking into account the colloidal structure of bitumen and the nature of the interaction of its components, it can be assumed that the additive particles, interacting with the maltenic medium, swell and are attracted to the most polar bitumen particles - asphaltenes, create a stable halo that prevents further interactions. Thus, it can be assumed that the separation of the phase (asphaltenes) and the maltenic medium occurs (Fig. 5).



1-Asphaltene phase, 2-Halo of additive in maltenic medium, 3-Maltenic medium

Fig. 5. Scheme of interaction of the additive in the dispersed structure of bitumen

It can be assumed that such an interaction will prevent the aggregation of asphaltene conglomerates and phase transitions of maltenes into asphaltenes, keeping the system stable over time under the influence of external factors, making such a system less prone to aging processes.

The measured dynamic viscosity (Fig. 6) shows that an increase in viscosity is observed in samples with an additive concentration of 2–5%.

For the sample with an additive content of 1%, the viscosity curve was lower than that for the original bitumen sample throughout the entire test cycle in the temperature range of 120–200 °C. These results confirm the assumptions on the influence of Viscogel on the rheological properties of bitumen. It can be assumed that the decrease in the colloid viscosity is associated with the effect of the additive on the structural bonds within the system. In addition, the obtained viscosity allows us to assume that in the future, bitumen modified with 1% Viscogel will have more stable rheological properties.

The determined contact angles of the bitumen samples confirm the viscosity data on the stability of the rheological properties of the sample modified with 1% Viscogel (Table 3).

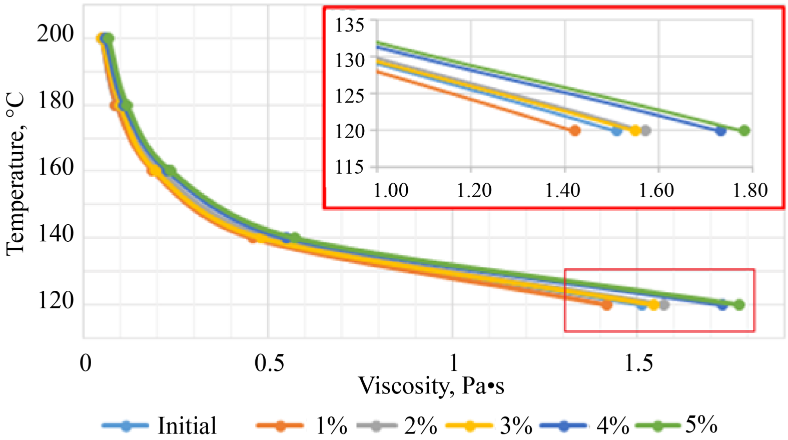


Fig. 6. Viscosity of bitumen modified by the additive

Table 3. Contact angle of the modified bitumen samples

Aging time, hours	Modifier concentration, %			
	0	0,5	1.0	2,5
0	95.52	101.89	94.00	96.52
24	103.37	102.25	94.24	101.23
48	115.77	108.78	96.61	110.31

The presented data show that the sample with 1% of the modifier, there was practically no change in the contact angle after 24 h of testing. After 48 h the increase in the indicator is much less than in all other cases.

According to studies [36], the contact angle may indicate the quality of the bituminous binder used in the asphalt concrete mixture (Fig. 7).

Wetting describes the behavior of a liquid upon contact with a solid surface when the system behavior is determined by the surface tension. In our case, this liquid is the bituminous colloid. It can be assumed that if a 1% rheological additive is introduced into bitumen, stable cohesive bonds are formed, which can keep the drop stable under the influence of high temperatures over time.

Obviously, due to an increase in cohesion inside the original bitumen and binders modified with a non-optimal additive content, the surface wetting deteriorates and the system rigidity increases due to an imbalance in the colloidal system manifested in the depletion of the maltenic medium. In this case the main characteristic of the state is the mechanical coupling of the phases involved, caused by the strengthening of the molecular interaction in the boundary layer. According to the theory of adsorption and wetting, the binder modified with the 1% additive maintains thermodynamic equilibrium during the entire process of thermostating. If the boundary layer of the bituminous colloid is thermodynamically unstable, the drop changes.

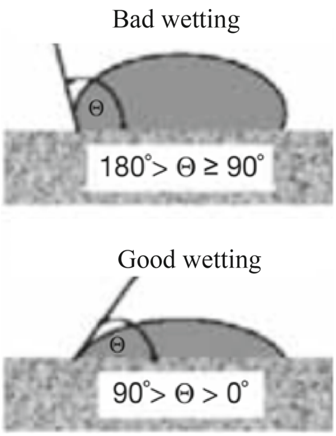


Fig. 7. Contact angle of a bituminous drop [34]

Further we introduce the Δ coefficient, denoting the ratio of the characteristics of bitumen samples before and after aging, and obtain the following data (Fig. 8).

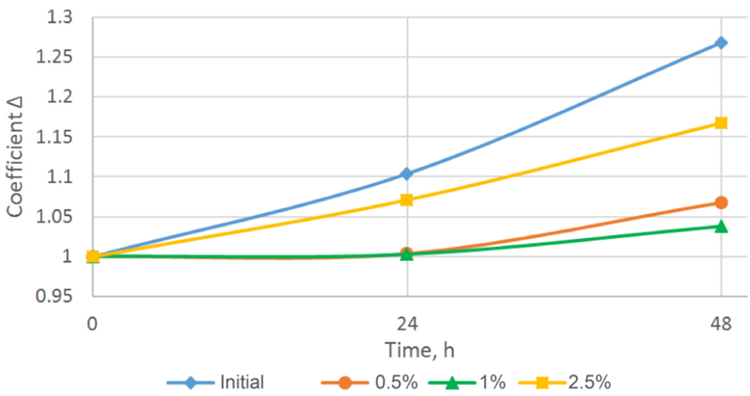


Fig. 8. Dynamics of change in the bitumen viscosity during aging

The graph shows that the sample modified with 1% rheological additive has the smallest deviation from the initial bitumen parameters.

4 Conclusions

A scheme for the interaction of a rheological additive with a dispersed colloidal structure of bitumen is proposed.

Viscosity and contact angle of wetting were determined. The rational content of the additive was established, which makes it possible to control the rheological and technological parameters of bitumen. It can be concluded that the introduction of the

1% Viscogel additive has the best effect on the bitumen performance, reducing the viscosity, but at the same time maintaining the cohesive properties of the bitumen.

The efficiency of the Viscogel additive as a tool maintaining the colloidal system stability during thermostating was proven. This modifier enables to protect bitumen from the harmful effects of aging processes while maintaining the stable properties of the asphaltenes-maltenes system.

The results of the study indicate the need for further investigation of the effect of the rheological additive not only on bitumen but also on the properties of the asphalt concrete mixture.

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