Aging of bitumen on the surface of crushed granite at high temperatures

M G Salikhov, E V Veyukov, R Y Kalugin and A O Yendeletov
Volga region state University of technology, 17, Panfilova Str., Yoshkar-Ola, 424000, Russia
E-mail: VeukovEV@mail.ru

Abstract. When exposed to high temperatures, bituminous materials including mixtures of crushed stone and bitumen (black gravel) quickly change their physical and mechanical properties. In the process of heating up, the structure and composition of the bitumen binding agent go through complex transformations due to the processes of polymerization, polymerization of carbons, evaporation of volatile components, etc. These processes depend on the thickness of bitumen films on the surfaces of mineral particles, depending on the type and size of mineral particles, exposure to air, magnitude and intensity of the process, high temperatures and other factors. Since bitumino mineral mixtures contain mineral particles that can vary in size hundreds of times, films of different thickness and directivity are formed on their surfaces in the process of mixing with bitumen. This raises the need for a differential study of their behavior at high temperatures and changes in their adhesive properties in particular. At this, due to the lack of a standard methodology for analysis of these processes, a special estimating experimental method has been developed (see the Patent of the Russian Federation for the invention No. 2654954 [22]). The aging of the bitumen binding agent on the surfaces of mineral materials was analysed using a dimensionless aging factor for local indicators of physical and mechanical properties. According to the research based on this method, the most sensitive indicator is the compressive strength limit at 50 degrees Celsius for standard cylindrical samples, formed from bituminous mixtures pre-heated at high temperatures. The aging of crushed granite mixtures of fr. 5...10 mm with petroleum road bitumen 90/130 was calculated at various ratios – 1:25; 1:30; 1:35; 1:40, pre-aged at + 150 °C. The aging dynamics was assessed by the values of aging intensity according to the aging coefficient. Due to the experiments, the optimum ratio of bitumen and mineral part (crushed granite) with the best resistance to aging at high temperatures and the dynamics of changing the aging intensity at different time intervals was determined. The results also include mathematical models describing the aging of mixtures under study, analysis of the experimental results and conclusions.

Key words: crushed granite, petroleum road bitumen, bitumen film, heating, high temperature, aging coefficient and intensity, compressive strength limit, mathematical model.

1. Introduction
It is known that at the stage of composing asphalt concretes and other bituminous materials, large fillers are subject to strict requirements: they must ensure good compatibility with a binding agent and meet the required values for strength, durability, frost resistance and other indicators. Crushed acidic rock (granite) with negative surfaces of its grains is often used for that purpose.
As road bitumens are considered acidic environments, the interaction of their surfaces is mostly physical due to the Van der Waals forces [1–4]. As a result, in the process of making bituminous mixtures, surfaces of crushed granite get covered with poorly oriented bitumen films with a low degree of stratification by the group composition [2, 4].

It is also known that the specific surface of crushed stone fillers in the asphalt concretes of the optimal structure is 2.8...3.0 m$^2$/kg, for mineral powder – 300...500 m$^2$/kg [2]. As a result, the share of oriented bitumen on the crushed stone surfaces is relatively small. Since crushed stone is the main framework (skeleton) of bituminous mixtures, combining it into a single whole with an adhesive substance – bitumen – is of great importance for ensuring the carrying capacity of this material in general.

Ensuring that the crushed stone frame, consisting of separate stone pieces, is functioning well altogether under the influence of external forces in a constructive layer of road clothing is one of the key requirements for successful functioning of bituminous materials. Thus, resistance to mechanical stresses arising in the body of bituminomineral materials is provided by the mechanical strength of grains of stone materials (crushed stone), the cohesion strength of bitumen films and adhesive strength (adhesion) of the binding agent to the crushed stone surfaces.

The required values of the above indicators are to be provided starting from the stage of composing them. However, it is known that due to natural processes and under the influence of water, high changing positive and negative temperatures, solar radiation, dynamic and cyclical loads when being used individually or jointly during the operation, the properties of all components change as well, usually for the worst.

This process is especially evident in organic components. The result is a change in operational properties of structural layers of road surfaces, such as cracks, potholes, etc. These processes often cause deep irreversible structural changes in materials resulting in weakening of intergranular bonds of stones, less deformability, less corrosion resistance, crack resistance, wear resistance, frost resistance of the coating material, etc. Such processes are called aging.

2. Setting the problem and research objective

The speed and intensity of aging of bituminomineral materials over time seems to depend on the thickness and structure of bitumen films, size and type of grains of mineral materials, the ratio of bitumen and filling agent, etc. [2]. It is evident that aging of bitumen also depends on exposing to oxygen of contact areas, contamination and electrochemical state of mineral material surfaces and the magnitude of current temperatures.

With these considerations in mind, one should expect that the aggressive environment affects the structure of dispersed mineral materials formed on the surfaces of bitumen films (particles of mineral powder, sand and crushed stone) in different ways. There is little information in the literature on the study of this problem [1, 2, 4–16]. While it is of high practical importance and theoretical interest.

The objective of this research study is justification of the optimal ratio of bitumen and crushed stone in bituminomineral mixtures, in terms of the highest resistance to their aging at high temperatures. For experiments, a mixture of crushed granite M 1200 fr. 5...10 mm and petroleum road bitumen 90/130 in the ratios of 1:25, 1:30, 1:35 and 1:40 were used, pre-warmed up at 150 degrees Celsius for 0, 1, 3, 5 and 7 hours.

3. Justification of selected methods of the experimental research.

To date, the aging of bitumen is studied according to the PNST-2012 (Preliminary National Standard) [18] and GOST 33140 (State Standard) [19] methods, which assess the aging of bitumen in terms of changing the mass loss of the bitumen sample under study after heating it at the temperature of +163 °C. The drawback of this method is neglecting the influence of the lining surface on aging. Moreover, the structure and thickness of bitumen films are different from their values on the surface of stone materials.

There is also a method [1], that studies changes in the properties of bitumen extracted from their bituminous mixture after heating it with solvents. This method is complex and does not take into
account possible changes in properties during the dissolution and extraction of bitumen from the bituminous mixture. As for the study of the aging of bituminous mixtures in general, there are no standard methods so far.

In this regard, a few methods were proposed based on the study of changes in the physical and mechanical and rheological properties of the samples of bituminous mixtures after the exposure to ultrasound, successive exposure to the elevated temperature, freezing-thawing, etc. [12, 18–20].

The above methods are generally complex and require special expensive equipment or long-term and not fully simulating the aging processes of bitumen films within bituminous mixtures. Considering the above mentioned shortcomings of the methods available at the Department of Building Technologies and Roads of the Volga region state University of technology has developed and proposed a new method [22]. It allows studying the aging processes of both multi-component bituminous mixtures, as well as two-component ones – of bitumen and powder, bitumen and sand, bitumen and crushed stone, etc. At this, testing does not take long and requires standard equipment available in construction laboratories, while aging is assessed using a dimensionless, independent of the scale parameter – the aging intensity factor.

The proposed method is as follows:

- Selecting samples of crushed stone, drying them to the constant weight at 150...160 °C.
- Making samples of bitumen by dewatering and heating up to the operating temperature.
- Making mixtures of crushed stone and bitumen (CS:B) in various ratios by thorough mixing.
- Placing the resulting mixtures evenly on separate metal trays and then into a preheated to the estimated temperature (in this case + 150 degrees Celsius) ventilated oven. Then, heating them up during the planned period of time (0, 1, 3, 5, 7, etc. hours).
- After the time expires, taking trays with mixtures out of the oven and molding standard cylindrical samples (of 71.4 mm diameter and height) from the heated mixtures at pressure of 40 MPa for 3 minutes. After 1 day of exposure to air at room temperature, the samples are tested according to standard GOST 12801-98 [17] methods in order to determine values of their physical and mechanical properties.
- According to experimental results, calculating the aging factor values based on the determined value of the physical and mechanical parameter $K_{Ag}^{Ind}$ and aging intensity $I_{Ag}^{Ind}$.
- Determining mathematical models and evaluating aging processes according to parameters $K_{Ag}^{Ind}$ and $I_{Ag}^{Ind}$.
- Developing proposals for determining the optimal ratio of bitumen and crushed stone (B:CS) in terms of the highest resistance to aging at high temperatures and selecting measures for reducing them.

4. Results of the experiments and their analysis

This research study used samples of crushed granite M 1200 fr. 5... 10 mm and viscous petroleum road bitumen 90/130 in the bitumen to crushed stone (B:CS) ratios of 1:25, 1:30, 1:35 and 1:40, which were carefully mixed at 140... 160 °C, then placed on separate trays and heated at the temperature of 150 °C for 0, 1, 3, 5 and 7 hours.

After expiration of the estimated period of time, standard cylindrical samples were made of them and then tested. In particular, the compressive strength limit at 50 °C was determined. Some of the results of these experiments are presented in Table 1.

Mathematical models with a high degree of approximation obtained in CurveExpert [23] are as follows:

a) for $K_{Ag}^{R50°C.ReadString}$:

$$K_{Ag}^{R50°C.ReadString} = 9,8999 \cdot 10^{-002e^{-1.008e^warm}}$$

$S = 0,0639$ (standard error); $r = 0,9909$ (correlation coefficient);
According to the table data analysis, maximum values of medium density and tensile strength of bituminous mixtures are at the ratio of bitumen and crushed stone (B:CS) of 1:25 (see lines 4 and 5).

Further analysis of experimental findings indicates that mixtures of bitumen and crushed stone of all ratios are aged within first 3–5 hours of heating. It means that such mixtures reach their limit in
terms of aging, and structural layers of road clothing in this state should be expected to have the least resistance to destruction at external influences. It is evident that polymerization processes in bitumen films end in 3...5 hours.

To explain the experimental data pattern, let's have a look at conditions for formation of bitumen films on surfaces of crushed stone grains. At the bitumen:crushed stone ratios of 1:25, 1:30, 1:35, 1:40, the actual content of bitumen in bituminous mixtures is 3.99; 3.34; 2.86 and 2.50 % respectively. According to I.V. Korolev [2], the specific surface of crushed granite fr. 5...10 mm is 0.71 m$^2$/kg.

At the bitumen:crushed stone ratios of 1:25, 1:30, 1:35 and 1:40, the proportion of blackened surfaces at the average thickness of the bitumen film of $6.4 \cdot 10^{-4}$ cm is 88.5; 73.7; 63.2; and 63.0 % respectively. This implies that the highest adherence of bitumen films is in the mixtures with the most blackened surface of crushed stone grains: the mixture of bitumen and crushed stone with the ratio of 1:25, that was confirmed by the tests results as well.

Analyzing the samples aging dynamics during the heating, we can see that samples with a high bitumen content have higher speed and intensity of aging (columns 6 and 7 of Table 1). The maximum aging values in all samples are during the first hour of heating, then this process is reduced.

Therefore, in order to reduce the aging process in early periods of life of bituminous mixtures, we should search for technological and other methods. According to studies by Bahrah G.S.[ 6], Korolev I.V. [2], Gezentswy L.B. [1], Uglovaaya E.V. [9], Skripkin A.R., Starkov G.B., Kolesnik D.A. [12], Bratchun V.I. and Stukalov A.A. [8], Saenko S. S. [11], American, Chinese and Japanese scientists [15, 16], scientists from Belgorod State University of Technology [24] and others [20], to achieve this, mixtures should be made at the lowest technological temperature, in the environment of inert gases, with adding of special anti-aging and surface active agents, using binding agents of polymer and bitumen, rubber and bitumen, sulfur and bitumen, etc.

5. Conclusions
1. Experimental findings let us conclude that bituminous mixtures with the 1:25 ratio of bitumen and crushed stone have the highest resistance to the aging of bitumen at high temperatures. This corresponds to bitumen content in the mixture of about 4.0% of the crushed stone mass.
2. At high temperatures (150 °C), bitumen in the mixtures of bitumen and crushed stone ages intensely during the first hour of heating, then this process stabilizes.
3. Resistance of samples of the bitumen and crushed stone mixtures compressed at 50°C is sharply reduced due to aging. In order to ensure the resistance of structures using mixtures of bitumen and crushed stone, methods for regulating this process at all stages of their life cycle should be developed.

References
[1] Gezentsway L B, Gorelyshev N V, Boguslavsky A M and Korolev I V 1985 Road asphalt concrete (Moscow: Transport)
[2] Korolev I V 1986 Ways of saving bitumen in road construction (Moscow: Transport)
[3] Kuchma M I 1980 Surfactants in road construction (Moscow: Transport)
[4] Kovalev Y N 1990 Activation-technological mechanics of road asphalt concrete (Moscow: Transport)
[5] Rybiev I A 1969 Asphalt concretes (Moscow: Vysshaya shkola)
[6] Bahrah G S 1973 Considering the aging process at planning the composition of bituminous mixtures Avtomobilnye dorogi 9 8–9
[7] Gohman L M and Amosova N V 1988 Study of the effect of bitumen quality on the processes of its aging in thin films Oil chemistry and refining 2 6–8
[8] Bratchun V I, Gulyak D V and Bespalov V L 2008 On certain patterns of the aging of concrete mixtures and concretes on organic binders using tar concrets as an example Vestnik Kharkovskogo Natsionalnogo Avtomobilnogo dorozhnogo univer. (Kharkiv: HADI)
[9] Iliopolov S K, Mardirosova B V and Uglova E V 1994 Development of bitumen aging processes in asphalt concrete pavements of motor roads Izvestia vuzov. Series: Construction 3 48–52
[10] Uglova E V 1993 Increasing the resistance to the aging of bitumen in asphalt concrete pavements in the South of Russia environment Master of technical sciences’ thesis

[11] Saenko S S 2008 Methods for minimizing the aging of bitumen in a working boiler when making hot asphalt mixtures PhD dissertation thesis

[12] Skripkin A D, Starkov G B and Kolesnik D A 2010 Aging of bitumen in the technological process of its preparation for production of asphalt mixtures Collection of articles and reports of the annual scientific session of the Associat. of researchers of asphalt concrete (Moscow: MADI) pp 46–53

[13] Stukalov A A 2015 Aging of asphalt concrete mixtures and ways to increase their thermal oxidation stability PhD dissertation

[14] Salikhov M G, Ilivanov V Yu, Malyanova L I and Veyukov E V 2018 Studying the temperature aging of modified crushed stone and mastic asphalt concrete with limestone crushing waste Transport facilities. Ecology 1 70–4 (Perm: PNIIPU)

[15] Siddiqui M M 2002 Use of X-ray diffraction in assessing the aging pattern of asphalt fractions Fuel 1 51–8

[16] Zhao Zhaohui A 2003 Study on aging kinetics of asphalt based on softening point Petroleum Sci. and Technol. 10 1575–82

[17] GOST 12801-98 1999 Materials based on organic binders for road and airfield construction Experimental methods Enforced by Resolution of the Gosstroy of Russia

[18] PNST 8-2012 (Preliminary national standard) 2014 Public roads. Viscous petroleum bitumen. Method for determining bitumen resistance to aging under the influence of high temperature and air (Moscow: Standartinform)

[19] GOST 33140-2014 2015 Public motor roads. Viscous petroleum road bitumens. The method of determining bitumen resistance to aging under the influence of high temperature and air (RTFOT method)

[20] Kalgin Y I, Strokin A S and Tyukov E B 2014 Promising technologies for the construction and repair of road surfaces (Voronezh: Voronezh state univer. of architect. and construct.)

[21] Tarashchansky E G and Wilmsen I I 1975 Study of the asphalt concrete aging using impulse ultrasonic method Improving the efficiency of cement and asphalt concrete in Siberia (Omsk: SibADI) pp 40–61

[22] Salikhov M G, Veyukov E V and Sabirov L R and Malyanova L I 2018 Method for determining the speed and intensity of aging of asphalt concretes Patent of the Russian Federation for the invention no. 2654954

[23] Mazurkin P M add Filonov A S 2006 Mathematical Modeling. Identification of one-factor statistical patterns (Yoshkar-Ola: MarGTU)

[24] ODM 218.3.021-2011 2012 Methodical recommendations on the selection of asphalt concrete mixtures, taking into account the effect of adhesive additives on the aging of organic binder components in bituminous mixtures Federal Road Agency (Moscow: Rosavtodor)

[25] ODM 218.3.020-2012 Methodical guidelines for ensuring the bitumen sustainability against aging in the technological processes of manufacture and application of asphalt concrete mixtures (Moscow: Rosavtodor)

[26] Anasuke M 1971 Method for preventing embrittlement and destruction of asphalt concrete coatings The patent of Japan no. 51-41766