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Effect of Mechanically Activated Additives on the Thermal Decomposition of Bitumen*

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Abstract

The thermal decomposition of the samples of bitumen of the winter storage (heating with water vapour), that was worked out to remove water according to the regulations and with the excess of the regulated treatment temperature and time has been studied by the method of the thermogravimetric analysis. The effect of the mechanically activated mineral additive and additive imitating pyrobitumen on thermolysis was considered. Calculated activation energies of the thermal decomposition of bitumen samples are reported.

Key words: mechanochemical activation of additives, thermolysis of bitumen

INTRODUCTION

The most widespread kind of road paving in the world is asphalt concrete and its numerous varieties. The total length of motor roads in the world is 70 million km, among them 6.5 million km in the USA and 1.0 million km in RF. Bitumen acts as an organic binder for the mineral component (mechanical basis), filler (sand) and inorganic binder (cement). A complicated heterogeneous system manufactured from these components possesses a number of outstanding characteristics including a good thermal stability and weather resistance.

Bitumen is complex organic systems originating from petroleum of oil origin. A high stability of bitumen to external actions is defined by their internal structure. The preparation of bitumen to work includes several stages: obtaining bitumen from petroleum at petroleum refinery, winter accumulation/storage with water vapour heating, preparation after the winter accumulation to the summer season by heating and removing the accumulated water. Both during preparation and during maintenance of road paving, the thermal decomposition of bitumen is possible, with the changes of its composition and structure, and therefore alteration of properties. This process is accompanied by the evolution of volatile components into the environment, which worsens the ecological situation. An increase in bitumen stability will allow one to improve the ecology of road communications, *viz.*, the environment, where modern people spend a substantial part of their lives.

One of the ways to increase the stability of bitumen is the introduction of additives into it. As a rule, surface-active substances (SAS) and mineral additives are used for this purpose [1, 2].

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The authors of [1] substantiated the use of the mineral component to improve the structure of asphalt concrete and compared different methods of introducing additives (mainly into the bitumen binder). It was demonstrated that mechanochemical treatment of mineral components, for example, traditionally used calcite, allows one to enhance the efficiency of additive. Much attention of researchers is attracted to the change of viscosity of adhesion ability to the mineral component of asphalt concrete. It is assumed that the ordering of the components of the binder occurs near the surface of particles of mineral supplements.

The introduction of nanocarbon additive (up to 0.5 mass %) during processing heavy oil residues was studied in [3]. It is assumed that the additive intensifies changes in the structure of molecules of petroleum components near the surface of particles during thermolysis. The authors of [3] did not consider long-term aging of the obtained object. The products of thermal decomposition of bitumen were studied in [4]. The formation of ecologically dangerous aromatic oxygen- and sulphur-containing compounds was detected.

The goal of the present work was to study thermal decomposition of bitumen and the effect of mechanochemically activated solid additives of calcite and carbon nature on thermolysis.

EXPERIMENTAL

The initial raw material for sample preparation was BND-90/130 bitumen from the Omsk Petroleum Refinery. Sampling and storage were performed according to standards [5, 6]. The following bitumen samples were prepared for studies. Sample No. 1 is initial, with high water content after winder storage. According to the data reported in [7], the water content in bitumen after the winter storage sis stable and equal to approximately1 mass %. For this reason, separate experiments on the determination of water content in the samples were not carried out. When preparing sample No. 2, water was evaporated from it according to the standard requirements [6]. Treatment time was determined from reaching the temperature of 140–145 °C in the bitumen bath. Sample No. 3 was bitumen overheated during evaporation: bitumen was heated to 180 °C and kept at this temperature for 4 h.

We studied the effect of additives of the carbon nature (samples Nos. 4, 5) and mineral nature (calcium carbonate, samples Nos. 6, 7). The carbon additive was nanotubes (2×20)–(2×200) nm (China). The additives were introduced in the amount of 10 and 100 mg per 100 g of bitumen prepared normally (sample No. 2) when melting temperature was reached.

Chemical and thermal analyses of bitumens were carried out. The chemical analysis included the determination of the group composition of pyrobitumen, tar and oil, according to the known procedure developed at the IPC of the SB RAS (Tomsk) and it is similar to that reported, for example, in [8].

Thermogravimetric and differential thermal analyses of bitumen samples were carried out with a Paulik-Paulik-Erdey Q-1000 derivatograph (MOM, Hungary). Analysis conditions: air atmosphere, heating rate 10 °C/min, temperature range 20–1000 °C, weighted portion 100 mg.

The mechanical activation of additives was carried out with the help of attritor Courtesy of Union Process (the USA), rotation frequency 200 min^{-1}, the cylinder was thermostated with water. The mass of balls 15 mm in diameter was 2000 g. The ratio of the charge mass to ball mass was 1 : 10, activation time was 1–3 min.

RESULTS AND DISCUSSION

The group composition of bitumen samples is listed in Table 1. One can see that the oil content decreases during thermal treatment, while pyrobitumen content increases.

The thermal analysis of tar and pyrobitumen shows that thermal destruction starts at a temperature higher than 300 °C [7, 9]. Our results on bitumen samples also show the threshold decom-

TABLE 1

Group composition of samples of bitumen

Sample No.	Asphaltenes	Resins	Oils
1	13.9	14.9	71.2
2	16.0	21.3	62.7
3	21.9	18.4	59.7

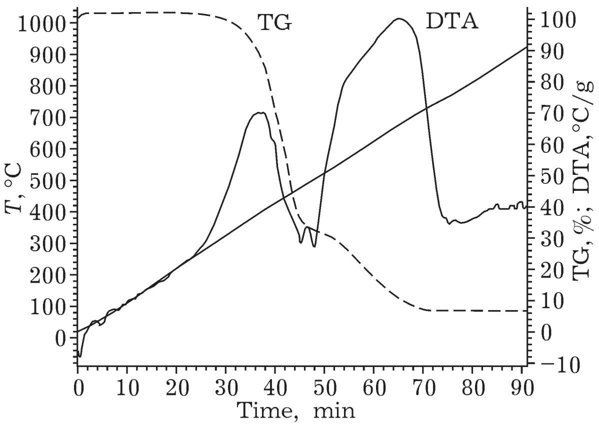

Fig. 1. Thermogram of bitumen sample heated during water evaporation (sample No. 3).

position temperatures. The diagrams of thermal analysis for sample No. 3, which exhibits a typical sequence of gaseous product evolution, are shown in Fig. 1. It was established that for all the samples the first exothermal effect is observed near 400 °C, endothermic effect appears at 500 °C, the second exothermal effect appears near 700 °C. Such a combination and positions of peaks are characteristic also for related objects, for example, for asphalt-tar-paraffin deposits formed in oil pipes during oil pumping [10].

The heat evolution at 400 °C is usually connected with air oxidation of the oil component [11] or with hydrogen redistribution and destruction of heteroatomic bonds, first of all carbon-oxygen [4]. Deep thermal decomposition of tar and pyrobitumen, removal of volatile products and destruction of the carbon framework of molecules occur in the field of 500 °C [12]. This process is accompanied by a substantial change of the sample mass. At the final stage, the residual molecular structure becomes denser, similarly to atomic layers in graphite crystal, and the condensed component burns. A decrease in mass in this temperature region is accompanied by the noticeable exothermal effect. The conservation of peak positions within the studied temperature range is the evidence that thermal decomposition in the samples is realized according to the same scheme.

Below we report the data on mass losses for bitumen samples Nos. 1–7 during thermal decomposition:

Samples	1	2	3	4	5	6	7
Mass loss, %	60	85	92	90	98	50	80

For samples 1–3, with a decrease in the content of oil component we observe more complete transformation during thermolysis. The protective action of the oil component is known [1, 7].

Calculating activation energy, we used the results of thermogravimetric analysis at the first stage of thermal decomposition. Previously related reactions (for example, coal pyrolysis) were studied using Erofeev–Kolmogorov equation. Considering the results of thermogravimetric experiments [9], it is reasonable to attract this model because, unlike other non-isothermal models, it is suitable for heterogeneous systems and does not require knowledge of reaction order [13]. The authors of [13] also described the transformation of the time dependence of transformation degree into the temperature dependence for the constant heating rate. The following equation was obtained for the description of the curve near the point of maximal transformation rate:

$$\ln(-\ln\alpha) = [E_a(T - T_m)]/(RTT_m)$$

Here α is the transformation degree at the current temperature; E_a is the process activation temperature; T and T_m are current temperature and the temperature of the maximal transformation rate, respectively; R is the universal gas constant.

Activation energy values (E_a) reported in literature varies from 75 kJ/mol for diffusion-controlled processes to 227 kJ/mol for the destruction of pyrobitumen matrix [9]. On the other hand, E_a for bitumen aging process reported in [7] are within the range 43–72 kJ/mol.

Below we present E_a values for the first stage of thermal decomposition of bitumen samples Nos. 1–7 (kJ/mol):

Samples	1	2	3	4	5	6	7
E_a	157	92	87	90	103	120	129

The E_a values obtained for samples Nos. 2–7 (90–120 kJ/mol) are usually related to the case of the radical reaction mechanism. It is necessary to stress that E_a decreases during thermal treatment of bitumen: from 157 kJ/mol for sample No. 1 with the maximal water and oxygen content to 87 kJ/mol for sample No. 3. A decrease in the content of oxygenated compounds and the oil component as a result of evaporation [14] promotes an increase in the rate of decomposition of the remaining hydrocarbon component.

It is known [7] that the weather stability of oxidized bitumen may be improved due to an increase in oil and pyrobitumen content, enlargement of pyrobitumen molecules, addition of oxidation inhibitors etc. The authors of [7] chose fine carbon in the form of soot as an additive to enlarge molecules and associates of pyrobitumen; in our case carbon nanotubes 20–200 nm in size were used.

The results obtained demonstrate that the introduction of an additive in the amount of 10 mg/100 g of bitumen does not affect transformation degree and activation energy of decomposition. An increase in the amount of the additive to 10 mg/100 g is accompanied by an increase in activation energy of the first stage but the overall transformation proceeds more completely. It may be stressed that the introduction of carbon nanoparticles as an additive only insignificantly increases thermal stability of the bitumen system at the initial stage of decomposition.

On the other hand, the improvement of the weather stability is possible due to the addition of natural carbonates into bitumen [1, 7]. These compounds are recommended for use even in warm countries to prevent the coke formation. Fine calcite was chosen as the second additive. The introduced calcite additive composed of the particles 0.5–5 μm in size possesses noticeable inhibiting action, both on the value of transformation degree and on activation energy of thermal decomposition. Analyzing literature [1, 7] one may assume that calcite additive is adsorbed on the surface of pyrobitumen core prone to oxidation. Then the growth of the oil shell occurs, which prevents further oxidation (decomposition).

CONCLUSION

1. The thermal decomposition of bitumen samples of different origin was studied. It was shown that with the help of chosen equation of the thermal decomposition it is possible to describe the kinetics of bitumen mass decrease and evolution of gaseous products. Activation energies of sample thermolysis were determined; they were 90–157 kJ/mol.

2. The introduction of mechanically activated additives composed of calcite particles and carbon nanotubes leads to an increase in the activation energy of the decomposition, a decrease in the rate of the first stage of the thermal decomposition of pyrobitumen and change of the degree of the decomposition.

3. The introduction of additives increases the stability of bitumen materials within the road paving. This effect may be used to improve the ecological situation at road communications.

REFERENCES

1 Gezentsveya L. B. (Ed.), Dorozhny Asfaltobeton, Transport, Moscow, 1993.
2 Rudenskaya I. M., Rudenskiy A. V., Organicheskie Vyazhushchiye dlya Dorozhnogo Stroitelstva, INFRA-M, Moscow, 2010, 256.
3 Tumanyan I. B., Sinitsyn S. A., *Khim, Tekhnol. Topliv Masel*, 6 (2007) 39.
4 Kovaleva O. V., *Neftekhim.*, 44, 6 (2004) 459.
5 GOST 22245–90 Bitumy Neftyanye Dorozhnye Vyazkiye. Tekhnicheskiye Usloviya.
6 GOST1510–84. Neft' i Nefteprodukty. Markirovka, Upakovka, Transportirovaniye i Khraneniye.
7 Gun R. B., Neftyanye Bitumy, Khimiya, Moscow, 1973.
8 Grudnikov I. B., Proizvodstvo Neftyanykh Bitumov, Khimiya, Moscow, 1983.
9 Syunyaeva Z. I. (Ed.) Khimiya Nefti, Khimiya, Leningrad, 1984, 360.
10 Khalikova D. A., Ganeeva Yu. M., Yusupova T. N., VII Mezhdunar. Konf. "Khimiya Nefti i Gaza" (Proceedings), Tomsk, 2009, pp. 507–511.
11 Tsamaeva P. S., Strakhova N. A., *Vestn. AGTU. Khim. Tekhnol.*, 6 (2005) 126.
12 Grin'ko A. A., Serusoderzhashchiye Strukturnye Fragmenty Smolisto-Asfaltenovyh Komponentov Nefti (Author's Abstracts of Candidate's Dissertation in Chemistry), Tomsk, 2011.
13 Fialko M. B., Neizotermicheskaya Kinetika v Termicheskom Analize, Izd-vo TGU, Tomsk, 1981.
14 Mamylov S. G., Donchuk A. I., Lomovskiy O. I., VII Mezhdunar. Konf. "Khimiya Nefti i Gaza" (Proceedings), Tomsk, 2009, pp. 367–370.