Obtaining Binders for Road Building from Mixtures of Brown Coal, Oil Residues and Polymeric Wastes

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Abstract

Joint treatment of brown coal, oil residues and wastes of synthetic polymeric materials, resulting in high-quality binders for road building and distillate hydrocarbon products, is investigated. The technology includes the stage of thermal dissolution of brown Kansk-Achinsk coal in oil residue (1 : 1) in the presence of polymeric material added, and thermal treatment of the formed high-boiling products in water vapour on activated ferrioxide catalysts of ore origin. It is shown that the main products of the process are high-boiling fractions of the liquid products of transformation of coal, oil and polymeric material (bitumen) as well as distillate fractions of hydrocarbon products. Technological parameters of the process were chosen to allow obtaining bitumen with the yield of 56.6–62.1 mass % and distillate hydrocarbon products – 17.6–23.0 mass %. Addition of a number of synthetic polymeric materials (polyethylene, polypropylene, rubber based on butyl caoutchouc at the concentration of 25 mass %) at the stage of thermal dissolution of coal allows one to increase the yield and to improve the main characteristics of bitumen. The resulting bitumen corresponds in its main characteristics to the requirements of the State Standard (GOST) for high-quality oil bitumen; the composition of distillate products allows one to consider them as a raw material for the production of petrol and organic solvents.

INTRODUCTION

At present, paving bitumen is produced mainly by the oxidation of residues of oil refining by oxygen of the air. The quality of the formed binders is to a great extent determined by the type of the initial oil raw material [1]. A substantial part of thus obtained oil bitumen possesses insufficiently high performance characteristics.

A promising raw material for the production of binding materials is shale, brown and sapropelite coal due to their large resources and low cost in comparison with oil, as well as relatively high degree of transformation into the target products in thermal treatment processes [2–5]. However, in the majority of cases, thus obtained products cannot be used directly as binding materials because they do not meet the requirements to bitumen.

It was shown in a number of works that the quality and performance characteristics of the materials based on oil bitumen could be improved by means of modification involving synthetic polymeric materials. Polymeric bitumen compositions are usually prepared by mixing the components and heating at a temperature of 200–250 °C for several hours until a homogeneous mixture is formed. The substances used as polymeric modifying agents included polyethylene [8–12], atactic polypropylene [8, 13–15], chlorosulphonated polyethylene [8, 9], *etc*. Much attention is attracted to the development of bitumen compositions with synthetic caoutchouc [6, 7]. A specific feature of caoutchouc is its ability

to large elastic deformations. It is assumed that the presence of the modifying agents of this kind in polymeric bitumen compositions will allow one to increase elasticity and plasticity within a broad temperature range. However, in order to achieve the required result, it is necessary to use substantial (up to 50 %) amounts of polymer added; in some cases this does not lead to any noticeable improvement of the properties of bitumen. In addition, not very high stability of polymeric bitumen mixtures at elevated temperature is observed, which hinders obtaining high-quality pavement on their basis.

These results are likely to be due to poor compatibility of bitumen with some polymeric materials. It is known that oil bitumen is a dispersed system composed mainly of three groups of substances: oil, resin and pyrobitumen. The dispersion medium is composed of petrolene (a sum of oil and resin), the dispersed phase is pyrobitumen. The stability of the system depends on the degree of affinity between petrolene and pyrobitumen, which can be estimated to a definite approximation as the difference in their aromaticity. The smaller is this difference, the more stable is bitumen system [16]. In this connection, the addition of polymers having non-aromatic structure can decrease the stability of bitumen compositions.

We demonstrated previously [17–19] that the joint thermal transformations of brown Kansk-Achinsk coal and polyethylene involve chemical interaction between the components of the mixture resulting in the formation of products including both the aromatic fragments of coal structure and aliphatic fragments of a polymer. These data allow us to assume that the compatibility of polymeric bitumen compositions obtained by thermal dissolution of a mixture of brown coal and polymeric materials in oil residue will be better in comparison with bitumen modified simply by the addition of polymers.

In the present work we investigate the process by which organic binding materials and distillate fractions are obtained from a mixture of brown coal and polymeric materials. The process includes their thermal dissolution in oil residue followed by thermal treatment of the formed products with water vapour in the presence of iron ore oxide catalyst.

EXPERIMENTAL

Brown coal of B-2 grade from the Borodino open-pit mine of the Kansk-Achinsk Basin (KAB) with particle size below 0.1 mm was used in the investigation. Coal dried at 100–105 °C had the following composition (calculated per dry de-ashed mass), mass concentration, %: C 70.8, H 4.9, N 0.8, S 0.2, O 23.3. The residue from refined west Siberian oil was used as the solvent; its composition was, mass concentration, %: C 85.9, H 12.5, N 0.2, S 0.4, O 1.0.

Commercial samples of middle-pressure polyethylene (PE) (molecular mass 20 000) and atactic polypropylene (A-PP) (molecular mass 900), as well as the waste material (with the content of butyl caoutchouc 55 mass %) from the Krasnoyarsk plant of general mechanical rubber goods.

Thermal dissolution of the mixtures of brown coal and synthetic polymeric materials in oil residue was carried out in a set-up with rotating steel autoclaves 0.25 l in volume. The coal : oil residue ratio was 1 : 1. The necessary amount of the mixture components was charged into the autoclave. To remove the air, a 10-fold volume of argon was blown through the vessel. The autoclave-heating rate was 9–10 °C/min. The moment of achieving the required temperature was accepted to be the start of reaction. The process duration was 60 min.

After cooling the autoclave, we collected the gaseous products into a gasometer to determine the volume. Then the autoclave was opened; its content was removed quantitatively. The condensed products were subjected to extraction with an ethanol-benzene mixture in Soxhlet's apparatus. Coal conversion level was calculated on the basis of the amount of solid residue. After solvent removal, the extract was separated into the fraction boiling below 350 °C and the residue (by distillation at a pressure of 10 mm Hg).

Thermal treatment of the condensed products of thermal dissolution was carried out with water vapour in a flow laboratory set-up with the reactor 0.1 l in volume. The ratio of the raw maerial to water was equal to 1 : 0.5 (mass). The catalyst was added in the amount of 5 % of the organic raw mass. Sintered iron ore manufactured at the Abagur plant and

containing more than 53 mass % of iron in the form of oxides was used as a catalyst. The sintered ore was preliminarily treated in AGO-2 activator mill with water added; acceleration of milling bodies was 600 m/s^2. Activation time was 30 s; the specific surface of the sample increased up to 65 m^2/g within this time. Activation conditions were chosen on the basis of results obtained in preliminary investigation of the effect of intensity, time and medium of activation on changes in texture parameters of the samples under treatment and their catalytic activity during hydrogenation of brown coal [19].

The formed products were separated into gaseous and condensed phases in a cooler separator. The volume of gaseous products was determined with the help of a wet gas meter. Water was separated from condensed products by decantation. The hydrocarbon part of the products was separated into the fractions boiling below 200 °C, within the range 200–350 °C, and starting to boil above 350 °C.

The composition of gas products was determined with LKhM-80-1 gas chromatograph with katharometer detection. Concentrations of individual hydrocarbons in distillate fractions were determined by means of gas chromatography – mass spectrometry with Agilent 6890 instrument equipped with the detector of selective masses Agilent 5973 (70 eV). The products were separated with a capillary column Optima I No. 726839.50 (50 m × 0.2 mm with OV-1) with temperature programmed from 40 to 185 °C at a rate of 3 °C/min. The compounds were identified using the computer database NIST98.

High-boiling fractions of the products were tested using the standard procedures for oil bitumen [20–24].

In some experiments, pyrobitumen content of bitumen was determined by means of dissolution in hot benzene followed by precipitation with light petroleum. Resin and oil content of asphalt-free oil was determined by means of adsorption chromatography in a glass column [25].

RESULTS AND DISCUSSION

Thermal dissolution of the mixtures of brown coal with polymeric material in oil residue

Investigation showed that the yield of the substances extractable by the ethanol-benzene mixture during thermal dissolution of the oil refining residue at 320–410 °C is only weakly dependent on the process temperature and makes up 72–77 % of the organic raw mass (ORM) (the organic mass of carbon + the mass of oil residue). However, the composition of the formed condensed products changes substantially (Fig. 1). The content of the high-boiling fraction, which may presumably be used as an organic binding agent decreases for the process temperature above 350 °C. At the same time, the content of the fraction boiling within the range 200–350 °C increases in the products. The content of the solid residue decreases noticeably; a likely reason is an increase in coal conversion into liquid and gaseous products.

Addition of synthetic polymeric materials chosen in the present work causes an increase in the concentration of compounds extractable from the condensed products with an ethanol-benzene mixture (Table 1). For instance, with an increase in the mass concentration of atactic polypropylene in the initial mixture to 50 %, the concentration of the fraction starting to boil at 350 °C increased by 9 mass %, while that of

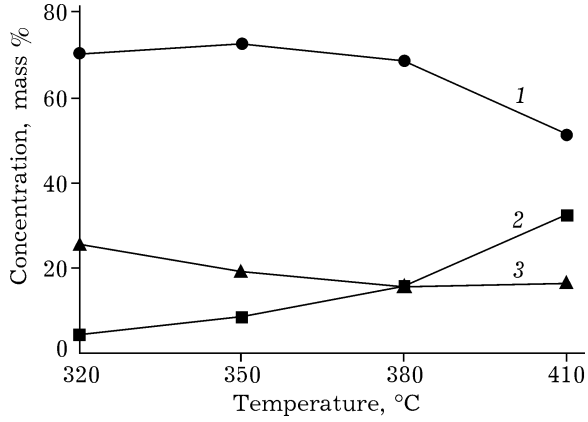

Fig. 1. Effect of temperature of thermal dissolution of the brown coal from the KAB in oil residue on the composition of products extractable with a mixture of ethanol and benzene, and the content of: *1* – fraction boiling above 350 °C, *2* – fraction boiling below 350 °C; *3* – solid carbon residue.

TABLE 1

Effect of atactic polypropylene (A-PP) on the composition of condensed products and the degree of brown coal transformation during its thermal dissolution in oil residue at 350 °C

Concentration of A-PP*, mass %	Composition of products, mass %			Transformation degree of OMC, mass %
	Fractions		Solid carbon residue	
	boiling below 350 °C	starting to boil at 350 °C		
–	8.4	72.7	18.9	64.1
10	9.0	74.9	16.1	65.9
25	10.1	77.9	12.0	69.9
35	10.3	80.1	9.6	70.5
50	10.5	82.0	7.5	71.8

*Calculated per ORM (organic mass of coal (OMC) + oil residue mass + polypropylene mass).

the solid residue decreased by a factor of 2.5. It is necessary to stress that the conversion of coal into liquid and gaseous products increases noticeably under the action of polypropylene addition. A similar effect was previously observed for the joint thermal transformation of brown Kansk-Achinsk coal with polyethylene, which was explained by chemical interaction between the products of thermal depolymerization of coal and the polymer [25–27].

Some characteristics of thermal dissolution of coal in oil residue in the presence of polymers of different types are presented in Table 2. One can see that the main transformation products are high-boiling fractions; their yield in the presence of polymers (25 % of ORM) is 72.6–73.6 mass %. The maximal yield of distillate fraction (boiling below 350 °C) and gaseous products was observed in the experiments involving the wastes of general mechanical rubber goods (GMRG) as an additive. Gaseous products of thermal dissolution of coal consist of carbon oxides by more than 75 mass %; they are likely to be formed as a result of thermal decomposition of oxygen-containing functional groups of the organic mass of coal. The low yield of hydrocarbon gases points to the fact that oil residue does not undergo profound thermal destruction under the chosen conditions.

Thermal treatment of the high-boiling coal dissolution fractions in water vapour

Tests of high-boiling fractions of coal thermal dissolution for evaluation of the outlooks of their use as organic binders for

TABLE 2

Effect of the type of the added polymeric material on the yield of products during the joint thermal dissolution with brown coal in oil residue at 350 °C

Type of polymeric material	Yield of products, % per ORM				Degree of coal transformation, mass %
	Gaseous	Liquid fractions		Solid carbon residue	
		boiling below 350 °C	starting to boil at 350 °C		
Without additives	4.7	8.0	69.3	18.0	64.1
PE	4.9	8.3	73.9	12.9	65.6
A-PP	5.6	9.5	73.6	11.3	69.9
GMRG	6.0	10.3	72.6	11.1	70.3

Note. The content of the organic mass of polymeric material in the mixture was 25 % per ORM (OMC + oil residue mass + organic mass of polymeric material).

TABLE 3

Effect of temperature of thermal treatment of the products of joint thermal dissolution of coal and polypropylene at 350 °C on some characteristics of the resulting bitumen

Process temperature, °C	Needle (0.1 mm) penetration depth, at 25 °C	Stretchability at 25 °C, cm	Composition of bitumen (concentration), mass %		
			Pyrobitumen	Resin	Oil
350	250	50	12	25	63
380	170	66	20	31	49
400	150	60	22	30	48
440	87	45	45	20	35

paving according to the standard procedures [20–24] showed that they do not correspond to high-quality oil bitumen in such characteristics as stretchability and needle penetration depth. Because of this, in order to render the necessary properties to the products of coal thermal dissolution, these products were subjected to thermal treatment in water vapour in the presence of catalysts of ore origin containing iron oxides as the main crystal phase. It was supposed that the following main chemical processes will take place within the chosen temperature range of thermal treatment:

– hydrocarbon oxidation on the surface of iron oxides;

– condensation of oxidation products with the formation of the compounds with high molecular mass providing the necessary elasticity of the resulting bitumen;

– interaction of the reduced forms of the catalyst with water, resulting in the formation of iron oxides and hydrogen.

In addition, hydrogen formed in the process can take part in hydrogenation of the compspounds with unsaturated bonds, which will promote an increase in the stability of the final product in storage and in use.

Investigation of the effect of temperature, at which the high-boiling fractions of the joint thermal dissolution of coal and polypropylene are treated, on the group composition of the resulting bitumen showed that an increase in the process temperature is accompanied by the transformation of oil into pyrobitumen and resin (Table 3). High temperature initiates the reactions leading to the transformation of resin into pyrobitumen, which causes a sharp increase in the viscosity of the products and a decrease in their elasticity. The maximal stretchability characterizing cohesion strength of bitumen was discovered in the products obtained at 380 °C. Comparison of the results with the requirements of the State Standard (GOST) for oil bitumen shows that the best characteristics are those exhibited by the products obtained within temperature range 400–380 °C.

The results of determination of the yield of products formed during water-vapour thermal treatment of the high-boiling fractions obtained at the stage of thermal dissolution of a mixture of coal with synthetic polymers of different types are shown in Table 4.

One can see that the main product of the transformation is distillation residue; within the chosen temperature range, its yield changes from 74.2 to 84.1 %, calculated per the mass of raw material charged in. An increased yield of distillate fractions is characteristic of the experiments involving atactic polypropylene as an additive.

On the basis of the results presented above, we compiled the mass balance of the process including the organic mass of the initial raw material and the organic mass of products (Table 5). One can see that bitumen, up to 62.1 mass %, and distillate hydrocarbon products (a sum of fractions boiling within temperature ranges: 200 and 200–350 °C), up to 23.0 mass % may be obtained from brown coal, oil residue and synthetic polymeric materials chosen in the present investigation. The use of thus obtained bitumen as binders for paving is of special interest. In this case, it is not necessary to isolate the solid residue from the formed bitumen; this simplifies the technology and decreases the cost of the products. It is known from literature that the addition of powdered coal into bitumen-based paving asphalt improves the performance characteristics of the latter [1].

TABLE 4

Yield of the products of water-vapour thermal treatment of the high-boiling fractions of the joint thermal dissolution of brown coal with different polymeric materials. Polymer content of the initial mixture: 25 %, temperature of thermal dissolution: 350 °C

Polymer type	Temperature, °C	Product yield, mass %			
		Gas	Fraction boiling:		Distillation residue
			below 200 °C*	200–350 °C	
PE	380	3.2	4.0	8.7	84.1
	400	4.5	4.9	11.4	79.2
A-PP	380	4.7	4.1	14.2	77.0
	400	5.3	5.2	15.3	74.2
GMRG wastes	380	2.7	3.9	12.3	81.1
	400	4.1	5.3	14.4	76.2

*The yield of a fraction was calculated as 100 % – percent of the yield of (gas + fraction 200–350 °C – residue of distillation products) (in mass %).

Investigation of the properties of bitumen and the composition of distillate products

Distillation residue comprising high-boiling products (>350 °C) were tested according to the standard procedures used to determine the quality of bitumen. Some results of the tests are presented in Table 6. For comparison, the standard requirements with respect to the parameters under analysis for some grades of oil bitumen samples are shown here. One can see that the bitumen obtained from mixtures of brown coal and oil residue without any addition of synthetic polymeric materials corresponds in some parameters to the requirements to high-boiling bitumen. At the same time, it does not meet the requirements of the State Standard (GOST) in one of the basic parameters, *i.e.* stretchability (characteri-zing cohesion strength of bitumen). Addition of the herein-chosen synthetic polymeric materials at the stage of thermal dissolution of coal in oil residue allows one to improve the quality of bitumen substantially. The type of an additive has an

TABLE 5

Mass balance with respect to the organic mass of raw material and products of the process of obtaining binders for paving and the distillate hydrocarbon fractions from brown coal, polymeric wastes and oil residue. Temperature of thermal dissolution: 350 °C, of thermal treatment with water vapour: 380 °C

Raw material and products	Concentration, mass %		
	Taken		
BC	37.5		
OR	37.5		
PM*	25.0		
Total	100		
	Obtained**		
GP	7.3	9.0	8.0
Fraction boiling below 200 °C	6.9	7.5	7.9
Fraction 200–350 °C	10.7	15.5	14.1
Bitumen	62.1	56.6	59.0
Solid carbon residue 13.0	11.4	11.0	
Total	100	100	100

*Concentration of the polymeric material (PE, A-PP, GMRG wastes) in the mixture was 25 mass % per ORM.

**The first value: with PE, the second value: with A-PP' the third value: with GMRG wastes.

TABLE 6

Characteristics of bitumen obtained by means of the joint transformation of brown coal and oil residue

Characteristics	Without additives	Obtained by thermal dissolution with additive			Standards for the grades of oil bitumen (GOST 22245–76)	
		PE	A-PP	GMRG wastes	BND 90/130	BND 40/60
Depth of penetration of a 0.1 mm needle, at a temperature of:						
25 °C	56	97	105	13	91–130	41–60
0 °C	15	29	29	35	≥28	≥13
Softening temperature according to KiSh, °C	40	48	41	43	≥43	≥51
Stretchability at a temperature of, cm:						
25 °C	33	60	55	63	≥60	≥40
0 °C	–	4.2	3.5	4.5	≥4.2	–
Brittle temperature, °C	−19	−15	−19	−17	−17 and below	−10 and below
Flash point, °C	210	230	220	220	≥220	≥220
Cohesion to marble or sand	Endures as a reference sample No. 2					
Changes in softening temperature after heating, °C	6	6	6	6	≤6	≤7
Content of water-soluble compounds, %	–	–	0.3	–	≤0.3	≤0.2

essential effect on these quality characteristics. The highest stretchability is achieved with polyethylene and GMRG production wastes as additives. The least viscous bitumen was obtained with atactic polypropylene and GMRG wastes.

According to examination by means of gas chromatography–mass spectrometry, the fractions boiling below 200 °C contain mainly alkanes (mass concentration 70–75 %) with the maximal number of carbon atoms in molecule equal to 13, and aromatic hydrocarbons (mass concentration 23–25 %), represented by alkylated benzene derivatives. The structure of alkane hydrocarbons is to a large extent determined by the type of the synthetic polymer used as an additive to coal. Thus, in the experiments with polyethylene as an additive, mainly normal-structure hydrocarbons are obtained. Addition of polypropylene causes an increase in the concentration of structural isomers in the products.

Fractions boiling within the range 200–350 °C contain alkanes with the number of carbon atoms from 12 to 26. The concentration of olefin hydrocarbons reaches 7 mass %. In addition to benzene derivatives, aromatic hydrocarbons contain indans, tetralin, naphthalene an its alkyl derivatives with total concentration not more than 5 mass %.

It follows from the results obtained in the investigation that the distillate fractions can be considered as a raw material for the production of petrol, solvents, etc., or they can be used as fuel in nozzle-type furnaces, which are often used in industrial bitumen-producing units.

CONCLUSIONS

Bitumen obtaining process based on a combination of thermal dissolution of a mixture of brown coal and synthetic polymeric materials in oil residue at 350–380 °C with subsequent thermal treatment of the products in water vapour at 350–400 °C and pressure not higher than 5 atm were investigated. Technological parameters of the process allowing one to obtain bitumen with a yield of 56.6–62.1 mass % and distillate hydrocarbon products with a yield of 17.6–23.0 mass % were chosen.

It was shown that polyethylene, polypropylene, or rubber based on butyl caoutchouc, in

the amount of 25 mass %, added at the stage of thermal dissolution of coal, allows one to increase the yield of bitumen and to improve its main characteristics substantially.

The process under investigation allows one to utilize the industrial and household wastes of synthetic polymeric materials and at the same time to obtain hydrocarbon products with high consumer characteristics. Thus obtained bitumen corresponds to the requirements of the State Standard (GOST) to high-quality oil bitumen in the main characteristics; the composition of distillate products allows one to consider them as a raw material for the production of petrol and organic solvents.

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