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Thermal Solution of Waste Tire in Heavy Commercial Solvents

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Abstract

Thermal solution of the rubber chips of waste tire in high-boiling commercial solvents in the absence of molecular hydrogen is considered. High conversion of rubber to liquid products takes place at 300 °C and above this temperature. The yield of the gas is less than 1 % at 300 °C. Solution of rubber chips in commercial solvents can give products in the form of suspensions of finely granular carbon black in bitumenlike materials. Thermal solution combined with thermal oxidation with air permits one to vary the softening point and the plastic properties of the products. The thus obtained modified bitumens have a weaker temperature dependence of the plastic properties, which is important for improving resistance to cracks and cold in road coatings.

INTRODUCTION

Waste tire utilization demands working out environmentally safe technologies, affording valuable goods [1, 2].

One of possible solutions to this problem is destructive hydrogenation of waste tire [1–3]. Hydrogenation of rubber chips obtained by grinding tire at a hydrogen pressure of 7.0 MPa and at a temperature of 700 K can give liquid fuel products [4]. Co-hydrogenation of coals and rubber chips also leads to positive results [3, 5–7].

A simpler technology that may be used by analogy with destructive hydrogenation of coal is thermal solution in the absence of molecular hydrogen at a pressure depending on the solvent and reaction temperature. Thermal solution of waste tire under supercritical conditions using toluene, alcohols, pentane, and water as solvents was studied previously [8, 9]. Major products of this process are liquid products of rubber transformation and a solid residue consisting primarily of carbon black and inorganic additions. Due to reduced gas formation, the yield of liquid products is much higher than during pyrolysis.

If carried out in low-boiling solvents, the thermal solution process should include subsequent isolation of the solvent from the reaction mixture and utilization of liquid products and the insoluble residue.

Thermal solution of waste rubber in high-boiling oil products affords pitch- and asphalt-like materials [10–12]. These products may be used (without being separated, by analogy with bitumens) in road building, or as anticorrosive, waterproofing, and other materials. The process will be much less expensive if the stages of solvent isolation and product separation are excluded. To obtain modified road bitumen it was suggested that road tar be co-oxidized at 210–220 °C with up to 1 mass % additions of rubber ships [13]. Data about the nature of the products and the degree of rubber solution at different temperatures are not given in the above references. These issues are discussed in the present work, which deals with thermal solution of rubber chips derived from waste tire in heavy commercial solvents of varying nature: road tar, coal tar product, and anthracene fraction.

EXPERIMENTAL

Rubber chips obtained by grinding waste tires after removal of metallic cord and characterized in Table 1 were used. For heavy organic solvents we employed commercial products of petroleum and coal tar processing [road tar and the anthracene fraction (AF)].

Characteristics of the anthracene fraction:

– density 1150 kg/m^3;

– boiling range 280–360 °C;

– element analysis, %: C 92.3, H 5.8, S 0.5, (N + O) = 1.4;

– H/C = 0.75;

– substances soluble in hexane 92.6 %.

Characteristics of road tar:

– density 1013 kg/m^3;

– softening point (ring and ball method) 34 °C;

– asphaltenes 16.7 %;

– element analysis, %: C 85.68, H 10.66, S 3.66;

– H/C = 1.49;

– substances soluble in hexane 83.3 %.

Thermal solution was carried out in a 30 ml rotating steel autoclave at 300–400 °C. The autoclave was charged with rubber chips (3 g) and a solvent (9 ml); steel balls were placed in the reactor for better mixing. Atmospheric pressure was set as the initial pressure; working pressure was 5–15 atm depending on the solvent and temperature used. Run time was 30 min after the required temperature had been attained. Experiments were also carried out in an open system without pressure, namely, in a 150 ml metallic reactor equipped with a propeller stirrer; run time was 30 min after the required temperature had been attained. The scheme of experiments is presented in Fig. 1.

Conversion of rubber chips into soluble products was defined as the difference between the mass of the solid residue insoluble in tetrahydrofuran (THF) and the mass of the starting rubber chips. Road tar and the anthracene fraction completely dissolve in tetrahydrofuran.

The liquid products of thermal solution and the THF-insoluble residue were characterized by element analysis, derivatography, and IR and PMR spectroscopy.

The PMR spectra of the oils were recorded on a Bruker DRX 400 spectrometer at room temperature using $CDCl_3$ as a solvent and tetramethylsilane as an internal standard. The hydrogen distribution in the oils was determined from the PMR spectra using the known procedures [14, 15]. IR spectra were measured on a Perkin Elmer Spectrum BX-II Fourier-transform spectrometer; the samples were suspended in a KBr pellet. The average molecular mass of the oils was determined cryoscopically in naphthalene. Derivatography was performed on a Mom OD-102 Paulick-Paulick-Erdey derivatograph [heating rate 5 °C/min to 800 °C; inert atmosphere (nitrogen)].

RESULTS AND DISCUSSION

Tables 2 and 3 show the results of experiments on solution of rubber chips. Conversion of rubber chips into soluble products reaches high values at 300 °C and continues to grow insignificantly above this temperature. The resulting product is a mixture of the starting solvent and liquid oils soluble in hexane.

TABLE 1

Characteristics of rubber chips

Size, mm	Technical analysis, %			Element composition, %			
	W^a	A^d	V^{daf}	C^{daf}	H^{daf}	S^{daf}	$(N + O)^{daf}$
1–3	0.03	3.1	68.8	87.8	7,9	1.5	2.8

Note. W^a is analytical moisture; A^d is the ash content; V^{daf} is the yield of volatile substances based on the dry ashless mass.

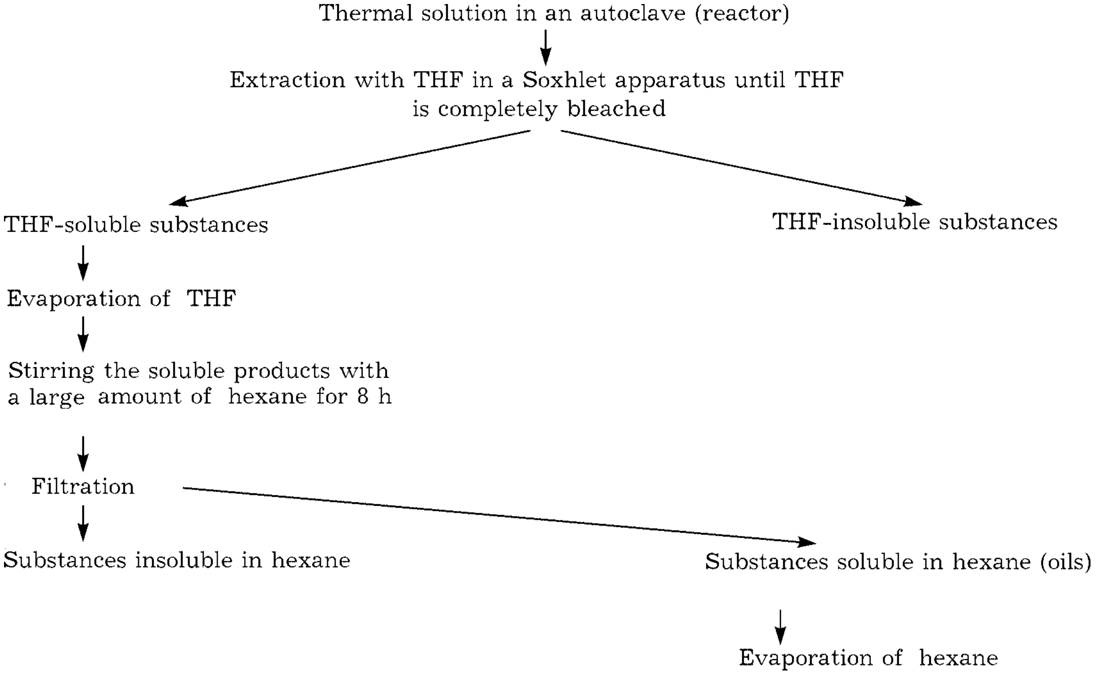

Fig. 1. Scheme of experiment.

According to DTA data, thermal decomposition of rubber chips starts at 300 °C; the rate of the process reaches its maximal values at 330–400 °C, decreasing drastically after mass loss has become 60 % of the initial mass.

When thermal solution is performed in an open system, some liquid products evaporate together with the gas from the reactor. The yield of the gas is less than 1 % when the reaction is carried out in road tar at 300 °C. At this temperature, liquid products do not evaporate unless the anthracene fraction is used; the liquid products are the low-boiling part of this solvent.

The residue that is insoluble in THF is a finely divided powder consisting of carbon black particles (rubber extender) with organic compounds adsorbed on their surface in amounts of up to 25–30 % (DTG data). Note that completely adsorbed organic compounds were also revealed on the surface of carbon black obtained by vacuum pyrolysis of tire rubber and were not removable by treatment with toluene [16].

Table 4 presents the results of oil analyses. The oils obtained by solution of rubber chips and road tar at 300 °C have a higher H/C ratio than that of the starting road tar and the oil obtained from it; the ratio decreases at elevated temperatures. According to the PMR spectra, the oils obtained at 300 °C contain considerable amounts of olefinic protons, vanishing at

TABLE 2
Thermal solution of rubber chips in an autoclave

Experiment No.	Solvent	Temperature, °C	Conversion of rubber to products (%) soluble in	
			THF	hexane*
1	AF	300	60.3	57.6
2	»	400	66.3	60.6
3	Road tar	300	60.0	57.0
4	»	400	64.8	59.1

*Conversion to products soluble in hexane; calculated using data on solution of AF and road tar in hexane.

TABLE 3

Solution of rubber chips in a reactor at atmospheric pressure

Experiment No.	Conditions of solution	Fraction, %		Products (% of charge) soluble in		Conversion of rubber to products soluble in THF, %
		Liquid products	Gas	THF	hexane	
5	Road tar (60 g), rubber (30 g), 300 °C	No	0.6	84.9	74.0	56.7
6	The same, 400 °C	16.2	7.3	63.6	51.8	61.0
7	Road tar (92 g), 400 °C	12.1	3.0	84.5	66.0	–
8	AF (74 g), rubber (37 g), 300 °C	9.8	0.3	77.4	71.7	62.0
9	Road tar (73 g), rubber (36 g), 300 °C, then oxidation of the total product of solution in the same reactor	2.0	5.0	87.7	64.7	70.0

400 °C, as contrasted to the oils obtained from road tar. Moreover, at high temperatures, the content of aromatic protons increases. These data indicate that at elevated temperatures the solution products undergo cyclization and aromatization involving compounds with double and conjugated bonds by analogy with processes that take place during rubber pyrolysis [17]. When thermal solution is performed in an open system, the content of aromatic protons is much lower, probably because of the competing removal of unsaturated low-molecular compounds in distillate form from the reaction sphere.

Figure 2 presents the IR spectra of the oils obtained from road tar in the present work and the spectra of the oils prepared by thermal solution of rubber chips in dodecane after complete solvent evaporation under vacuum [18]. The latter spectra acquire new bands compared to the former, namely, the 835 and 967 cm^{-1} bands arising from the C=C bond vibrations and absorption bands in the range 746–814 cm^{-1}, relating to C–H bond vibra-

TABLE 4

Composition of the products of solution of rubber chips in road tar

Experiment No.	Type of product	H/C	H_{arom}	H_{olef}	H_a	H_b	H_g
3	Oils	1.65	4.5	1.9	17.4	57.5	18.7
4	»	1.54	7.3	0.3	17.0	55.6	19.8
5	»	1.73	3.8	3.5	20.2	57.6	14.9
6	»	1.46	4.8	–	14.2	56.6	24.4
8	»	0.94	45.1	3.0	16.2	29.7	6.0
9	»	1.65	5.1	2.0	15.0	58.5	19.4
Starting road tar	»	1.49	8.5	1.3	13.2	54.9	22.1
6	Distillate	1.53	4.3	5.2	16.8	54.9	18.8
7	»	1.68	3.4	2.1	15.5	53.3	25.7
9	»	1.70	7.8	2.1	15.1	56.4	18.6

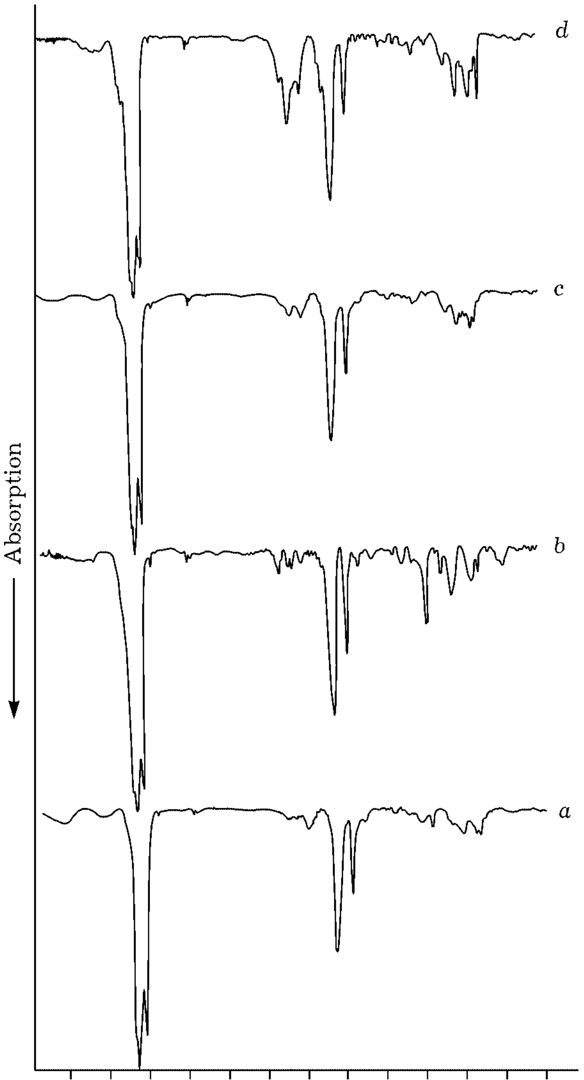

Fig. 2. IR spectra of oils obtained by thermal solution of rubber chips in different solvents: *a*, *c* – road tar, 300 and 400 °C, respectively; *b* – dodecane, 300 °C.

tions in the benzene ring. The 835 cm^{-1} band, as well as the 967 cm^{-1} band, is observed in the oils obtained in dodecane as an inert solvent at 300 °C (see Fig. 2, *b*) and relates to vibrations of the C–H *cis*- and *trans*-double bonds. In experiments with road tar at 300 °C (see Fig. 2, *a*), the 967 cm^{-1} band corresponding to the vibrations of the C–H *trans*-double bond was present, but the 835 cm^{-1} band was not. It is assumed that the absence of the 835 cm^{-1} band points to chemical interaction of road tar with the products of thermal solution of rubber chips.

At 400 °C the 967 cm^{-1} band becomes less intense for oils obtained in road tar (see Fig. 2, *c*), and new bands appear in the range 740–814 cm^{-1} due to the vibrations of the C–H bonds in benzene rings with varying degrees of substitution.

When thermal solution of rubber in road tar is carried out in an open system at 300 °C, nearly all the products stay in the reactor. At 400 °C some of the products of rubber solution and road tar thermolysis evaporate from the reactor. This is consistent with data on the mean molecular mass of the oils obtained in an autoclave after thermal solution of rubber chips in dodecane [18]. The oils obtained at 300 °C in dodecane have a mean molecular mass of 1000–2000. They primarily consist of aliphatic compounds and, to a lesser extent, of olefinic, aromatic, and naphthene structures. When the solution temperature increases to 400 °C, the oligomers are further split into compounds with a mean molecular mass of 400 and with decreased numbers of double bonds, while the content of naphthene and aromatic structures increases.

Thus dissolving rubber chips in road tar and anthracene fraction yields materials consisting of carbon black suspended in the mixture of the starting high-boiling solvent and liquid products of thermal solution of rubber. The latter products are primarily oils, whose aromaticity and double bond content depend on the reaction temperature.

Possible applications for such materials are traditional fields of use for bitumenlike substances such as binders for road building, waterproofing compositions, anticorrosive coatings, *etc.* The presence of finely disperse carbon black as a structure-forming component can have positive effects on the mechanical and some other properties of the materials.

Addition of carbon black to road bitumens improves the properties of the latter [19]. Thus the physical characteristics of bitumen become less dependent on temperature, and the mechanical properties of road coatings are also improved. Addition to bitumen of carbon black obtained by tire pyrolysis decreases the temperature dependence of penetration and viscosity, which is favorable for the lifetime of the road coating.

The basic characteristics used for assessing road bitumens are listed in Table 5 for the

TABLE 5

Physical and mechanical properties of materials obtained by thermal solution of rubber chips in road tar with and without further oxidation

Run No.	Drop point, °C		Penetration, mm at a temperature of		Expansibility, cm
	Softening point (ring and ball method), %		25 °C	0 °C	
Starting road tar	42	34	177	68	65
5	42	36	228	164	–
9	57	50	48	33	30

starting road tar and for the overall product of thermal solution of rubber chips in road tar at 300 °C with or without subsequent oxidation with air at 260 °C for 3 h [air consumption 240 dm^3/(h kg of raw material)]. Oxidation with air is a widespread technique for managing the major characteristics of bitumen employed in bitumen installations. As follows from Table 5, modification of road tar with carbon black and with liquid products of the thermal solution of rubber does not affect significantly the softening point, but increases the penetration drastically. Subsequent thermal oxidation of the total product of solution increases the softening point, but decreases the penetration considerably. The product of thermal oxidation is similar in these characteristics to BND 40/60 road bitumen, for which the softening point must be 51 °C or higher, and penetration must be 40–60 mm (at 25 °C). In agreement with the results of [19], modified road tar has a weaker temperature dependence of penetration. Moreover, as can be see from Table 4, oxidation permits one to reduce the number of double bonds (H_{olef}) in solution products, which is important for increasing the thermal stability of the material.

CONCLUSIONS

By varying the ratio between the rubber chips and the oil residue, as well as conditions of thermal solution and oxidation, one can obviously obtain modified bitumens with diverse characteristics, including bitumens whose basic parameters satisfy the norms of current standards. Heavy coal-tar chemical products modified with products of thermal solution of rubber chips may be used as additions to asphalt concrete mixtures [20] and in anticorrosive coating formulations [21].

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