STRENGTH AND THERMAL STABILITY OF PAVING ASPHALTS

V. D. Portnyagin

UDC 691.1.16:665.45

A clear interrelation has not yet been determined between the strength and durability of asphalts and their structures (supramolecular and spatial disperse). It is not clear, for example, how structures and structure formation affect thermal stability, determining the durability of asphalts and materials based on them, and which structures' content and ratios determine the strength of asphalts.

It is known that during the processing of viscous paving asphalts the greatest effect on their properties is exerted by the chemical processes oxidation, polymerization, and condensation. The conversions of the molecules begin with "burning" of side chains: oxygen atoms are introduced mainly into structures with aliphatic and acyclic C–H bonds, which leads to the formation of hydroperoxides [1, 2]. The latter are very unstable and rapidly decompose. The decomposition of the hydroperoxides is accompanied by termination of alkane chains and cycloalkane rings, after which processes of enlargement and densification of resin and asphaltene molecules occur intensely [1]. As a result, the performance of asphalts worsens sharply: during processing, the viscosity of the asphalts increases 1.5-2.5 times, the cohesion increases 2 times, the breaking point increases by 3-5° (sometimes by as much as 7°), and the temperature-dependence curve of the viscosity $\eta = f(t)$ becomes steeper [3].

The present paper is based on the following hypothesis. In a complex structural unit, first a core is formed and then a solvate shell, the thickness of which is determined by the composition and structure of the molecules of the dispersing medium [4]. Because the molecules of the disperse phase and the dispersing medium (asphaltenes, resins, and hydrocarbons) consist of identical components, namely, benzene and naphthene rings and paraffin chains, it is obvious that during the formation of complex structural units these molecules react not only at rings, but also at side chains. As a result, the side chains, which tend to oxidize, will be shielded. According to the concepts of N. M. Émanuél′ [5], shielding of chains by solvated species can lead to retardation of the oxidation reaction.*

To verify this hypothesis, we carried out complex investigations of viscous paving asphalts with various chemical compositions (Table 1) and structural-mechanical properties (Table 2) using rheological and radiophysical methods, differential thermal analysis, electron microscopy, and IR and UV spectroscopy. The temperatures at which physical association complexes of asphaltenes were "formed" and the properties of the system in this state were determined. It was found that beginning with this moment the main processes that determined the aging of asphalts (oxidation, polymerization, condensation, and evaporation) occurred not only quantitatively, but also qualitatively differently.

This is indicated by the data on the change of the viscosity and strength, the main performance characteristics of asphalts.

If an asphalt was processed at solution temperature $t_s = 140°C$ (when the asphalt was a molecular solution, i.e., the association complexes were broken down as a result of thermal motion, and the side chains of the molecules were exposed), the aging index† increased with decreasing temperature. This means that a change of the properties is manifested most sharply not at the temperatures of the technological process, but at the service temperatures, which is most dangerous: the mixture becomes rigid, and the asphalt concrete from it tends to undergo accelerated crack formation.

---

*F. F. Cheshko [6] showed that, with increasing degree of shielding of the C=O group, substitution of the carbonyl oxygen atom in it can be decreased from 82 to 74.6 and even further to 31.4%.

†This is the ratio of the viscosity of the asphalt after aging and the initial viscosity. The viscosity was measured on a Rheotest RV viscometer after establishment of the temperature conditions under conditions of equilibrium shear stress. The properties of the asphalts were compared in identical rheological states.

Institute for Improvement of Qualifications, Ministry of Automotive Transportation and Highways of the Russian SFSR. Translated from Khimiya i Tekhnologiya Topliv i Masel, No. 11, pp. 35-37, November, 1989.

0009-3092/89/1112-0578$12.50

TABLE 1

No.	Asphalt	Composition,* %			Penetration		Ductility, cm		Temperature, °C	
		oils	resins	asphaltenes	at 25°C (P^{25})	at 0°C (P^0)	at 25°C (D^{25})	at 0°C (D^0)	softening point, °C (R&B)	breaking point, °C
1	BN-90/130	49,0	24,1	26,9	98	11	45	6,0	48,5	—16
2	BN-60/90	48,1	33,8	18,1	68	6	100	5,5	49,5	—12
3	BN-90/130	46,3	30,2	23,5	102	8	100	8,0	45,5	—9
4	BN-60/90	49,8	20,0	30,2	69	11	95	3,5	57,0	—18
5	BN-60/90	36,5	48,4	15,1	90	8	100	0,0	52,5	—4,5
6	BN-60/90	50,6	21,3	28,1	86	18	45	2,5	59,5	—28
7	BND-90/130	44,2	34,0	21,8	92	36	60	6,5	51,0	—25
8	BN-90/130	45,3	33,7	21,0	111	32	100	3,9	45,5	—20
9	BND-40/60	46,7	29,1	24,2	55	20	48	2,5	51,0	—14
10	BND-90/130	50,1	28,5	21,4	100	32	100	4,3	44,5	—19

---

*Determined by adsorption chromatographic analysis.

TABLE 2

Asphalt No.	Viscosity, Pa·sec								
	140 °C	130 °C	120 °C	110 °C	100 °C	90 °C	80 °C	70 °C	60 °C
1	0,23	0,30	0,47	0,92	2,35	5,5	18,7	70,2	330
2	0,25	0,38	0,65	1,30	2,65	5,85	17,0	49,1	175
3	0,17	0,25	0,35	0,64	1,3	2,94	9,0	32,6	132
4	0,27	0,42	0,85	1,95	5,2	24,9	117,5	680	5800
5	0,43	0,68	1,25	2,55	5,8	14,1	70,1	147	610
6	0,32	0,49	1,00	2,56	7,9	22,3	170,0	910	6630
7	0,42	0,65	1,25	2,10	4,7	12,4	34,5	125	416
8	0,40	0,60	1,10	2,10	4,1	6,9	19,8	59,5	249
9	0,40	0,60	1,30	2,30	4,6	11,1	31,5	96	357
10	0,20	0,30	0,60	1,10	2,1	4,9	12,5	37,5	120,8

TABLE 3

Temperature, °C	Viscosity of asphalt, Pa·sec				
	initial	after aging with free air access (τ = 289.5 h)		after aging with limited air access (τ = 533.5 h)	
		at t_s = 140°C	at t_{ss}	at t_s = 140°C	at t_{ss}
Asphalt No. 9, t_{ss} = 114°C, η_m = 1.6 Pa·sec					
95	3,2	14,8 (4,6)	5,3 (1,7)	20,2 (6,4)	6,4 (2,0)
90	4,9	25,0 (5,1)	8,7 (1,8)	34,4 (7,0)	10,1 (2,1)
80	12,5	80,8 (6,5)	22,6 (1,8)	113,0 (9,0)	30,2 (2,4)
70	37,5	306,5 (8,2)	69,9 (1,9)	449,0 (12,0)	96,0 (2,6)
60	120,8	1321,0 (10,9)	278,0 (2,2)	—	368,0 (2,9)
Asphalt No. 10, t_{ss} = 112°C, η_m = 0.9 Pa·sec					
95	7,1	31,5 (4,4)	11,4 (1,6)	173,0 (24,4)	19,1 (2,7)
90	11,1	57,6 (5,2)	18,5 (1,7)	342,0 (30,8)	32,8 (2,9)
80	31,5	184,0 (5,8)	52,6 (1,7)	1292,0 (41,0)	100,0 (3,2)
70	96,0	710,0 (7,4)	193,5 (2,0)	—	369,0 (3,8)
60	357,0	—	700,0 (2,0)	—	—

Notes: 1. The maximum service temperature in summer is 60-65°C. 2. The aging index is in parentheses. 3. η_m is the lowest viscosity of the critically fractured structure.

If the asphalt was exposed to the temperature t_{ss} (when supramolecular structures are formed in it), the aging index was 3-10 times less than at 140°C (Table 3). It is especially important that at the service temperatures it was practically the same as at the temperatures of the technological process. Another conclusion is extremely important for practical purposes (see Table 3): with sealing of the equipment in which the asphalt was processed, the change of the asphalt's properties was retarded even more significantly. It is of interest that the mass of the specimens of all the studied asphalts increased in this case [3].

The strength change of the asphalts was studied by separation [7] from polished steel plates; the functional groups and types of intramolecular bonds were determined in parallel by IR spectroscopy. Special attention was paid to the oxygen-containing compounds that

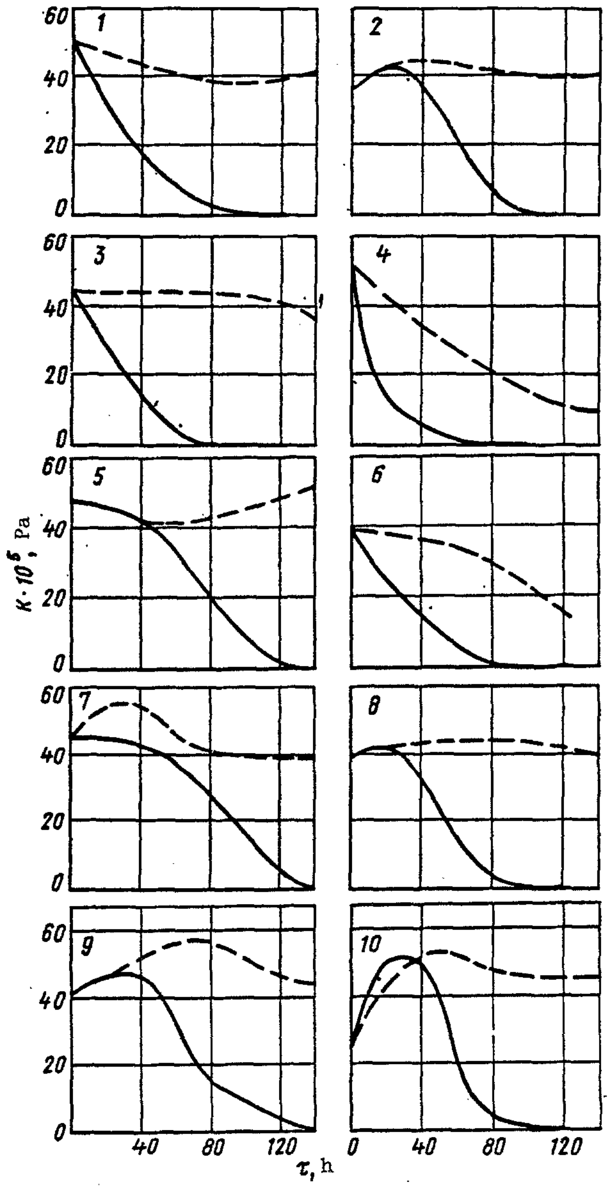

Fig. 1. Relation of the cohesion K of the asphalt to the aging time τ: ——) in the state of a Newtonian fluid (at 140°C); ---) at a temperature corresponding to the formation of supramolecular structures; 1-10) asphalt No.

formed during aging. However strange it may seem, these compounds have not yet been given attention, despite the known fact of intensification of aging of asphalts under the effect of oxygen. It was possible to determine that after 80 h of aging at 140°C the cohesion decreased to almost zero (Fig. 1). During aging at t_{ss}, the strength of asphalts of types II and III* did not change in comparison with the initial strength. For asphalts of type I, having the best service properties but most prone to undergo aging during processing, the cohesion was 50-80% of the initial cohesion.

Analysis of the infrared absorption spectra (Fig. 2) shows that the intensity of a band at 1705 cm^{-1} (vibrations of C=O groups) changed during aging from zero (in some initial asphalts these structures were contained in very insignificant amounts) to the maximum value. The cohesion increased in parallel to the increase of the intensity of the absorption band at 1705 cm^{-1}. The maximum strength values were attained at identical intensity of the bands at 1705 and 1610 cm^{-1} (vibrations of aromatic rings). With a further increase of the content of structures corresponding to the band at 1705 cm^{-1}, the cohesion decreased. If the aging was

---

*According to A. S. Kolbanovskaya's classification [8].

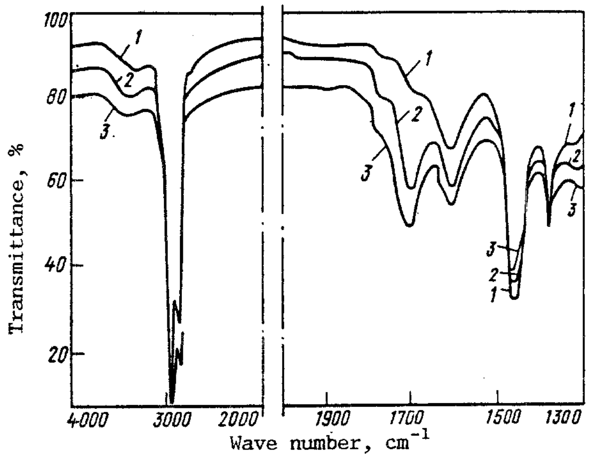

Fig. 2. IR spectra of asphalt (No. 1): 1) initial; 2, 3) after aging at 140°C for 24 and 72 h, respectively.

carried out at 140°C, the strength of most of the investigated asphalts decreased to zero when the correlation of the intensities of the mentioned bands was 1.6 ± 0.1.

The obtained data indicate that the most complete and objective information on the properties of asphalts can be obtained only in a complex investigation of several methods of analysis. As a result, the temperatures of formation of physical association complexes were determined: 115-135°C for asphalts BND-40/60, 110-130°C for asphalts BN-60/90 and BND-60/90, and 105-145°C for asphalts BN-90/130 and BND-90/130.

It was also determined that supramolecular structures were responsible for the thermal stability of the asphalts (volatilization of light fractions was retarded 3-8 times, and aging occurred 3-10 times more slowly, with the curve of the temperature dependence of the viscosity remaining flattened) and that oxygen-containing compounds (structures corresponding to a band at 1705 cm^{-1} and their correlation with structures corresponding to a band at 1610 cm^{-1}) were responsible for the cohesion of the asphalts. The potential possibilities of asphalts as binding materials have been used far from completely. For their realization, asphalts must be processed at temperatures where the side chains in the molecules of asphaltenes and resins, determining the most important service characteristics, i.e., the elasticity and the breaking point, are shielded by molecules of the dispersing medium that are adsorbed by them.

LITERATURE CITED

1. S. R. Sergienko, B. V. Taimova, and E. I. Talalaev, High-Molecular-Weight Nonhydrocarbon Compounds of Crude Oil [in Russian], Nauka, Moscow (1979).
2. K. I. Ivanov, Intermediates and Intermediate Autoxidation Reactions of Hydrocarbons [in Russian], Gostoptekhizdat, Moscow and Leningrad (1949).
3. V. D. Portnyagin, Characteristics of the Preparation of Asphalts and Asphalt-Concrete Mixes [in Russian], IPK Minavtodora RSFSR, Moscow (1988).
4. Z. I. Syunyaev, Applied Physicochemical Mechanics of Disperse Petroleum Systems [in Russian], MINKh i GP im. I. M. Gubkina, Moscow (1982).
5. N. M. Émanuél', G. E. Zaikov, and Z. K. Maizus, Role of the Medium in Radical-Chain Oxidation Reactions of Organic Compounds [in Russain], Nauka, Moscow (1973).
6. F. F. Cheshko, Chemical Structure of Molecules and Reactivity of Aliphatic Substances [in Russian], Khar'kovskii Gosuniversitet, Kharkov (1970).
7. I. V. Korolev, K. S. Drozdov, and B. I. Degtyarev, Izv. Vyssh. Uchebn. Zaved. Stroit. Arkhit., No. 3, 71-73 (1976).
8. A. S. Kolbanovskaya and V. V. Mikhailov, Paving Asphalts [in Russian], Transport, Moscow (1973).