VARIETY AND QUALITY OF ASPHALTS PRODUCED FROM COMMERCIAL WEST SIBERIAN CRUDE

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In connection with the increasing volume of construction and the more severe service conditions being imposed on structural objects and articles in which petroleum asphalt is used, we are finding more severe demands on asphalt quality, along with requirements for an increasing number of different types of products.

If we can resolve the question of quality improvement and expansion of the asphalt product line, with due allowance for specific conditions of asphalt application and service, this will undoubtedly lead to an increase in the service life of buildings, facilities, and other structural items. In turn, this will be one of the basic and most effective means for resolving the problem of how to satisfy more fully the demand for asphalts, where we are currently experiencing a severe shortage [1, 2].

It has been established by various studies that the chemical composition of the original crude oil is the main factor determining the manufacturing technology and the properties of the asphalt products.

In the USSR, residual stocks from more than 40 crude oils from different fields are being used in asphalt production, these crude oils being processed either separately or in mixtures. In the total volume of crude oil being processed, the relative amount of West Siberian crudes is increasing every year. A number of manufacturing plants in our industry-branch are currently receiving and processing a commercial mixture of West Siberian crudes, the residua from which are being used in asphalt production. Here we refer to the plants of the production associations "Omsknefteorgsintez" and "Angarsknefteorgsintez," and the Khabarovsk and Ufa Petroleum Refineries. Studies performed at BashNII NP and at MINKh i GP [Gubkin Moscow Institute of the Petrochemical and Gas Industry], along with the operating experience gained in these refineries and plants, have shown that West Siberian crudes are good starting materials for asphalt production.

In the present communication, we are setting forth requirements on feedstock and processing technology for the manufacture asphalts for various purposes, in the example of the commercial mixture of West Siberian crudes received at the Ufa Petroleum Refinery. The mixed crude contains 1.5% asphaltenes, 9.3% resins, 2.2% wax, and 1.2% sulfur. The yield of TBP residue distilling above 350°C is 49%, and the yield of residue above 500°C is 21.2%. The physicochemical characteristics of this crude indicate that it differs considerably from the corresponding commercial Romashkino crude formerly processed in most of the refineries of our industry-branch. In view of the low content of asphaltenes in the West Siberian crude, along with a relatively high content of resins and aromatic hydrocarbons (which are good solvents for the asphaltene materials), the straight-run residua and the asphalt obtained by propane deasphalting are distinguished by low viscosity (R & B softening point of the straight-run resid is 18-22°C, and softening point of the asphalt from deasphalting 34-36°C, in comparison with 37-49°C and 50-56°C for the respective products from Romashkino crude) [3]. This characteristic of the residua from the mixed West Siberian crude is reflected very significantly in the quality of the asphalt products that are obtained and also in the production technology and processing conditions.

In order to manufacture a wide variety of asphalts to meet present and future requirements, the following basic approaches are available in processing West Siberian crude for asphalt manufacture:

a) Oxidation of the straight-run resid or the precipitated asphalt alone, to give the required grade of asphalt.

b) Compounding the straight-run resid with the precipitated asphalt (obtained by de-

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TABLE 1. Variety and Quality of Asphalts Obtained by Oxidation of Different Residual Stocks from Commercial West Siberian Crude

Number	Original feedstock	Asphalt quality: softening point, °C	needle penetration at 25°C	needle penetration at 0°C	ductility (in cm) at 25°C	ductility (in cm) at 0°C	breaking point, °C	Asphalt grade
1	Straight-run resid with viscosity of 20-40 sec at 80°C	39	210	47	70		—22	BND 200/300*
		41	165	42	85	9,3	—20	BND 130/200*
		45	120	36	95	6,5	—19	BND 90/130*
		49	80	28	110	4,0	—17	BND 60/90*
		56	56	22	70	—	—12	BND 40/60*
		65	40	17	13	—	—	BNI -IV-3*
		75	28	13	5	—	—	BNI -IV*
		90	22	9	2,5	—	—	BNI -V*
2	Mixture of straight-run resid with precipitated asphalt (30-50% asphalt)	41	150	36	135	—	—19	BND 130/200
		43	124	30	140	—	—17	BND 90/130
		48	80	26	140	—	—16	BND 60/90
		52	56	19	140	—	—13	BND 40/60
		72	22	—	7,4	—	—	BN IV
		94	11	—	2,9	—	—	BN V
3	Precipitated asphalt oxidized to R and B 100°C and diluted with straight-run resid	39	220	52	100	—	—22	BND 200/300*
		43	160	44	130	8,6	—20	BND 130/200*
		47	108	32	140	—	—18	BND 90/130*
		49	85	27	100	4,5	—17	BND 60/90*
		57	45	16	44	—	—12	BND 40/60*
4	Precipitated asphalt with R and B softening point of 34-36°C	41	129	24	>140	—	—	BN 90/130
		45	78	16	>140	—	—	BN 60/90
		52	43	11	>140	—	—	BN 40/60
		92	8	—	2,0	—	—	BN V
5	Extra-light straight-run resid or blend of regular straight-run resid with vacuum gas oil	41	190	—	—	—	—	BNK 45/180*
							—	
		93	30	—	—	—	—16	BNK 90/30*

*With State Seal of Quality.

asphalting the straight-run resid) or with other residual stocks, followed by oxidation of the blend to give the required grade of asphalt.

c) Over-oxidation of a resid (for example, the asphalt recovered in straight-run resid deasphalting), with subsequent dilution of the oxidized product with straight-run resid or with an extract from lube oil solvent treating, to give the required grade of asphalt.

We should note that all of these approaches include an oxidation process, in one stage or another. Thus, the rather widespread practice of manufacturing asphalts by direct blending of propane-precipitated asphalt with a straight-run resid or with extracts is not feasible when processing West Siberian crude resids, in view of their low viscosities in comparison with resids from other commercial crudes processed in the fuel/lube scheme.

In Table 1 we show the quality requirements for residual stocks from commercial West Siberian crude as a feedstock for the oxidation process and the assortment of asphalts obtained from these stocks, in application to processing of these resids in an oxidation tower as currently practiced in 16 refineries of our industry-branch.

As can be seen from these data, a wide variety of high-quality asphalts conforming to new GOST standards can be produced by using the regular straight-run resid as an oxidation feedstock (this resid has a cut point of approximately 480-490°C and a viscosity at 80°C generally within the range 20-40 sec); among the asphalts that can be produced by this method we may mention paving asphalts, waterproofing asphalts, roofing asphalts, and compositions for sealing cable boxes and battery containers. Most of these asphalts will meet the requirements for products with the State Seal of Quality.

When using a mixture of the SR resid with 30% precipitated asphalt as the feedstock, paving asphalt binders can be obtained in grades BND and BN meeting the new standard GOST 22245—76, as well as construction asphalts meeting GOST 6617—76 and asphalt potting compositions for cable boxes meeting GOST 6997—77. If the percentage of the precipitated asphalt is increased to 50%, it is no longer possible to produce grade BND paving asphalts, as the materials fail to meet the specifications for penetration at 0°C and breaking point. Any further increases in the amount of precipitated asphalt in the mixture will limit the assortment of asphalts that can be produced to an even greater degree.

The next method, which consists of over-oxidation of the precipitated asphalt to an R & B softening point of the order of 80°C, and then diluting with SR resid, will give satisfactory paving asphalt binders BND and BN. If the degree of over-oxidation of the precipitated asphalt is increased, so that the product is brought to a softening point of the order of 100°C and then diluted with the same SR resid, the paving asphalt binders can be obtained with the State Seal of Quality.

The precipitated asphalt (from propane deasphalting of the SR resid) is not a very good raw material for asphalt production when it is used by itself. When it is oxidized, the products obtained are usually paving asphalt binders in grade BN, construction asphalts in grades BN 50/50 and BN 90/10, and other types of low-melting, brittle asphalts, such as those used as binders in briquetting coal dust, or as structure-forming agents in oil-well drilling fluids.

In recent years, a number of major consumers (production of soft roofing materials, insulating and waterproofing operations, the electrotechnical industry, etc.) have been imposing particularly severe requirements on asphalts in relation to their heat and cold resistance, i.e., on their ability to remain in a viscoplastic state over a wide range of temperatures. With an R & B softening point corresponding to construction grades of asphalts (70-100°C), they must have a brittle point of -10 to -20°C, i.e., at the level of paving asphalt binders. The production of such asphalts involves considerable difficulty in practice, since the softening point and the breaking point, which nominally characterize the heat and cold resistance of the asphalt (with a given value of the penetration at 25°C), are opposed to each other. Hence, up to the present time there has been practically no production organized for highly plastic asphalts in the USSR, and the primary consumers of such products have been forced to use asphalts that are not up to the proper quality level and do not give products that are reliable or long-lived.

For the production of highly plastic asphalts, it is necessary to use a raw material that is rich in oil components of a certain distillation range and chemical composition, since these components are the carriers of cold resistance for asphalts. Heat resistance of asphalts is achieved at the expense of the asphaltenes, which are accumulated in the process of raw material oxidation.

In countries other than the USSR, an oxidation feedstock prepared by compounding an SR resid with oil fractions is used in producing highly plastic asphalts [4-6]. In the case of the mixed West Siberian crude, this general method of feedstock preparation is being used in the following version: The regular SR resid is compounded with a heavy vacuum distillate in amounts up to 10%, thus giving an oxidation feedstock with a viscosity of 5-15 sec at 80°C, containing 70-75% oil components (in comparison with 60-65% in the original SR resid). The heavy vacuum distillate used for blending must correspond approximately to the oil fraction IV, with a kinematic viscosity of at least 8 cSt at 100°C and a flash point no lower than 220°C. The oxidation of this sort of blended feedstock will give the following highly plastic asphalts: "Plastbit," roofing asphalts BNK 45/180, BNK 90/30, and BNK 90/40, with the State Seal of Quality.

The recommended formula and feedstock properties that are shown in Table 1 relate to the process of oxidation in a tower without internals, under conventional conditions: oxidation temperature 250-270°C, air load $4 m^3/m^2$ of vessel cross section.

If these feedstocks are oxidized in batch shellstills, the variety and quality limits on the resulting asphalt products are narrowed quite considerably. In order to produce a wide variety of asphalts in a shellstill, the feedstock must have a smaller amount of precipitated asphalt (methods 2 and 3) and a larger quantity of oil components (methods 1 and 5). For example, with method 5, the amount of vacuum distillate in the feedstock must be of the order of 20%. In contrast, when the oxidation process is performed in a tubular reactor, the feedstock may be a regular SR resid (methods 1 or 5) or blends of the SR resid with larger amounts of precipitated asphalt (methods 2 and 3). The tubular reactor, owing to the highly developed and constantly changing contract surface between the reacting phases, and also the shorter residence time of the oxidized product in the reaction zone, gives asphalts with better plastic and adhesive properties in comparison with products obtained from the same feedstock in other types of oxidation equipment. Oxidation towers are currently recommended for production of the large-volume grades of paving and construction asphalts, as such apparatus has the advantages of high capacity and simplicity in design and operation; however, for the production of highly plastic hard asphalts such as insulating, waterproofing, or roofing asphalts or "Plastbit," it is advisable to use tubular reactors.

It should be noted that the processing of residual stocks from West Siberian crudes to manufacture asphalts requires more severe conditions in the oxidation process (higher oxidation temperature and air input) in comparison with oxidation of the corresponding residual stocks from other crudes such as Romashkino, without any adverse effects on the variety and quality of the asphalt products obtained.

Thus, from a comparative evaluation of different commercial crudes being processed today in the manufacturing plants of Minneftekhimprom SSSR [Ministry of the Petroleum Refining and Petrochemical Industry of the USSR], we can conclude that the West Siberian crudes are the best from the standpoint of asphalt production, since appropriate processing of the residual stocks from these crudes will provide the widest variety of high-quality asphalts, in comparison with the processing of residual stocks from other USSR crudes.

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SOLUBILITY OF WATER IN NORMAL ALKANES AT ELEVATED TEMPERATURES AND PRESSURES

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The solubility of water in liquid hydrocarbons increases with increasing temperature. The data of the greatest interest are those on the solubility of water in the region of three-phase equilibrium, with coexistence of hydrocarbon liquid (solution of water in liquid hydrocarbon), aqueous liquid (solution of hydrocarbon in water), and gas phase (mixture of water and hydrocarbon vapors).

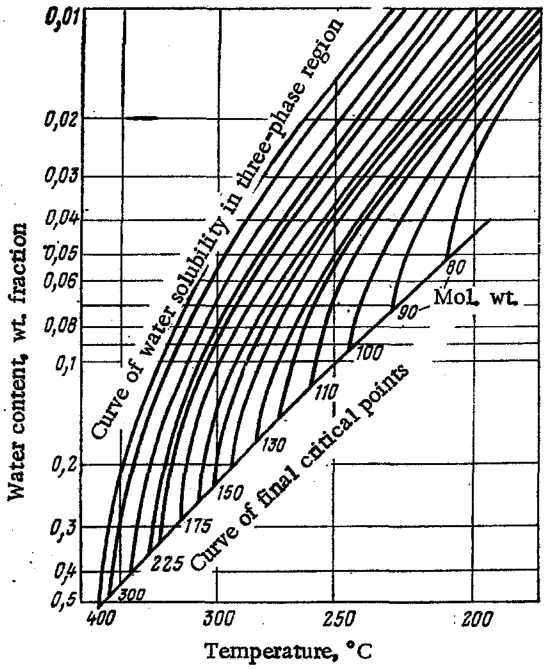

Fig. 1. Solubility of water in liquid hydrocarbons in relation to molecular weight of hydrocarbon (or temperature of final critical point of hydrocarbon/water system) and temperature of three-phase equilibrium.

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