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VISBREAKING RESIDUES AS COMPONENTS OF FEEDSTOCK FOR PAVING ASPHALTS

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A crude-oil residue visbreaking unit has been operating for a long time at the Moscow Refinery [1]; it solves the problem of boiler fuel production in the winter. In the summer, it does not run due to the difficulties of utilizing visbreaking residue (VR), although year-round operation is economically expedient. A rational way to use the residue could be in production of asphalt, for which the demand is very high in the summer construction season.

The use of VR as a component of feedstock for residual, oxidized, and mixed asphalts has been examined at different times by many investigators [2-4]. Viscous BN paving asphalts according to GOST 22245 and soft varieties – BN 60/90 and BN 90/130 – are usually manufactured with it, since they are relatively simple to produce with this technology. However, BN asphalt is difficult to sell due to its universal displacement by higher quality BND asphalt and also because there is a demand in the Moscow region for production of better paving asphalt than BND. This only complicates the problem of utilizing VR as asphalt feedstock.

The data obtained by the different investigators are poorly reproducible due to the differences in the quality of the initial crude oils and the implementation of the processes, and the use of certain technical methods not disclosed in the publications. For this reason, laboratory studies of different variants of using VR in production of asphalts from mixed west Siberian and Ukhta crudes were conducted at the Moscow Refinery to solve the problem of rational utilization of VR. The quality of the asphalt obtained was evaluated with the active GOST 22245.

TABLE 1

t_f, °C	t_s (R & B method), °C		t_{br}, °C		P, 0.1 mm			D, cm		
	before heating	after heating	before heating	after heating	at 25°C	at 0°C	at 25°C after heating	at 25°C	at 0°C	at 25°C after heating
					>500 °C Residues					
320	48	52	–8	–4	59	22	30	>100	2.0	>100
315	51	55	–10	–5	33	10	27	>100	1.0	88
310	50	55	–3	+1	25	5	15	>100	0.5	83
					>480°C Residues					
306	45	50	–12	–10	67	19	32	>100	5.2	>100
310	45	50	–10	–6	65	21	28	>100	1.5	90
315	48	54	–10	–8	36	11	20	>100	1.3	84

Note. t_f, t_s, t_{br}: flash, softening points, and brittleness temperature; P: penetration; D: ductility.

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TABLE 2

Added asphalt	t_s (R & B), °C		t_{br}, °C		P, 0.1 mm			D, cm		
	before heating	after heating	before heating	after heating	at 25°C	at 0°C	at 25°C after heating	at 25°C	at 0°C	at 25°C after heating
>500°C residue										
BND 60/90	49	53	–15	–12	60	21	36	>100	4.5	60
>480°C residue										
BND 40/60	48	51	–15	–11	68	20	37	>100	5.1	88
BND 60/90	47	50	–16	–13	71	20	48	>100	6.0	69

TABLE 3

Feedstock	t_s (R & B), °C		t_{br}, °C		P, 0.1 mm			D, cm		
	before heating	after heating	before heating	after heating	at 25°C	at 0°C	at 25°C after heating	at 25°C	at 0°C	at 25°C after heating
>360°C VR	51	56	–20	–16	57	24	43	97	5.3	30
The same	47	52	–20	–18	75	27	49	>100	7.8	49
>420°C VR	49	58	–14	–12	45	19	32	60	4.5	12
Mixed >360°C VR and vacuum resid	48	53	–15	–15	60	25	43	>100	5.7	62

It is necessary to note that asphalts made from cracked tars always have worse indexes than other asphalts and are even placed in a separate class [3]. Moreover, it is necessary to consider that visbreaking is a variant of the thermal cracking with low conversion conducted at the Moscow Refinery in relatively mild conditions. For this reason, the target product of this process, VR, is the >180°C cut obtained after taking off only the gas and naphtha cut from the reaction mixture [1].

A technologically possible variant of direct production of asphalt from VR by vacuum distillation, i.e., by concentration of VR to the condition of commercial paving asphalts, was investigated first. This method is attractive for production of essentially residual asphalts, for which there has been a recent tendency to develop production [5].

It is important to note here that GOST 22245–90, Am. 1, directly notes the feasibility of using cracked tar as a component of asphalt feedstock but not as asphalt. For this reason, we can suggest the possibility of producing a product that satisfies the standard. Nevertheless, it is clear that the notion of “component” does not give distinct limits for using VR in commercial asphalts, so that some degree of freedom is possible in this case.

Concentrated >480 and >500°C residues were produced in the laboratory from industrial >180°C VR by Manovyan distillation and the quality indexes were analyzed according to GOST 22245 and additionally according to GOST 18180 after heating them.

The results of the analysis reported in Table 1 show that the >500 and >480°C concentrated residues have a softening point from 48 to 51 and from 45 to 48°C, i.e., based on this index, they are on the level of the requirements of the standard for BND and BN paving asphalts. All of the residues have very high ductility at 25°C. However, penetration at 25 and 0°C was outside of the limits in the standards for BND asphalts and corresponded to BN 60/90 only for a low softening point (45°C).

TABLE 4

Asphalt	Vacuum resid content, wt. %	Asphalt quality indexes										
		before heating							after heating			
		t_s (R & B), °C	t_{br}, °C	*P*, 0.1 mm		*D*, cm		penetration index	t_s (R & B), °C	t_{br}, °C	*P*, (at 25°C), 0.1 mm	*D* (at 25°C), cm
				at 25°C	at 0°C	at 25°C	at 0°C					
>360°C Residue (t_s = 31°C with B & R, NV_{80}**=43 sec)												
Oxidized	0	47	–20	75	27	>100	7.8	–1.0	52	–17	49	49
Oxidized	0	57	–15	41	–	42	–	0	–	–	–	–
Mixed	20	49	–19	68	28	>100	4.9	–0.2	54	–12	40	45
Oxidized	0	72	0	16	–	5.1	–	+0.6	–	–	–	–
Mixed	50	47	–15	64	22	>100	5.6	–1.2	53	–12	44	60
>420°C Residue (t_s = 37°C with B & R, NV_{80}**=73 sec)												
Oxidized	0	49	–14	45	19	41	4.3	–1.7	56	–12	32	11.6
Oxidized	0	58	–10	38	–	19.3	–	+0.2	–	–	–	–
Mixed	20	48	–15	63	25	97	4.2	–1.0	53	–11	42	34
Oxidized	0	70	–16	18	–	5.3	–	+0.6	–	–	–	–
Mixed	45	47	–20	65	25	>100	3.5	–1.1	51	–16	45	48

Notes. * Determined with the nomogram in [3].
** Nominal [Engler] viscosity at 80°C.

In addition, all of the residues had unsatisfactory low-temperature properties: the brittleness temperature varied from –3 to –12°C, which does not satisfy the requirements for BND asphalts for the given penetration. Concentrated VR, like residual asphalts, do not correspond to commercial BND paving asphalts, but BN 60/90 asphalt, for which low-temperature indexes have not been standardized, can be obtained from them. Similar data are reported in [2].

After heating concentrated VR, the softening point changed within the limits of the standard, penetration was 45-85% of the initial penetration, the ductility remained high, the mass did not change, and the brittleness temperature increased by 2-5°C.

Evidence of the positive qualities of concentrated VR (high ductility before and after heating) led to experiments to improve their low-temperature properties to obtain compound asphalts, primarily the most popular BND 60/90 brand.

Concentrated VR was mixed with refinery heavy petroleum products in a laboratory mixer at 120°C for 20 min: vacuum resid with nominal [Engler] viscosity of 50 and 24 sec from AVT units, atmospheric resid with nominal [Engler] viscosity of 10°E, vacuum gasoil with IBP of 327°C, oxidized BND 40/60 and BND 60/90 paving asphalts with a softening point of 52 and 48°C, respectively. The amount of the added component was a function of the required softening point of paving asphalts (47-51°C) and was 3-20 wt. % in the case of unoxidized products and 50 wt. % in the mixture in the case of oxidized products.

It was found that the brittleness temperature of concentrated VR decreased insignificantly on addition of vacuum resid from the AVT-6 unit (maximum of 15% content of cuts under 500°C) – only by 3-4°C, and when vacuum resid from the AVT-3 unit (up to 26% content of cuts under 500°C), atmospheric resid, or vacuum gasoil was added, it only increased by 7-8°C, but the standards for this index have not been established for BND grades.

Mixing concentrated VR with commercial oxidized BND 40/60 and BND 60/90 asphalts demonstrated the possibility of incorporating these asphalts in up to 50% residues, since the product obtained satisfies the requirements

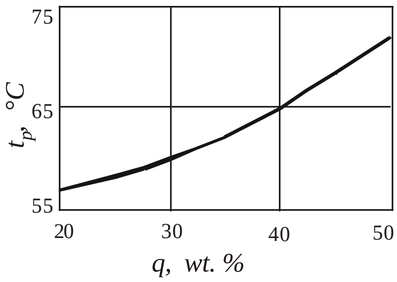

Fig. 1. Correlation of the softening point t_s of visbreaking residue oxidized in excess and amount q of vacuum resid mixed with it to produce BND 60/90 asphalt.

of the standard, including after heating. This method can thus be considered one direction for use of concentrated VR. It is technologically feasible when the vacuum towers of low-capacity VT units are freed. The quality indexes of the products obtained in mixing oxidized asphalts with concentration VR in the ratio of 1:1 (by wt.) are reported in Table 2.

The subsequent studies were aimed at determining the quality of the asphalts obtained by oxidation of VR with air with existing technology. High end-point >360 and >420°C VR were produced in laboratory conditions on an ARN-2 setup and oxidized in a laboratory still at 250±5°C and air flow rate of 4 liter/(kg×min). The quality indexes of the oxidized VR are reported in Table 3.

Their oxidation time was 1.5-2 times less than the oxidation time for vacuum resids and the amount of blowing was on average 9% (3% uncondensed oxidation gases, 6% black solar oil), i.e., slightly higher than what is usually observed in laboratory oxidation of asphalts (under 5%).

As follows from Table 3, standard grades of asphalt – BND 40/60 and BND 60.90, characterized by high ductility and improved low-temperature properties, were obtained by oxidation of high end-point VR (>360°C). Oxidation of more concentrated VR (>420°C) did not result in commercial grades of viscous paving asphalt.

Testing of asphalts produced by oxidation of >360°C VR for thermal stability according to GOST 18180 showed that their softening point increased by a maximum of 5°C, penetration after heating was 65-75%, ductility was 30-50% of the initial values, the weight did not change, and the brittleness temperature increased from –20 to –16°C.

The possibility of producing paving asphalts by oxidation of mixed >360°C VR and commercial vacuum resid in a 1:1 ratio (wt.) was also determined. The oxidation time was 1.5 times longer than for oxidation of pure VR, but BND 40/60 and BND 60/90 paving asphalts were also produced, although with a slightly worse brittleness temperature but better ductility after heating (see Table 3). It is thus possible to produce standard BND paving asphalts by oxidation of >360°C VR and a 1:1 mixture of VR with vacuum resid.

The method of producing standard paving asphalts by slightly excessive oxidation of high end-point >360 and >420°C VR with subsequent dilution of the product obtained with unoxidized vacuum resid from an AVT-6 unit was investigated as one of the possible industrial variants. Laboratory high end-point VR was oxidized in a still to different softening points (57-72°C) and diluted with vacuum resid with a nominal [Engler] viscosity of 62 sec (from an AVT-6 unit) in different ratios as a function of the softening point of the oxidized component.

The quality indexes of the oxidized and mixed products are reported in Table 4. For the indicated softening points of the oxidized part and the amounts of vacuum resid, commercial BND 60/90 paving asphalt was obtained with a more important quality margin in the case of a smaller degree of oxidation and dilution. Low penetration indexes were characteristic of all samples obtained with this method. We can hypothesize, however, that this index should be higher in industrial conditions, since we know [3] that for the same softening point, asphalts obtained by continuous oxidation in a tower are more plastic than asphalts produced by periodic oxidation in a still.

The method of so-called [4] peroxidation–dilution of VR can thus be used for production of commercial grades of asphalt according to GOST 22245. The experimentally obtained correlation of the softening point of the component oxidized in excess and the amount of vacuum resid required for dilution in production of BND 60/90 asphalt is shown in Fig. 1.

In generalizing the above, we can draw a conclusion concerning the suitability of visbreaking resids from mixed west Siberian and Ukhta crude oils for production of BND grade paving asphalts. Direct oxidation after removal of the solar oil cut and oxidation after mixing with vacuum resid are the most suitable variants. These residues can be oxidized in excess and then mixed with vacuum resid.

Finally, if necessary, exhaustively distilled VR can be added to ordinary oxidized BND asphalts while still satisfying the requirements in the standard. The reasonable combination of these methods as a function of the production situation should ensure continuous manufacture of standard grades of paving asphalt and year round operation of visbreaking units.

REFERENCES

1. A. A. Abrosimov, N. Yu. Belokon', V. G. Kompaneets, et al., *Khim. Tekhnol. Topl. Masel,* No. 2, 47-50 (1998).
2. A. V. Ishkil'din, S. L. Aleksandrova, and S. S. Mingaraev, *Ibid*., NO. 1, 17 (1997).
3. R. B. Gun, *Petroleum Asphalts* [in Russian], Khimiya, Moscow (1989).
4. I. B. Grudnikov, *Production of Petroleum Asphalts* [in Russian], Khimiya, Moscow (1983).
5. Yu. A. Kut'in, I. R. Khairudinov, S. S. Mingaraev, et al., *Neftepererab. Neftekhim.*, No. 9, 20-23 (1998).