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USAGE OF PYROLYSIS HEAVY RESIN FOR THE PETROLEUM BITUMEN PRODUCTION

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Abstract. *The investigation results of tar and pyrolysis heavy resin joint oxidation, as well as the results of commercial bitumen modification by pyrolysis heavy resin are presented. The possibility of the latter compound usage in the processes of petroleum bitumen production is shown.*
Keywords: bitumen; modification; oxidation; pyrolysis heavy resin; tar.

1. Introduction

Various technologies and different types of oil are used for bitumen production. It is well-known that bitumen operational properties most of all depend on its group composition. In particular, the high concentrations of resins and asphaltenes ensure the optimum operational properties. The residuals of paraffinic oils are usually reckoned as bad crude for bitumen production because during their oxidation the concentration of resins and asphaltenes is less than those while oxidation of aromatic oils. One of the possible decisions of this problem is the change of group composition due to the introduction of individual high-aromatic products into the crude.

2. Analysis of investigations and publications

Pyrolysis Heavy Resin (PHR) is one of the hydrocarbons pyrolysis by-products [Mukhina et al. 1987]. This product is characterized by high content of aromatic and unsaturated hydrocarbons [Lebedeva et al. 2010]. PHR may be used for the production of individual aromatic hydrocarbons, concrete plasticizer, dark petroleum resins, etc. [Lesokhina et al. 1977; Dumskyi 1988]. However the main application of the mentioned product is a fuel oil component. Authors [Kutsuev, Budnik 2012] studied EP-300 pyrolysis heavy resin to use as a crude component for compounded petroleum bitumen production. It was established that using PHR in amount of 20 mass % in the crude allows to double the installation productivity at the same technological parameters. Article [Kutsuev, Budnik 2012] deals with the study of bitumen production from aromatic oil residuals therefore the effect of paraffinic tar and pyrolysis heavy oil joint oxidation is unknown.

The **aim** of the work is to examine the effect of pyrolysis heavy resin on the oxidated bitumen obtained from paraffinic tar which was produced from the mixture of West-Ukrainian oils and to establish the possibility of such application.

3. Experimental part

To obtain oxidated petroleum bitumen we used a tar produced from West-Ukrainian paraffinic oils withdrawn at JSC "NPK-Galychyna" (Drogobych, Lviv region). Its characteristics are following: softening temperature by "ring and ball" method – 42ºC; ductility at 25ºC – 13 cm; penetration at 25ºC – 245x0.1 mm. We also used BNB-70/30 commercial building bitumen produced at JSC "NPK-Galychyna" (Drogobych, Lviv region).

To improve the petroleum bitumen properties we used pyrolysis heavy resin produced at JSC "Karpat-naftokhim" (Kalush, Ivano-Frankivsk region). Its characteristic is given in Table 1.

Table 1. PHR characteristics

Index	Index value
Density at 15°C, g/cm^3	1.085
Pour point, °C	5
Flash point, °C	89
Cokeability, %	15.1
Sulphur content, mass%	0.04
Water content, mass %	0.12
Ash content, %	0.01

The oxidation of tar and PHR mixture was carried out at the laboratory plant consisted of a reactor block, air supply system and system of cooling and volatile oxidation products trapping. The compounded bitumen was obtained at the laboratory mixing plant. The ductility at 25ºC (according to GOST 11505-75), penetration at 25ºC (according to GOST 11501-78) and softening temperature by "ring and ball" method (according to GOST 11506-73) were determined for the obtained samples.

To estimate the adhesion properties of the oxidated bitumen the index "adherence with glass" was determined in accordance with DSTU BV.2.7-81-98). The group composition was determined in accordance with [Isagulyants, Egorova 1965].

4. Results and Discussion

We studied the main regularities of tar and pyrolysis heavy resin (5–15 mass %) joint oxidations.

The results are represented in Table 2. The results of tar oxidation without PHR are given for the comparison. The oxidation was carried out at the laboratory plant at 250ºC and air volumetric rate of 2.5 h^{-1} for 3–12 hours. The PHR presence in the crude affects the oxidated bitumen properties. The introduction of 5–10 mass % of the pyrolysis heavy resin into the crude increases the softening temperature and ductility and reduces penetration.

Table 2. Characteristics of oxidated bitumen obtained while using the pyrolysis heavy resin

Index	Oxidation time, h			
	3	6	9	12
Crude – tar				
Softening temperature by "ring and ball" method, °C	45	46	47	48
Ductility at 25°C, cm	13	14	20	16
Penetration at 25°C, 0,1 mm	192	163	115	92
Adherence with glass, %	49	61	72	84
Group composition,%:				
asphaltenes	20.90	22.37	23.53	25.98
resins	24.50	24.63	25.38	24.83
oils	54.52	53.00	51.10	49.19
Crude – tar + 5 % PHR				
Softening temperature by "ring and ball" method, °C	47	48	49	51
Ductility at 25°C, cm	17	24	35	30
Penetration at 25°C, 0,1 mm	178	132	102	73
Adherence with glass, %	61	66	74	87
Group composition,%:				
asphaltenes	23.87	24.37	25.79	27.24
resins	25.50	26.19	27.11	26.87
oils	50.63	49.44	47.10	45.89
Crude – tar + 10 % PHR				
Softening temperature by "ring and ball" method, °C	46	47	49	50
Ductility at 25°C, cm	19	25	32	27
Penetration at 25°C, 0,1 mm	193	169	109	80
Adherence with glass, %	52	60	73	81
Group composition,%:				
asphaltenes	22.58	23.69	25.13	26.57
resins	24.65	25.18	26.03	25.63
oils	52.77	51.13	48.84	47.80
Crude – tar + 15 % PHR				
Softening temperature by "ring and ball" method, °C	45	47	49	50
Ductility at 25°C, cm	21	24	30	24
Penetration at 25°C, 0,1 mm	215	175	113	85
Adherence with glass, %	47	58	65	78
Group composition,%:				
asphaltenes	21.72	23.33	24.59	25.73
resins	23.33	24.12	25.14	24.88
oils	54.95	52.65	50.27	49.39

Note: oxidation temperature – 250°C, air volumetric rate – 2.5 min^{-1}.

The further increase of PHR amount slightly decreases ductility and softening temperature and increases bitumen penetration. Such dependence connects with the fact that the main part of PHR components has the increased reactivity during oxidation and positively affects the bitumen operational properties. On the other hand, the components of pyrolysis heavy resin which do not participate in the oxidation conduct themselves as diluents. The result is the decrease of bitumen hardness and refractoriness. The results of group analysis given in Table 2 confirm this fact. Moreover, using PHR we obtained bitumen with better adherence properties.

The optimum amount of PHR in the crude for bitumen production is 5–10 mass %. Such bitumen approaches to the road bitumen BND 60/90 by their main indexes. The drawback is insufficient ductility what is a specific property of all bitumen obtained from paraffinic tar.

We also studied the introduction of pyrolysis heavy resin into BNB 70/30 commercial bitumen. The results show (Table 3) that PHR introduction decreases the softening temperature and increases the penetration; bitumen ductility increases considerably.

To determine the PHR components capable to improve the bitumen properties most of all, we precipitated the pyrolysis heavy resin by petroleum-ether (ratio 1:5) at room temperature. The obtained product – a solid dark-brown substance – was used as a component for oxidated bitumen production. The investigation results show (Table 4) the increase of precipitated product amount increases the softening temperature and decreases the penetration; ductility decreases slightly. The modification of BNB-70/30 by PHR precipitated product does not give the noticeable results – the operational properties are not actually changed (Table 5).

5. Conclusions

The principal possibility of the pyrolysis heavy resin use has been established for the production of petroleum bitumen.

The main regularities of the joint oxidation of paraffinic tar and pyrolysis heavy resin have been studied. It was established that the introduction of 5–10 mass % of PHR into the crude allows to produce bitumen with the main indexes similar to those of BND-60/90 road bitumen.

The introduction of the pyrolysis heavy resin into the commercial bitumen increases its ductility.

The precipitation of PHR heaviest components out using petroleum-ether was carried out. The precipitated product was used as crude for the bitumen production.

Table 3. Modification of BNB-70/30 bitumen by the pyrolysis heavy resin

Index	PHR content, mass %			
	0	5	10	15
Softening temperature by “ring and ball” method, °C	67	57	49	44
Ductility at 25°C, cm	4	10	26	46
Penetration at 25°C, 0,1 mm	20	37	70	116

Table 4. Characteristics of oxidated bitumen obtained while using PHR precipitated product

Index	Content of PHR precipitated product, %		
	0	10	20
Softening temperature by “ring and ball” method, °C	46	50	55
Ductility at 25°C, cm	14	12	10
Penetration at 25°C, 0,1 mm	163	96	33

Note: oxidation time – 6 h; temperature – 250°C; air volumetric rate – 2.5 min^{-1}.

Table 5. Modification of BNB 70/30 bitumen by PHR precipitated product

Index	Content of PHR precipitated product, %		
	0	10 %	20 %
Softening temperature by “ring and ball” method, °C	67	67	68
Ductility at 25°C, cm	4	4	4
Penetration at 25°C, 0,1 mm	20	19	18

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І.В. Фридер[1], О.Б. Гринишин[2], Ю.Я.Хлібишин[3]. Використання важкої смоли піролізу у виробництві нафтових бітумів

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Наведено результати досліджень процесів сумісного окиснення гудрону і важкої смоли піролізу, а також модифікування товарного бітуму важкою смолою піролізу. Встановлено принципову можливість використання важкої смоли піролізу в процесах виробництва нафтових бітумів.

Ключові слова: бітум; важка смола піролізу; гудрон; модифікація; окиснення.

И.В. Фрыдер[1], О.Б. Гринишин[2], Ю.Я. Хлибишин[3]. Использование тяжелой смолы пиролиза в производстве нефтяных битумов

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Приведены результаты исследования процессов совместного окисления гудрона и тяжелой смолы пиролиза, а также модификации товарного битума тяжелой смолой пиролиза. Показано принципиальную возможность использования тяжелой смолы пиролиза в процессах производства нефтяных битумов.

Ключевые слова: битум; гудрон; модификация; окисление; тяжелая смола пролиза.

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