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## Thermal Transformations of Nitrogen-Containing Resin Bases of Heavy Oil from the Usinsk Field

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### Abstract

The paper presents results of a comparative study of composition and structure of nitrogen-containing resin bases of heavy oil from the Usinsk field before and after thermal effects at 450 °C for 30 min. Different molecular mass nitrogen-containing bases are isolated using sedimentation methods with hydrogen chloride and sulphuric acid extraction from initial and thermolysed resins. High molecular mass compounds comprise the bulk of bases in both cases, however, their fraction in thermolysed resins is substantially lower. Thermally transformed bases have lower masses compared to the initial ones. Structural group analysis and gas chromatographic-mass spectrometry techniques examine the composition of the isolated compounds. Middle molecules of nitrogen-containing resin bases of both types consist of polycyclic rings that include aromatic and saturated cycles with different alkyl frames, as demonstrated. Average species of thermolysed resin compounds are more aromatic due to a decrease in the fraction of naphthene and alkyl fragments. In the composition of bases of initial and thermolysed resins, there are alkyl derivatives of quinoline, benzoquinoline, dibenzoquinoline, and azapyrene, the maximum of the distribution of which falls at alkylbenzoquinolines. The fraction of alkylquinolines is elevated among azaarenes of thermolysed resins. A higher fraction of structures with a lower number of carbon atoms in alkyl substituents is typical for all types of bases of thermolysed resins. It may be assumed that the identified compounds would enter into the composition of distillate fractions during thermal processing of heavy hydrocarbon raw materials. This is necessary to consider in solving issues related to the preparation of high-quality fuels and lubricants based thereon.

**Keywords:** resins, nitrogen-containing bases, thermal transformations, content, structural group and individual composition

### INTRODUCTION

The presented paper continues studies [1] on characteristics of nitrogenous bases (NB) of resinous components of heavy oil of the Usinsk field. Furthermore, it is devoted to the exploration of directions of their transformations during the thermal effect. The interest towards such papers is related to the fact that resinous and highly resinous oils enter in an increasing amount to oil refineries. The search for the best ways to use them substantially depends on the structure of tarry matters that include the bulk

of oil heteroatomic compounds, in particular, NB. Their presence in hydrocarbon raw materials substantially complicates the occurrence of their catalytic processing and worsens the quality and operating characteristics of fuels and lubricants [2]. In a previous communication [1], we demonstrated that resins from the Usinsk field concentrate over 60 % of basic nitrogen determined in oil. Characteristics of distribution and structural group composition of high and low molecular mass resin components of NB were identified. The work goal was the comparative characteristic of tar NB of heavy Usinsk oil before and after thermal effect.

## EXPERIMENTAL

The study objects are NB of initial resins of heavy Usinsk oil with contents of total ( $N_t$ ) and basic ( $N_b$ ) nitrogen of 1.09 and 0.55 mass %, as well as NB of resins after their thermal treatment at 450 °C for 30 min in an inert medium with contents of  $N_t$  and  $N_b$  of 0.62 and 0.23 mass %, respectively. Temperature and tar thermolysis time were established on the basis of the data of thermal transformation of the concentrate of high molecular mass bases determining the bulk of oil NB [1, 3]. Thermal transformations of low molecular mass bases end at a temperature of 350 °C. Therefore, NB in thermolized resins are decomposition products of high molecular mass compounds.

The concentration of NB was performed from hexane solutions of initial and thermally transformed resins in accordance with a scheme that includes sedimentation stages with gaseous HCl (K-1), additional deposition of NB chloride using diethylamine (K-2) and extraction of low molecular mass NB with an acetic acid solution of sulphuric acid (K-3). K-1 and K-2 compounds were separated by hot hexane extraction onto components soluble (K-1<sup>HS</sup> and K-2<sup>HS</sup>) and insoluble (K-1<sup>HI</sup> and K-2<sup>HI</sup>) therein [4, 5].

Sample composition examination was carried out using the equipment of the Centre for Collective Use of the Tomsk Scientific Centre SB RAS. A complex of analytical methods included: 1) the determination of the elemental composition using Vario EL Cube CHNS analyzer; 2) the study of the functional composition of nitrogen compounds by non-aqueous potentiometric titration method [6]; 3) measurement of molecular masses by cryoscopy in benzene [7]; 4) NMR Fourier spectroscopy; 5) the structural group analysis (SGA) [8]; 6) gas chromatography-mass spectrometry (GC-MS).

The <sup>1</sup>H NMR spectra were recorded using AVANCE AV 300 Fourier NMR spectrometer (Bruker, Germany), operating power of 300 MHz, the solvent is CDCl<sub>3</sub>. Tetramethylsilane was used as the standard. The calculation of the relative content of protons in different structural fragments was carried out according to <sup>1</sup>H NMR spectra, proceeding from peak areas in the corresponding spectral regions:  $H_{ar}$  (the fraction of protons that are contained

in aromatic structures) was 6.6–8.5 ppm;  $H_\alpha$  (the fraction of protons at the carbon atoms in the  $\alpha$ -position to aromatic rings) is 2.2–4.0 ppm;  $H_\beta$  and  $H_\gamma$  (the proportion of protons for methylene and terminal methyl groups of aliphatic fragments of molecules, respectively) are 1.1–2.1 and 0.3–1.1 ppm correspondingly.

The SGA method was used to describe molecular structures of the following compounds: K-1<sup>HS</sup>, K-2<sup>HI</sup>, K-2<sup>HS</sup>, and K-3. Based on the data of molecular masses (MM), elemental composition and proton distribution between different fragments of their molecules, their average structural characteristics for the studied substances were calculated [8]. During the calculations, there were determined the following parameters:  $C_a$ ,  $C_n$ , and  $C_p$  are the number of aromatic, naphthenic, and paraffinic carbon atoms in average molecules, respectively;  $f_a$ ,  $f_n$ , and  $f_p$  are the fractions of carbon atoms in aromatic, naphthenic, and paraffinic structural fragments, respectively, %;  $m_a$  is the number of structural units in the average molecule;  $K_t^*$ ,  $K_a^*$ , and  $K_n^*$  are the total number, the number of aromatic and naphthenic cycles in the structural unit, respectively;  $C^*$  is the total number of carbon atoms in the structural unit;  $C_p^*$  is the number of alkyl carbon atoms in the structural unit;  $C_\gamma^*$  is the number of carbon atoms in terminal methyl groups non-bonded with aromatic rings.

The individual composition of NB, such as K-1<sup>HS</sup>, K-2<sup>HS</sup>, and K-3 was examined by the GC-MS method using the Thermo Scientific DFS instrument (ionizing electron energy of 70 eV, ionization chamber temperature of 270 °C, interface temperature of 270 °C, injector temperature of 250 °C). The DB-5MS column with a length of 30 m, a diameter of 0.25 mm, and phase thickness of DB-5MS phase of 0.25  $\mu$ m was used for chromatographic separation. Helium was used as a carrier gas, with a fixed flow rate of 0.8 mL/min. Thermostat program was as follows: an initial temperature of 80 °C (3 min), a rise to 300 °C (4 °C/min), ageing at the final temperature for 30 min. Scanning of mass spectra was carried out every second in the mass range up to 500 amu. Reconstruction of molecular mass separation of various compounds was carried out using characteristic ions based on chromatograms

TABLE 1

Isolation of nitrogen-containing bases from initial and thermolysed resins

Samples	Initial resins					Thermolysed resins				
	Yield, mass %	MM, amu	Content			Yield, mass %	MM, amu	Content, %		
			N <sub>t</sub> , mass %	N <sub>b</sub> , mass %	rel. %*			N <sub>t</sub> , mass %	N <sub>b</sub> , mass %	rel. %*
K-1	37.6	844	1.36	1.17	79.9	9.5	597	1.41	1.25	50.4
K-2	2.2	519	1.36	0.90	3.6	0.9	412	1.39	0.92	3.4
K-3	1.0	392	1.42	1.31	2.4	0.6	310	1.40	1.28	3.3

\* Relative to N<sub>b</sub> of resins.

of full ion current using Xcalibur software. To identify individual compounds, literature data of [9–11], and computer NIST 02 mass spectral library were used.

## RESULTS AND DISCUSSION

During thermal treatment under selected conditions, gaseous (19 %), coke-like (43 %), and benzene-soluble (38 %) products are generated. They consist of 17 rel. % of “secondary” asphaltenes and 83 rel. % of malthenes (hereinafter, thermolysed resins).

The concentrations, such as N<sub>t</sub> and N<sub>b</sub> in thermolysed resins are reduced by 1.8 and 2.4 times, respectively, unlike those in initial ones. As demonstrated by comparative analysis. The total contents of isolated K-1, K-2, and K-3 concentrates and the fraction of basic nitrogen of resins coupled with them are also decreased (Table 1). The totality of these data proves the suggestions [12, 13] made earlier about the fact that NB take part in forming coke-like products generated during thermolysis of oil raw materials.

The bulk of bases isolated from resins of both types is presented by high molecular mass compounds K-1 (see Table 1), however, the relative content of N<sub>b</sub> in thermolysed resins is lower than in initial ones. K-2 and K-3 concentrates of initial and thermolysed resins are almost identical by relative content of N<sub>b</sub> in the structure of their bases.

Products obtained from thermolysed resins are characterised by lower values of average MM (see Table 1).

According to fractioning results, NB of K-1 and K-2 concentrates of initial and thermolysed resins are different by the content of compounds soluble and insoluble in hot hexane (Table 2). The thermal decomposition process is accompanied by an increase in the fraction of hexane-soluble products. Thus, the relative content of K-1<sup>HS</sup> и K-2<sup>HS</sup> is 52 and 63 rel. % and 48 and 58 rel. % in the case of thermolysed and initial resins, respectively. The MM of K-1<sup>HS</sup> and K-2<sup>HS</sup> compounds for both samples is substantially lower compared to same name products from initial resins. The revealed differences may be related to the progression during thermal destruction of both reactions

TABLE 2

Fractionation of nitrogenous bases of initial and thermolysed resins

Samples	Initial resins					Thermolysed resins				
	Yield, mass %	MM, amu	Content			Yield, mass %	MM, amu	Content		
			N <sub>t</sub> , mass %	N <sub>b</sub> , mass %	rel. %*			N <sub>t</sub> , mass %	N <sub>b</sub> , mass %	rel. %*
K-1 <sup>HI</sup>	19.5	1566	1.25	1.03	36.5	4.5	748	1.15	0.95	18.4
K-1 <sup>HS</sup>	18.1	592	1.48	1.32	43.4	5.0	458	1.70	1.52	32.0
K-2 <sup>HI</sup>	0.9	647	1.91	0.56	1.0	0.3	497	2.05	0.80	1.0
K-2 <sup>HS</sup>	1.3	346	1.21	1.12	2.6	0.6	313	1.07	0.99	2.4

\* Relative to N<sub>b</sub> of resins.

TABLE 3

Computed parameters of medium-sized molecules of nitrogen-containing bases of initial resins

Parameters	Samples				
	K-1 <sup>HI</sup>	K-1 <sup>HS</sup>	K-2 <sup>HI</sup>	K-2 <sup>HS</sup>	K-3
<b>Number of carbon atoms of different types in medium-sized molecules</b>					
C <sub>a</sub>	39.4	12.9	12.0	12.0	5.6
C <sub>n</sub>	60.6	14.5	24.7	24.7	7.2
C <sub>p</sub>	22.7	11.8	6.0	6.0	13.3
<b>Distribution of carbon atoms, %</b>					
f <sub>a</sub>	32.1	32.9	28.1	20.4	21.5
f <sub>n</sub>	49.4	37.0	57.8	69.5	27.6
f <sub>p</sub>	18.5	30.1	14.1	10.1	50.9
<b>Parameters of average structural units</b>					
m <sub>a</sub>	3.0	1.5	1.5	1.0	1.1
K <sub>t</sub> <sup>*</sup>	8.2	4.4	5.9	4.9	2.7
K <sub>a</sub> <sup>*</sup>	3.2	2.1	2.0	1.0	1.2
K <sub>n</sub> <sup>*</sup>	5.0	2.3	3.9	3.9	1.5
C <sup>*</sup>	40.6	25.6	28.2	23.8	24.4
C <sub>p</sub> <sup>*</sup>	7.5	7.7	4.0	2.3	12.5
C <sub>γ</sub> <sup>*</sup>	2.6	2.2	2.0	2.3	3.0

TABLE 4

Computed parameters of medium-sized molecules of nitrogen-containing bases of thermolysed resins

Parameters	Samples				
	K-1 <sup>HI</sup>	K-1 <sup>HS</sup>	K-2 <sup>HI</sup>	K-2 <sup>HS</sup>	K-3
<b>Number of carbon atoms of different types in medium-sized molecules</b>					
C <sub>a</sub>	25.6	12.8	10.9	6.0	5.3
C <sub>n</sub>	17.3	12.4	17.9	10.4	14.1
C <sub>n</sub>	9.1	6.3	3.0	4.6	1.1
<b>Distribution of carbon atoms, %</b>					
f <sub>a</sub>	49.3	40.6	33.8	28.5	25.9
f <sub>n</sub>	33.2	39.4	61.8	49.8	68.7
f <sub>n</sub>	17.5	20.0	4.4	21.7	5.4
<b>Parameters of average structural units</b>					
m <sub>a</sub>	2.1	1.5	1.4	1.1	1.1
K <sub>t</sub> <sup>*</sup>	4.8	4.0	4.9	3.5	7.3
K <sub>a</sub> <sup>*</sup>	2.8	2.0	1.9	1.2	1.1
K <sub>n</sub> <sup>*</sup>	2.0	2.0	3.0	2.3	6.2
C <sup>*</sup>	24.5	21.3	23.0	19.7	19.6
C <sub>p</sub> <sup>*</sup>	4.3	4.3	2.1	4.3	1.1
C <sub>γ</sub> <sup>*</sup>	1.3	1.5	1.0	1.4	1.1

of dealkylation and naphthene ring expansion that leads to the generation of relatively low molecular mass compounds [12]. K-1 and K-2 compounds of initial resins may take part in these reactions.

Comparison of SGA data made it possible to establish the similarity and differences in the structures of NB of initial and thermolysed resins. The computed parameters given in Tables 3 and 4 attest to the fact that medium-sized molecules of fractionation products of high molecular mass K-1, K-2 compounds (K-1<sup>HI</sup>, K-1<sup>HS</sup>, K-2<sup>HI</sup>, K-2<sup>HS</sup>) and low molecular mass K-3 compounds generate systems consisting of aromatic (C<sub>a</sub>), naphthenic (C<sub>n</sub>), and paraffinic (C<sub>p</sub>) structural fragments.

Most carbon atoms (50.7–79.6 %) in all samples fall on saturated fragments (f<sub>n</sub> + f<sub>p</sub>); an aromatic carbon fraction (f<sub>a</sub>) is 20.4–49.3 %. Herewith, average size species of NB of thermolysed resins are more aromatic due to a decrease in the fractions of naphthenic (f<sub>n</sub>) and paraffinic (f<sub>p</sub>) carbon atoms. The changes in the structure of NB appear most clearly for middle molecules of K-1<sup>HI</sup> compounds. The number (from 3.0 to 2.1) and the size of average

structural units (m<sub>a</sub>) in their composition are reduced during thermolysis. A decrease in their total size characterised by such parameters as (C<sup>\*</sup>, K<sub>t</sub><sup>\*</sup>) proceeds mainly due to a reduction in the number of saturated rings (K<sub>n</sub><sup>\*</sup>) from 5.0 to 2.0 and the number of carbon atoms in the alkyl framing (C<sub>p</sub><sup>\*</sup>) from 7.5 to 4.3. Among the latter, there is a two-fold decrease (from 2.6 to 1.3) in the number of carbon atoms in methyl groups removed from the aromatic ring (C<sub>γ</sub><sup>\*</sup>), which attests to a decrease in the number and/or the degree of branching of substituents. There are similar changes in the composition of structural units for middle molecules of the entire series of the studied NB.

Nitrogenous bases of initial and thermolysed resins have similar group compositions, as demonstrated by qualitative analysis of K-1<sup>HS</sup>, K-2<sup>HS</sup>, and K-3 products *via* the GC-MS method. Among them, there are alkyl-substituted quinolines, benzo-, dibenzoquinolines, and azapyrenes, the maximum in the distribution of which falls on benzoquinolines (Table 5). An elevated content of alkylquinolines is a characteristic of NB. Unlike initial resins, where they are present in minimum amounts, their

TABLE 5

Composition of alkyl azaarenes of initial and thermolysed resins of Usinsk oil

Compounds	Homologues		Content, % rel. of identified structures	
	Initial resins	Thermolysed resins	Initial resins	Thermolysed resins
Quinolines	C <sub>2</sub> -C <sub>8</sub>	C <sub>2</sub> -C <sub>7</sub>	0.4	42.0
Benzoquinolines	C <sub>1</sub> -C <sub>5</sub>	C <sub>1</sub> -C <sub>5</sub>	88.8	53.8
Dibenzoquinolines	C <sub>1</sub> -C <sub>5</sub>	C <sub>1</sub> -C <sub>5</sub>	5.1	0.5
Azapyrenes	C <sub>1</sub> -C <sub>5</sub>	C <sub>1</sub> -C <sub>5</sub>	5.7	3.7

content (42.0 rel. %) is comparable with that of alkyl benzoquinolines (53.8 rel. %).

This increase in the fraction of bicyclic azaarenes may be related to the molecular structure of K-1<sup>HS</sup>, K-2<sup>HI</sup> bases of initial resins. According to SGA data (see Table 3), the structure of their middle units contains a bicycloaromatic ring ( $K_a^* = 2.0-2.1$ ) and two-four naphthene ones ( $K_n^* = 2.3-3.9$ ). Most likely, alkyl quinolines are the main products of thermal destruction of such bases.

Comparison of GC-MS data on the structure of prevailing compounds allowed determining that a fraction of structures with shorter alkyl substituents was higher in the composition of benzoquinolines of thermolysed resins. Figure 1 gives the distribution of alkyl benzoquinolines in K-3 of initial and thermolysed resins as an example.

## CONCLUSION

Based on the comparative study of the distribution and composition of nitrogen-

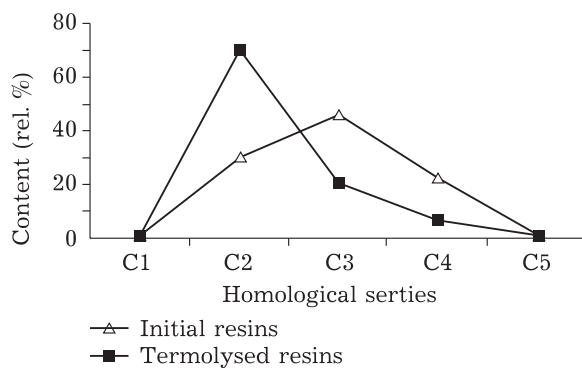


Fig 1. Distribution of alkylbenzoquinolines in K-3 samples of initial and thermolysed resins.

containing and thermally treated resinous components of heavy oil from the Usinsk deposit, it has been found that high molecular mass compounds constitute the bulk of nitrogenous bases of initial and thermolysed resins. However, their fraction in thermolysed resins is substantially lower. Thermally transformed bases have lower average molecular masses compared to initial. Their middle molecules are characterised by elevated aromaticity due to a decrease in the fractions of naphthenic and alkyl fragments. Among bases of initial and thermolysed resins, there are alkyl quinolines, benzoquinolines, dibenzoquinolines, and azapyrenes. Alkyl benzoquinolines make up the bulk of the identified compounds. An elevated fraction of bicyclic species is a particularity of azaarene composition of thermolysed resins. A higher fraction of structures with a lower number of carbon atoms in alkyl substituents is typical for the resulting low molecular mass nitrogen-containing bases. The identified compounds are part of distillate fractions during thermal treatment of heavy oil raw materials, which should be considered during selection of technical solutions for obtaining high-quality oil products based therein.

## REFERENCES

- 1 Gerasimova N. N., Klassen A. S., Min R. S., Sagachenko T. A., *Chem. Sust. Dev.* [in Russian], 2016, Vol. 24, No. 6, P. 739-744.
- 2 Pashigreva A. V., Klimov O. V., Bukhtiyarova G. A., Kochubey D. I., Prosvirin I. P., Chesalov Yu. A., Zaikovskii V. I., Noskov A. S., *Catalysis Today*, 2010, Vol. 150, No. 3-4, P. 164-170.
- 3 Kamyranov V. F., Aksenov V. S., Titov V. I., *Heteroatomic Compounds of Oils* [in Russian], Nauka, Novosibirsk, 1983, 238 p.

- 4 Bolshakov G. F. (Ed.), *Chemical Composition of Western Siberia Oils* [in Russian], Nauka, Novosibirsk, 1988, 288 p.
- 5 Cheshkova T. V., Gerasimova N. N., Sagachenko T. A., Min R. S., *Bulletin of the Tomsk Polytechnic University* [in Russian], 2017, Vol. 328, No. 8, P. 6–15.
- 6 Galpern G. D. (Ed.), *Methods of Analysis of Oil Organic Compounds, Their Mixtures and Derivatives* [in Russian], Moscow, Publishing House AN SSSR, 1960. P. 141–169.
- 7 Bogomolov A. I., Temyanko M. B., Khotyntsev L. I. (Eds.), *Modern methods of a Research of Oils: Reference Benefit* [in Russian], Leningrad, Nedra, 1984. 431 p.
- 8 Golovko A. K., Kamyayov V. F., Ogorodnikov V. D., *Russian Geology and Geophysics*, 2012, Vol. 53, No. 12, P. 1374–1381.
- 9 Li M., Larter S. R., *Org. Geochem.*, 2001, Vol. 32, P. 1025–1030.
- 10 Bakel A. J., Philp R. P., *Org. Geochem.*, 1990, Vol. 16, No. 1–3, P. 353–367.
- 11 Schmitter J. M., Arpino P. J., *Mass-Spectrometry Reviews*, 1985, No. 4, P. 87–121.
- 12 Speight J. G., *Petroleum Chemistry* [in Russian], 1989, Vol. 29, No. 6, P. 723–730.
- 13 Antipenko V. R. *Thermal Conversion of Sulphurous Rich Native Asphaltite: Geochemical and Technological Aspects* [in Russian], Novosibirsk, Nauka, 2013. 184 p.