Investigation of a Microcrystalline Wax

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With 1 figure

Summary

This paper deals with the separation of microcrystalline wax (ceresin) from the Soviet Tuimasa heavy oil, using an ABT mixture. Structure investigation was performed using different methods of analysis such as fractional crystallisation, n-d-M-method, Grodde analysis, elementary analysis, urea adduction and adsorption analysis. It was concluded, that this wax was mostly composed of di- and tricyclic paraffinic compounds.

Methods and Results

The microcrystalline wax was obtained from the Soviet Tuimasa vacuum residue. This residue was deasphalted by liquid propane in a pilot deasphalting unit.

The oil was dewaxed[1]) with an ABT mixture (30:30:35 by volume) of acetone, benzene and toluene with a ratio to the oil of 4:1 by weight at a temperature of −30 °C. The slack wax obtained was deoiled in the same way at the same dewaxing temperature. The properties of the wax are given in table 1.

Table 1
Properties of the wax, dewaxed at −30 °C and deoiled at −30 °C

Yield	11.0 wt. %
Solidification pt. (S_p) °C	58.2
Oil content wt. %	5.8
n_D^{90}	1.4575

The wax obtained and deoiled at −30 °C was further separated into saturates, aromatics and resins by adsorption chromatography over silicagel and the saturate was further fractionated by repeated silicagel chromato-

[1]) S. GIPP, Dissertation Leipzig (1962).

graphy[2)3)] and urea adduction. For the purpose of chromatography a column of 2 m height and 4 cm diameter, filled with silicagel of particle size 0.1 to 0.4 mm was used. The elution was performed with 2.5 liter petroleum ether 50/70, 1.5 liter benzene and 1.0 liter acetone. The results are given in table 2.

Table 2
Chromatography analysis of the wax

Saturate (petroleum ether eluate)	155.0 g = 90.2 wt. %
Aromatics (benzene eluate)	13.92 g = 8.1 wt. %
Resins (acetone eluate)	4.35 g = 2.5 wt. %

The petroleum ether eluate had the following properties:

Solidification point °C	58 °C
Refractive index at 70 °C	1.4572
Refractive index at 90 °C	1.4528
Refractive index at 70 °C (of benzene eluate)	1.4712

The dearomatised wax (petroleum ether eluate) was further fractionated in a similar column filled with fresh activated silicagel of particle size 0.1 to 0.4 mm, using petroleum ether as the eluent. Fractions were obtained by using a siphon of 76 ml capacity. After evaporation of the eluent, fractions of the same solidification point were added together. As a result 5 fractions were obtained as shown in table 3 together with their properties.

Table 3
Physical properties of the chromatographic fractions

Fraction No.	Yield %wt.	S_p °C	n_D^{90}	n_D^{70}	d^{70}	d^{90}	M	C % wt.	H % wt.	S % wt.
1	17.2	55.5	1.4483	1.4552	0.8201	0.7981	704	85.84	14.02	0.08
2	26.2	53.9	1.4503	1.4578	0.8250	0.8040	726.4	85.93	13.98	0.14
3	29.8	54.2	1.4529	1.4593	0.8293	0.8125	790	85.96	13.94	0.24
4	16.6	56.8	1.4597	1.4669	0.8215	0.8215	766	85.98	13.73	0.57
5	10.2	67.4	1.4692	1.4808	0.8781	0.8647	645	85.24	12.86	—

From these properties the n-d-M-structural group analysis was derived, the chemical formulae were calculated (table 4), and from GRODDE formulae[4)] the assymetry value As_v, ring value R_v and sum value S_v were found (table 5).

[2)] M. LEDERER, Chromatography, Elsevier Pub. Corp. (1953), P. 67.
[3)] Die chromatographischen Adsorptionsmethoden, Wien (1938).
[4)] H. GROSS u. K. GRODDE, Öl und Kohle **38**, 419 (1942).

Table 4

Fraction	$C_{A}\%$	$C_{N}\%$	$C_{P}\%$	$C_{R}\%$	R_T	R_N	R_A	X in C_nH_{2n} X	Formula	
1	3	11	86	14	1.1	1.0	0.1	−2.0	$C_{50.4}$	$H_{98.8}$
2	3	13	84	16	1.45	1.1	0.35	−1.4	$C_{52.07}$	$H_{102.75}$
3	3.8	12.3	83.9	16.1	1.5	1.15	0.35	−3.4	$C_{56.6}$	$H_{109.8}$
4	6	10	84.0	16	2.2	1.55	0.65	−4.8	$C_{64.8}$	$H_{123.8}$
5	7.8	25.2	67	33	3.5	2.7	0.7	−14.1	C_{47}	$H_{79.9}$

Table 5
Structural analysis after GRODDE

Fr. No.	As_v	R_v	S_v	Z ring No.	R_T (n-d-M)
1	28.6	11.9	40.5	0.7	1.1
2	29.5	18.0	47.5	1.1	1.4
3	32.1	24.0	56.1	1.6	1.5
4	28.0	34.8	62.8	2.2	2.05
5	15,4	82.7	98.1	4.0	3.5

Table 6

Fraction	Yield % wt.	Sp °C	n_D^{70}	n_D^{90}	d^{70}	d^{90}	M	C %	H %
1	17.2	55.5	1.4552	1.4483	0.8201	0.7981	704	85.84	14.02
added part	24.8	66.3	1.4524	1.4450	0.8153	0.7933	687	85.42	14.41
non added part	68.7	44.5	1.4561	1.4488	0.8325	0.8270	700	85.62	14.17
2	26.2	53.9	1.4578	1.4503	0.8250	0.8040	726	85.93	13.98
added part	26.2	65.6	1.4549	1.4478	0.8188	0.7858	700	85.04	14.22
non added part	67.6	42.5	1.4581	1.4510	0.8342	0.8286	757	85.38	13.89
3	29.8	54.2	1.4593	1.4529	0.8293	0.8128	784	85.96	13.94
added part	18.9	67.0	1.4559	1.4485	0.8297	0.8228	714	85.64	14.11
non added part	83.0	44.6	1.4598	1.4525	0.8317	0.8256	765	85.89	13.88
4	16.6	56.8	1.4669	1.4597	—	0.8402	766	85.18	13.73
added part	9.5	72.0	—	1.4481	—	—	—	—	—
non added part	96.6	56.5	1.4650	1.4579	0.8399	0.8370	769	85.68	13.64

The 5 chromatographic fractions were further fractionated by urea adduction[5][6][7]. The fractions obtained were characterised by their physical properties (see table 6). The structural analysis is given in table 7.

[5] W. SCHLENK, Liebigs Ann. Chem. **565**, 204 (1949).
[6] F. BENGEN, Angew. Chem. **63**, 207 (1957).
[7] U. HESSLER u. Q. MEINHARDT, Fette und Seifen **55**, 441, 786, 855 (1953).

Table 7

Fraction	R_V	As_V	Z Grodde	R_T n-d-M	R_A	% C_A	% C_R	% C_N	% C_P
1	13.0	27.4	0.8	1.3	0.1	3	14	11	86
added part	9.1	18.7	0.6	0.93	0.1	1	11	10	89
non added part	41.5	36.6	2.2	1.7	−0.3	0.05	28.5	28.5	71.5
2	18.0	29.5	1.1	1.45	0.35	3	16	13	84
added part	17.1	19.6	1.0	1.2	0.12	2.5	17.8	15.3	82.2
non added part	29.0	51.2	1.8	2	−0.2	−2.5	21.5	21.5	78.5
3	24.0	32.1	1.6	1.5	0.35	3.8	16.1	12.3	83.9
added part	37.4	19.3	2.2	2.25	0.1	−3	20.5	20.5	79.5
non added part	39.2	37.0	2.2	2.5	0.17	−2.2	17.0	14.8	83
4	34.0	28.0	2.2	2.05	0.65	6	16.0	10.0	84
added part	—	—	—	—	—	—	—	—	—
non added part	29.6	29.1	3.2	2.3	0.45	5	20.0	15	80

Table 8
Elementary analysis of the fractions obtained from chromatography and urea adduction

Fraction	M	C%	H %	X in C_nH_{2n+x}	Formula
1	704	85.84	14.02	−2	$C_{50.4}H_{98.8}$
added part	687	85.42	14.41	+0.96	$C_{48}H_{96.96}$
non added part	700	85.62	14.17	−1	$C_{50}H_{99.0}$
2	726	85.93	13.98	−1.4	$C_{52.07}H_{102.7}$
added part	700	85.04	14.22	0.0	$C_{57.1}H_{114.2}$
non added part	757	85.39	13.89	−2.7	$C_{54.06}H_{105.4}$
3	784	85.96	13.94	−3.4	$C_{56.6}H_{109.8}$
added part	714	85.64	14.11	−1	$C_{51.4}H_{101.8}$
non added part	765	85.89	13.88	−3.3	$C_{54.8}H_{106.3}$
4	766	85.18	13.73	−4.8	$C_{64.8}H_{125.8}$
added part	—	—	—	—	—
non added part	769	85.68	13.64	−5	$C_{55.2}H_{105.4}$

Discussion

The microcrystalline wax was obtained from heavy lube oil fractions (neutral oil II) and asphaltic residue[8]). In this work the asphaltic residue was deasphalted by liquid propane and the heavy oil obtained was further dewaxed by an acetone benzene toluene mixture to separate the wax. The deoiled wax had an oil content of 5.8 wt.% (table 1). To investigate

[8]) K. Triems u. G. Heinze, Chem. Technik 17, 350 (1965).

the structure of the wax, it is further dearomatised and deresined over silicagel columns (table 2). From the structural group analysis of the chromatographic fractions (table 3), we could observe the increase of the aromatic hydrocarbons from the 1st. to the last 5th. fraction. The high aromatic content of the 5th. fraction is confirmed by the values of x in C_nH_{2n+x} obtained by elementary analysis and from $C_{A\%}$-value (derived from n-d-M-method) (see table 4) and as observed from infra-red analysis (spectra NO. 4827, 4828, 4829, 4830 and 4831) at the band 1610^{-cm}. The IR-spectra of the fractions 1—5 are given in fig. 1. The interpretation of the values obtained from the GRODDE-formula confirms that the 1st. fraction contains one ring per average-molecule (R = 1.1 and Z = 0.7), the 2nd., 3rd. and 4th. contain maximum di- and tri-cyclic paraffinic hydrocarbons (R_T = 1.4, 1.5, 2.0 and Z = 1.1, 1.6, 2.2 respectively). The 5th. fraction contains 3 to 4 rings per average molecule. (R_T = 3.5 and Z = 4.0). The fractions contain a little amount of aromatic hydrocarbons, which could not be separated by chromatography. This may be due to the presence of long paraffinic side chains in the ring giving it the property of paraffinic hydrocarbons.

To give a deeper idea about the structure of the wax constituents, the fractions were further fractionated by urea adduction (the 5th. fraction is not included due to its small amount). Table 4 showes, that the long paraffinic chains are mostly in the added part of the 1st. fraction and decrease in the other three fractions (C_p in the added part of the 1st. fraction was 89% in the 2nd. 82% and in the 3rd. 79.5%). Table 7 showes that the added part of the 1st. fraction has ring No. of 0.6 per average molecule. This means, that in this fraction the average molecule is composed of one ring, which has long paraffinic side chains, that could form an adduct with urea. The C_p % increases from 86 in the mother fraction to 89% in the added part of the fraction, while it decreases to 71.5% in the non added part of the fraction. This last part contains two rings in the average molecule. It is also to be noticed, that the 3rd. fraction gave an added part, which included two rings in the average molecule. This means, that the rings had long side chains with more than 20 carbon atoms[9]).

The difference in the branching of the side chains of the added and non added part of the fraction, could be clearly identified by the assymetry values of these fractions. The added parts have the lowest assymetry values.

From the chemical formula C_nH_{2n+x}, it is found, that the added part of the 1st. fraction had an x-value of +0.96, which means, that this fraction

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[9]) L. MCLAUGHLIN, The chemistry of petroleum hydrocarbons, (1955) 249.

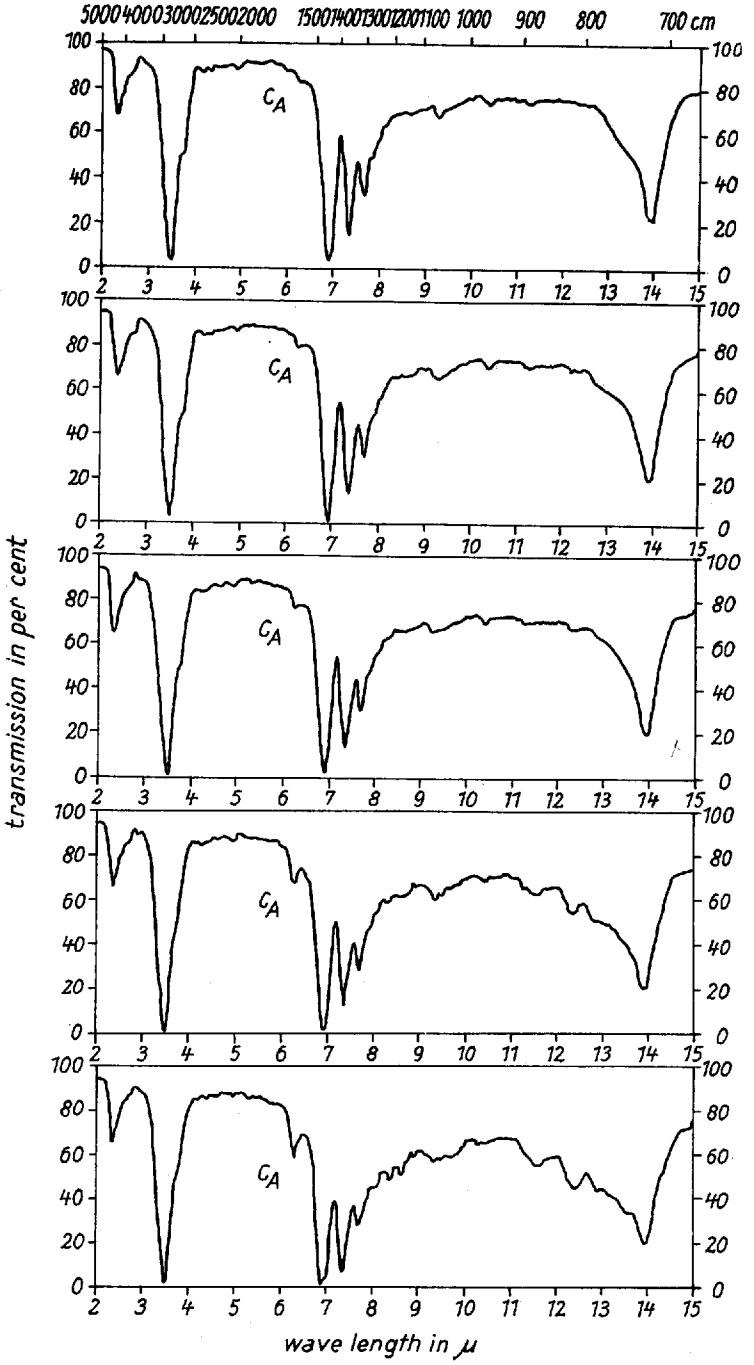

Fig. 1.
IR-spectra of the fractions 1—5

contains n-paraffins besides the cyclic paraffinic compounds. It is also clear, that the number of carbon atoms in the average molecule ranges from 48 to 57 carbon atoms (see table 8).

Conclusion

The wax obtained from the Soviet Tuimasa heavy oil is naphthenic in nature including mostly di- and tri-cyclic paraffinic compounds in the average molecule together with small amounts of n-paraffins.

Thanks for the help given from Mr. FRIEDRICH HOLLSTEIN in the carrying out of the dewaxing processes.

Cairo (VAR), Petroleum Research Unit, National Research Centre.

Bei der Redaktion eingegangen am 20. August 1965.