Journal für praktische Chemie

4. REIHE, BAND 33 NOVEMBER 1966 HEFT 5-6, S. 225-336

Analysis of a Residual Wax

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Summary

This work deals with the chemical structure of a microcrystalline wax obtained from a Soviet Tuimasa deasphalted oil residue. Fractional crystallisation of the wax was carried out and the obtained fractions were further separated using silicagel adsorption chromatography column and urea adduction. It was found, that the ring No. and the branching of the molecules increased with descrease of the crystallisation temperature.

Methods and Results

1. The wax obtained was deoiled at a temperature of −30 °C using an acetone, benzene, toluol (30:35:35) mixture in a ratio to the oil of 4:1 by weight and further fractionated by crystallisation. The temperatures of

Table 1
Physical constants of the crystallised fractions

Fraction °C	Yield wt. %	Sp. °C	V_K 90 °C cSt	V_K 100 °C cSt	$\overline{M}$	d^{70}	d^{90}	n_D^{70}	n_D^{90}
20	40.6	69.0	21.0	16.0	679.5	0.8259	0.8023	1.4560	1.4480
10	18.0	48.0	23.5	18.0	709.0	0.8385	0.8198	1.4607	1.4529
0	13.0	36.4	23.8	18.0	730.0	0.8513	0.8273	1.4625	1.4545
−10	1.48	29.6	24.6	20.4	762.0	0.8616	0.8357	1.4652	1.4564

Table 2
Structural analysis by different methods

Fraction crystallised at °C	V_K 100 °C cSt	R_v from viscosity	As_v from viscosity	S_v from viscosity	S_v from molecular weight	S_v from Ivanosky formula
+20	16	14.5	21.0	35.5	34.6	33.0
+10	18	29.3	38.5	67.8	67.8	65.5
0	18	36.8	47.2	84.0	83.5	78.4
−10	20.4	44.1	53.5	97.6	98.5	88.0

crystallisation were +20, +10, 0, −10 °C. The physical constants of the fractions are given in table 1. From the physical constants the structure of the fractions was found by calculatuon of the ring-, assymetry- and sum-values after GRODDE and from the structural group analysis (n-d-M-method). The results are given in table 2 and 3.

Table 3
Structural analysis after GRODDE and n-d-M-method

Crystallisation temp. °C	R_V	As_V	Z GRODDE	R_T n. d. M	R_A	% C_R	% C_A	% C_N	% C_P
+20	18.7	15.85	1.6	1.7	0.1	13.5	0	18.5	81.5
+10	34.6	33.2	2.04	2.7	0.08	23.0	0	23	77
0	41.2	42.3	2.5	3.1	−0.58	31.2	0	31.2	68.8
−10	49.2	49.3	3.7	4.0	0	36.5	0	36.5	63.5

2. A combination of elementary analysis with the n-d-M-method was applied to find the number of carbon atoms in naphthenic structure X_N, in aromatic structure X_A and paraffinic structure X_P. The number of carbon atoms per ring was also calculated. The results are given in table 4.

Table 4

Fr. °C	% C	% H	% S	$\bar{M}$	X	Y	Z	X_A	X_N	X_P	R_T	A	N
20	85.6	14.10	0.2	680	48.5	95.2	0.04	0	8.97	39.5	1.7	0	5
10	85.7	14.09	0.3	709	50.6	99.96	0.06	0	11.6	39.0	2.7	0	4.5
0	85.98	13.96	0.46	730	52.3	101.5	0.1	0	16.2	36.1	3.7	0	4.3
−10	85.8	13.6	0.7	768	54.6	101.4	0.16	0	19.9	34.7	4.0	0	4.1

X = number of carbon atoms in the molecule.

3. The crystallised fractions were further fractionated by urea adduction. The added part and the non-added part were investigated by structural group analysis and elementary analysis. The results are given in tables 5 and 6.

Table 5

Fraction	Yield % wt.	S_p °C	d^{70}	d^{90}	n_D^{70}	n_D^{90}	M	C %	H %
Fr. 20 °C	61.6	69	0.8259	0.8023	1.4560	1.4480	679.5	85.53	14.18
add part	56.0	74	0.8267	0.8020	1.4521	1.4449	801.0	85.58	14.29
non add. part	40.2	54	0.8367	0.8047	1.4593	1.4513	677	85.73	13.84

Table 6
Elementary analysis of the fraction +20 °C before and after urea adduction

Fraction °C	formula	Y in C_nH_{2n+y}	Ring No. from x	Ring No. from n. d. M
+20	$C_{48.5}H_{96.5}$	−2.5	2	1.7
added part	$C_{57.1}H_{111.2}$	0.0	1	1.3
non added part	$C_{48.6}H_{93.8}$	−3.4	2.7	2.5

Discussion

Fractional crystallisation of the wax under investigation separates it in to different fractions of different structural properties (see table 1). This was confirmed by the assymetry values, which are a measure of the branching of the molecules (table 2). It increases in the fractions from 21 to 53.5 by the decrease of the crystallisation temperature. This proves, that the alkyl chains present in the separated fractions become more branched by lowering the fractionating temperature. The ring values also increase with the decrease of the crystallisation temperature. This is further confirmed by the n-d-M-method values (table 3), where % C_R and % C_N increased with the decrease of the temperature of crystallisation. It could be also concluded, that the wax is of naphthenic nature.

A combination of elementary analysis with the n-d-M-method was applied to find the number of carbon atoms in naphthenic structure xN, aromatic structure xA and in paraffinic structure xP. The number of carbon atoms per ring was calculated, from which (table 4) the decrease of the average number of carbon atoms per naphthenic ring indicates a higher grade of condensation of the rings by decreasing of the crystallisation temperature. By further fractionation of the crystallised fractions using urea adduction, it was found, that the 1st. fraction crystallised at +20 °C formed 56 wt. % added part, the 2nd. at +10 °C forms 8.6 wt.% added part and the other two fractions form no adduct with urea. This means, that the long straight paraffinic chains are mostly concentrated in the first fraction (at +20°) due to their higher solidification point. From structural group analysis (n-d-M and Grodde analysis) and elementary analysis (see table 6), it is clear, that the added part of fraction +20 °C has one ring in the average molecule with a long side chain. The non added part has from 2 to 3 rings per average molecule. The ring values obtained from the n-d-M-method are confirmed by the ring values calculated from Y in the general formula C_nH_{2n+Y}. The calculated values from the elementary analysis depend upon the fact, that the formation of one ring causes a difficiency of two hydrogen atoms. An Y-value of +2 means n-paraffin, a value of 0.0 means one ring

(or double bond) and a value of -2 means two rings and so on. Further fractionation of the fraction $+20\,^{\circ}C$ was performed over a silicagel column of one meter height and 3 cm diameter. The silicagel had a particle size of of 0.1 to 0.4 mm and the column was thermostated at $50\,^{\circ}C$. Elution was carried out with n-heptane. It was found, that the first fraction eluted had the properties:

wt. %	Solidification point °C	M	H %	C %	Formula	Y
39	73	697	14.43	85.61	C 49.7 H 100.4	+ 1

This means, that this fraction contains n-paraffinic hydrocarbons besides one naphthenic ring per average molecule.

Conclusion

Fractionation of this type of wax by fractional crystallisation and urea adduction was not efficient enough to separate the different components of the wax, therefore the authors suggest the following separation methods.

1. Separation by fractional crystallisation, where by the long chained paraffinic constituents accumulate in the first highmelting fractions. The fractions could be differentiated in the branching degree of the side chains, in the ring values and in molecular weights.

2. Further separation of the crystallised fractions by adsorption chromatography, where separation depends on the molecular weight and on the polarity of the different molecules in the fraction.

3. Further separation of the chromatographic fractions by urea adduction, where the n-paraffinic hydrocarbons and long straight side chains can be separated.

4. Distillation of this type of wax at a pressure of 0.5 Torr causes the decomposition of the product. Therefore separation should be carried out by molecular distillation, where at very low pressures (10^{-7} Torr) the decomposition might be avoided.

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Bei der Redaktion eingegangen am 20. August 1965.