COMPOSITION OF MACRO- AND MICRO-CRYSTALLINE PARAFFINS OBTAINED FROM ROMASKINO PETROLEUM

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Introduction

CLERC [1] was the first to use adsorption-elution chromatography for the separation of hydrocarbon groups in mixtures of hydrocarbons. SNYDER [2] summarized the theoretical conclusions in this field, drawn from experiences collected in the years that followed. The chromatographic study of liquid hydrocarbon mixtures has been intensively pursued also by Hungarian authors [3, 4, 5].

CHERNOZHUKOV's paper [6] was the first report on elution chromatography used for analytical separation of macro- and micro-crystalline paraffins. In the course of his studies he dealt with solid paraffins obtained from distillates and residues of Tujmaz petroleum. Since then also others have utilized chromatography for separation of solid paraffins [7—13] either alone or in combination with other methods.

CSIKÓS et al. [13] studied the determination of the composition of slack wax and petrolatum obtained by laboratory extraction of Romaskino fractions and residues, with mixtures of methyl-ethyl ketone and benzene, as well as that of macro- and micro-crystalline paraffins obtained in the course of the separation from oil and further refining of these stocks, with the help of chromatography on silica gel. One of the most important of their conclusions is that by separation from oil and further refining, the quality of paraffins can be varied at will.

The substances used in the studies to be described were products obtained by a given technology which, in the case of macro-crystalline paraffins, is closely similar to one practised on a commercial scale by one of the Hungarian refineries.

For the separation of the several hydrocarbon groups a combined method of chromatography on silica gel and adsorption on a molecular sieve was utilized.

It is well known that a disadvantage of the separation of normal hydrocarbons from mixtures by adduct formation with urea is the rather tedious and time-consuming experimentation necessary to find the most suitable urea to hydrocarbon ratio to provide for analytical accuracy. This prompted me to

attempt the determination of normal hydrocarbons in paraffins with a separation method utilizing molecular sieves.

Though in the domain of lower molecular weights the determination of normal hydrocarbons with molecular sieves is a routine method, in the domain of molecules built of a higher number of carbon atoms this method involves some difficulties. There is only one publication in the literature [14] that deals with the separation of macro-crystalline paraffins on a molecular sieve.

There is no mention made in the literature either of the separation of micro-crystalline paraffins with molecular sieves or of macro-crystalline paraffins with molecular sieves combined with chromatography, for a thorough elucidation of the structure of macro-crystalline paraffins.

A number of publications [15—17] point out that besides the chemical properties of paraffins, also their mechanical and rheological characteristics are governed by their chemical composition. In view of the fact that functional requirements stipulated by users of paraffins become more stringent day by day, an extension of the methods by which the composition of these products can be studied seems not to be without purpose.

The separation methods applied in my work enabled to determine the normal paraffin contents, and the aromatic contents, of the solid hydrocarbons studied, separately and their naphthene and iso-paraffin contents together. Experience showed these three groups of hydrocarbon to affect the functional properties of solid hydrocarbons in different ways.

Fractions have been characterized by their refractive indices at 80 °C, sometimes by the refraction as a function of temperature, by setting points, by molecular weights measured according to MILLS [18], as well as by ring-asymmetry and -sum values* introduced by GROSZ and GRODDE [19].

The quantitative distribution of aromatic hydrocarbons, i.e. proportion of benzene, naphthalene, phenanthrene, and anthracene derivatives was determined according to the spectrophotometric method of SIRJUK and ZIMINA [20]. The selectivity of separation with molecular sieves was checked by mass-spectrometry [21].

The aromatic content of the paraffins was determined according to two methods. One of them was chromatography on silica gel, delivering percentages by weight of molecules containing aromatic rings, referred to the starting substance. Ultra violet spectrophotometry was the other method used, delivering percentages by weight of carbon in aromatic bonding. These data helped to determine the distribution of aromatic compounds according to ring number and ring type.

* Ring-asymmetry and -sum values are zero for single normal hydrocarbons; for branched and cyclic hydrocarbons these values are various positive figures depending on the concentration of each substance.

The normal hydrocarbon contents of the paraffins were estimated by the molecular sieve method. The selectivity of separation was checked by the absence of normal paraffins in the fraction of a micro-crystalline paraffin sample, not adsorbed by the molecular sieve, using mass spectrometry.

The starting substances used for these studies were paraffins obtained from light and medium oils, and from residual oils after asphalt extraction with propane, all of Romaskino crudes.

	Paraffinic light and medium oil	Residual oil
Solvent composition, benzene : acetone : toluene	1 : 1 : 1	1 : 1 : 1
Solvent to oil ratio	3—3.5	4.5
No. of stages used in deparaffination	2	2
Temperature at filtration, 1st stage	—25 °C	—30 °C
Temperature at filtration, 2nd stage	—15 °C	—15 °C

Table 1

Characteristics of primary substances used in the experiments

	Macro-crystalline paraffin		Micro-crystalline paraffin
Sample No.	1.	2.	3.
Setting point, °C	52.5	58	70—75
Refraction, n_D^{80}	1.4265	1.4295	1.4410
Mol. weight	355	390	570
Density, n_{20}^{80}	0.7701	0.7800	0.8058
ASTM standard oil percentage	0.33	0.40	3.38
Asymmetry value	2	0.5	10
Ring value	1.5	4	6
Sum value	3.5	4.5	16
Colour	white	white	yellow ochre
Odour	—	—	slight

The starting substance of Sample 1 was a paraffinic light oil, that of Sample 2 a paraffinic medium oil, and that of Sample 3 the residual oil. The starting substances were slack waxes and petrolatums made in the paraffin solvent extraction unit of the Duna Petroleum Refinery, and the technological parameters of the process were as follows. Removal of oil from slack wax and

petrolatum was carried out in two, essentially different ways under laboratory conditions.

Oil was removed from slack wax by heat, in a laboratory sweating chamber. The crude paraffin thus obtained was further refined with sulphuric acid and adsorptive clay. Oil from the petrolatum was removed in two steps with a 1 : 1 : 1 mixture of benzene, acetone and toluene, solvent to oil ratio was 5 : 1 in both steps. Filtration in the first step was at + 15 °C, in the second at + 25 °C. With this method ceresin could be obtained from petrolatum in a 20 per cent yield.

Some of the more important characteristics of the starting materials are shown in Table 1.

Chromatography on silica gel

Compared to samples for laboratory studies, rather great quantities have been used as starting materials in order to have available material enough for the necessary tests, in spite of the sharpness of separation. As it will be seen as a result of the sharp separation of macro-crystalline paraffins, even with this precaution quite a number of fractions were obtained in quantities too small to be tested.

Elution chromatography has been applied to separate the paraffin, naphthene, and aromatic compounds of the initial substance. Adsorbent was a 0.09—0.2 mm grain size silica gel from the GFR. The surface area of the silica gel, measured according to the BET method, was 660 m^2/g, its average pore radius was 27 Å. Prior to use, the silica gel was activated for 5 hours at 180 °C. Coefficient of activity was 0.219 ml/g.

The column was a stainless steel tube 220 cm long and 3.2 cm inner ⌀, with a heating mantle. 890 g activated silica gel was filled into this column, the silica gel being suspended in light naphtha free of aromatics to assure the uniformity of the filling and to eliminate disturbance by heat of wetting.

For separation 40 g of the initial substance dissolved in light naphtha free of aromatics was fed on the column, corresponding to a 4.5 per cent load on the adsorbent. Elution of compounds of saturated character (paraffins and naphtenes) was carried out with a light naphtha free of aromatics, that of compounds of aromatic character, with a 1 : 1 by vol. mixture of chloroform and ethanol. Based on experiences gathered in preliminary tests, to achieve sharp separation, in the first part of naphtha elution, fractions of 500, 300, 200 and 100 ml each, and subsequent to the desorption of the bulk of the substance, fractions of 1000 ml each were separated. Rate of elution was 250 ml/hour throughout. Because of the resistance of the sorbent layer, this rate was achieved by forcing

Table 2

Characteristics of the fractions obtained by chromatography of Sample 1

No. of fraction	Eluatum		Percentage of desorbed substance from total yield in 100 ml eluatum	Rotat. setting point, °C	n_D^{50}
	quant., ml	solvent* qual.			
1	1000	b	3.94	52	1.4265
2	100	b	34.78	52	1.4265
3	100	b	16.39	52	1.4265
4	100	b	6.69	52	1.4265
5	100	b	0.63	—	1.4278
6	100	b	0.13	—	1.4340
7	200	b	0.089	—	1.4450
8	300	b	0.050	—	1.4450
9	1000	b	0.029	—	1.4465
10	1000	b	0.011	—	—
11	1000	b	0.006	—	—
12	1000	b	0.006	—	—
13	1000	b	0.005	—	—
14	1000	b	0.005	—	—
15	1000	b	0.004	—	—
16					
17	1000	ke	0.005	—	—
18	1000	ke	0.047	—	—
19	1000	ke	0.015	—	—
20	1000	ke	0.011	—	—
21	1000	ke	0.010	—	—

* b = naphtha, ke = chloroform–ethanol 1 : 1 mixture

the eluent under nitrogen gas pressure applied in the eluent feed tank. This pressure was measured with a mercury manometer, the pressures needed for the rate mentioned were 0.25—0.35 atm gauge in the case of paraffins, and 0.6—0.8 atm gauge for ceresin.

Macro-crystalline paraffin samples were chromatographically tested at room temperature. The sample of micro-crystalline paraffin (ceresin) was hardly soluble in naphtha, therefore it was chromatographed at 50 °C. Higher temperatures could not be considered since the initial boiling point of the solvent was low (60 °C). The solubility of ceresin at 50 °C was sufficient for chromatography. The main part of the solvent was removed by distillation of the fractions, then the samples were evaporated to constant weight on a water bath. Weight was

Table 3

Characteristics of the fractions obtained by chromatography of Sample 2

No. of fraction	Eluatum		Percentage of desorbed substance, of total yield in 100 ml eluatum	Rotat. setting point, °C	n_D^{20}
	quant., ml	solvent qual.			
1	500	b	0.12	—	—
2	250	b	0.29	—	—
3	250	b	25.94	57.5	1.4300
4	100	b	23.68	57.5	1.4300
5	100	b	6.70	57.5	1.4300
6	100	b	0.96	57.5	1.4300
7	100	b	0.12	—	—
8	100	b	0.12	—	—
9	250	b	0.147	—	1.4532
10	250	b	0.111	—	1.4551
11	1000	b	0.031	—	1.4515
12	1000	b	0.012	—	—
13	1000	b	0.013	—	—
14	1000	b	0.013	—	—
15	1000	b	0.013	—	—
16	1000	b	0.014	—	—
17	1000	b	0.011	—	—
18	1000	b	0.013	—	—
19	1000	ke	0.011	—	—
20	1000	ke	0.043	—	—
21	1000	ke	0.043	—	—
22	1000	ke	0.017	—	—
23	1000	ke	0.017	—	—
24	1000	ke	0.020	—	—

* b = naphtha, ke = chloroform—ethanol 1 : 1 mixture

accepted as constant when it decreased by less than 1 mg within 3 hours of heating.

Data of the fractions received during adsorption of the samples are shown in Tables 2, 3 and 4, chromatograms are shown in Figs 1, 2 and 3, setting points and refractive indices in Figs 4, 5 and 6. In these latter, eluated material quantities are taken as abscissae. Yields of individual chromatographic runs are listed in Table 5.

For better presentation the co-ordinate scales are not uniform in Figs 1, 2 and 3 which show the chromatograms. The scale of the ordinate is changed

Table 4

Characteristics of the fractions obtained by chromatography of Sample 3

No. of fraction	Eluatum		Percentage of desorbed substance of total yield in 100 ml eluatum	Rotat. setting point, °C	n_D^{80}
	quant., ml	solvent*			
1	500	b	—	—	—
2	300	b	0.83	63	1.4460
3	200	b	11.02	64.5	1.4402
4	100	b	10.71	66.0	1.4405
5	100	b	8.00	67.5	1.4406
6	100	b	5.47	68.5	1.4408
7	100	b	4.33	69.2	1.4410
8	100	b	6.15	69.2	1.4435
9	250	b	1.74	71.0	1.4445
10	250	b	3.00	73.0	1.4502
11	1000	b	0.361	—	1.4475
12	1000	b	0.220	—	1.4469
13	1000	b	0.183	—	1.4456
14	1000	b	0.170	—	1.4460
15	1000	b	0.120	—	1.4460
16	1000	b	0.100	—	1.4464
17	1000	b	0.114	—	1.4466
18	1000	b	0.160	—	1.4456
19	1000	b	0.133	—	1.4453
20	1000	b	0.096	—	1.4453
21	1000	b	0.082	—	1.4470
22	1000	b	0.037	—	1.4483
23	1000	ke	0.079	—	1.4468
24	1000	ke	0.083	—	1.4569
25	1000	ke	0.053	—	—
26	1000	ke	0.023	—	—
27	1000	ke	0.038	—	—
28	1000	ke	0.011	—	—

* b = naphta, ke = chloroform—ethanol 1 : 1 mixture.

after the sixth, the eighth and the tenth elution fraction for Sample 1, Sample 2, and Sample 3, respectively. This change consists in that for Samples 1 and 2 the order of magnitude is reduced but the numerical values of the divisions are retained (thus they do not figure on the second ordinate scale), for Sample 3, however, both order of magnitude and numerical values had to be changed.

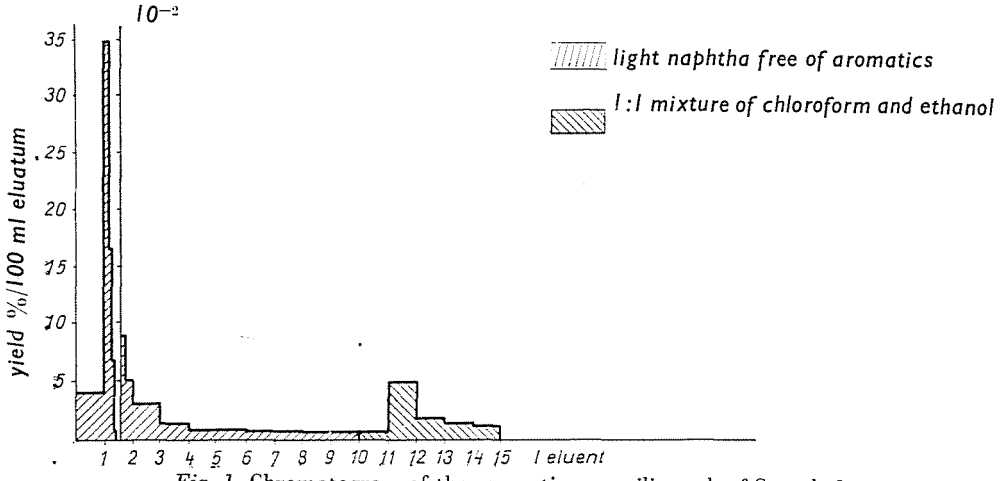

Fig. 1. Chromatogram of the separation, on silica gel, of Sample 1

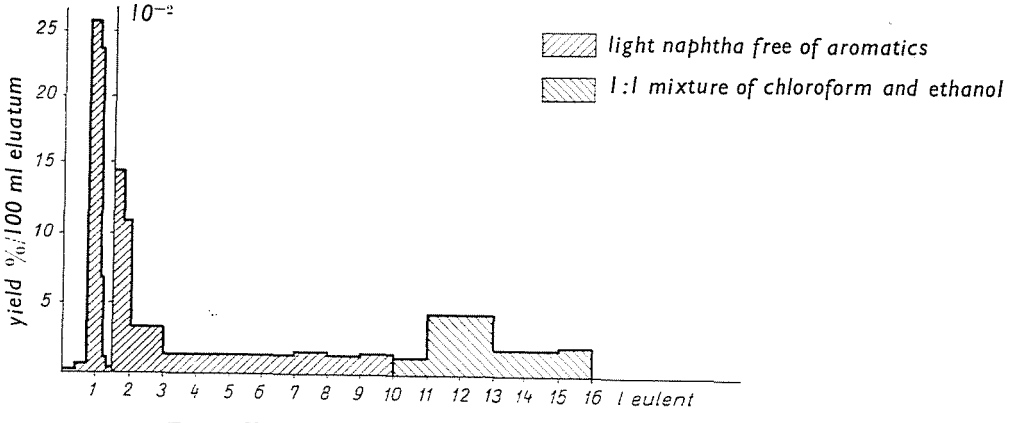

Fig. 2. Chromatogram of the separation, on silica gel, of Sample 2

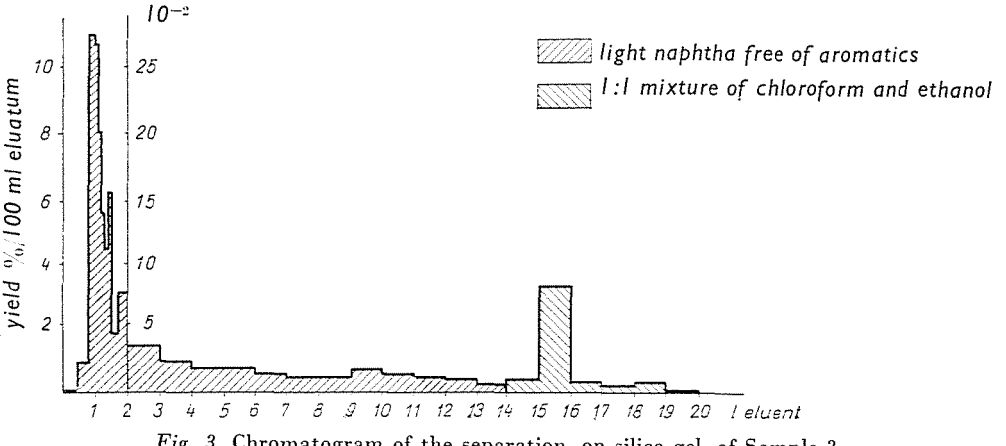

Fig. 3. Chromatogram of the separation, on silica gel, of Sample 3

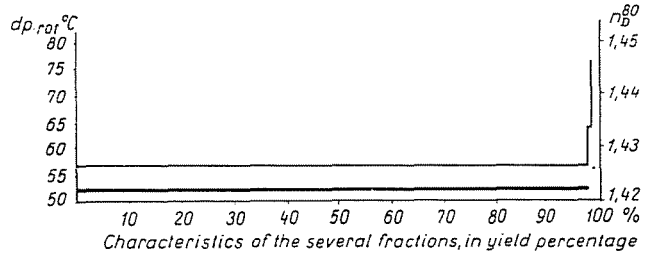

Fig. 4. Setting points and refractive indices of hydrocarbons separated by chromatography, from Sample 1; ▬▬▬ rotational setting point, - - - - - n_D^{80}, measured

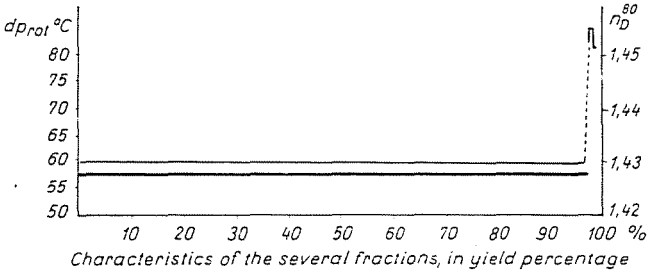

Fig. 5. Setting points and refractive indices of hydrocarbons separated by chromatography, from Sample 2*; ▬▬▬ rotational setting point, ——— n_D^{80}, measured

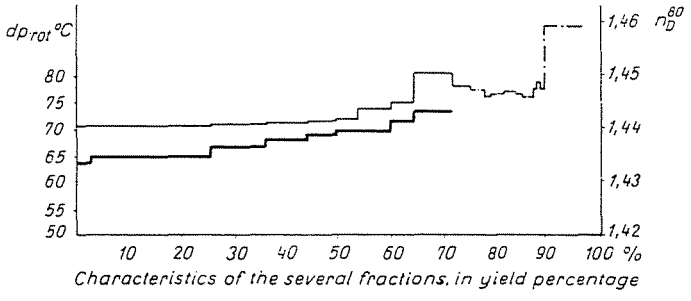

Fig. 6. Setting points and refractive indices of hydrocarbons separated by chromatography, from Sample 3**; ▬▬▬ rotational setting point, ——— n_D^{80} measured, — — — — n_D^{80} calculated

With the progress of chromatography the later fractions contained substances in quantities so small that the second peak, characteristic of the aromates — should its emergence be well discernible — could not be drawn else but by

* Due to lack of sufficient substance, for the part indicated by the dashed line no measurements could be carried out.

** For the part indicated by the dotted line, refractive indices were calculated from figures obtained in measurements over 80 °C.

Table 5

Yields of chromatographic runs

No. of sample	1.		2.		3.	
	g	%	g	%	g	%
Weight of sample	40.0008	100	40.0001	100	40.1780	100
Yields	40.1442		41.0062		39.1775	97.51
Total percentage of saturated fractions, of the yield	39.8085	99.16	40.4230	98.57	35.0846	89.55
Percentage of unsaturated fractions, of the yield	0.3357	0.84	0.5832	1.43	4.0929	10.45

changing the scale if it was to be shown in the same chromatogram as the saturated peak.

Ultra violet spectrophotometry was done in a Spectromom 201-type instrument. Samples for the determination of aromatic compounds were dissolved in iso-octane. This solvent was purified from aromatic components by repeated passage through a silica gel bed. Referred to water twice distilled, the extinction of this purified iso-octane was 0.2 at 200 millimicrons.

Separation with molecular sieves

Normal hydrocarbon contents of macro- and micro-crystalline samples have been determined by adsorption on molecular sieves. The samples were 2 g each, weighed to mg accuracy. Iso-octane was the solvent, from which normal hydrocarbons were removed by a molecular sieve.

To the solution of the sample, 40 g of a Linde 5 A type activated molecular sieve was added and the mixture boiled under a reflux condenser. The times needed for the adsorption of macro-crystalline and of micro-crystalline paraffins were 4 hours and 6 hours, respectively. After adsorption, the solution was filtered and the molecular sieve containing the normal hydrocarbons was collected. The solution contained all the "non-straight chain" hydrocarbons, the amount of which was found by evaporating the solvent and drying the residue to constant weight. Normal paraffins were recovered from the molecular sieve by desorption through boiling in n-hexane.

Duration of boiling was 10 hours, but the desorption of the normal hydrocarbons could not be achieved in one step, therefore the adsorbent was separated by filtration and boiled again in fresh n-hexane. For a practically complete desorption of paraffins nine steps, and of ceresin eight steps were necessary. Desorption was accepted as complete when further desorption failed

to produce more than a 0.1 per cent increment of paraffin referred to the paraffins desorbed in the given step and evaporated to constant weight. Quantitative data showing the results of separation with molecular sieves are presented in Table 6.

Table 6

Yields of separation with molecular sieves

	1.		2.		3.	
No. of sample	g	%	g	%	g	%
Weight of sample	2.000	100	2.000	100	2.000	100
Not adsorbed on mol. sieve	0.185	9.4	0.346	17.3	1.565	78.3
Adsorbed on mol. sieve	1.815	90.6	1.654	82.7	0.435	21.7
Recovered from mol. sieve	1.781	89.1	1.551	77.7	0.391	19.6
Recovered percentage of the adsorbed part		98.5		94.2		89.8

Evaluation of experimental results

The results of chromatography and separation by molecular sieves of the two macro-crystalline and one micro-crystalline paraffins (ceresin) can be summarized as follows.

Sample 1

The sample tested by chromatography was desorbed in a total of 21 stages or steps, and recovered to 99.8 per cent by weight. 16 fractions were obtained with light naphtha, and 5 fractions with the chloroform and ethanol solvent mixture. The substance recovered by evaporation of the solvent from the first six naphtha fractions (total eluate volume was 1.5 litre or 10 per cent of the solvent used for elution) amounted to 98 per cent by weight of the overall yield, the solid hydrocarbon content of the further 10 fractions was not more than 1 per cent by weight of the total yield. The quantity of all solid hydrocarbons of saturated character was 99.16 per cent by weight, the quantity of the substance desorbed with the chloroform–ethanol mixture was 0.84 per cent by weight. Yields are shown in Table 6, the chromatogram in Fig. 1, the characteristics measured and calculated for the individual fractions are listed in Tables 2 and 7.

Fig. 1 shows how sharp a separation was obtained. In consequence of this, several fractions yielded quantities of substance quite sufficient for per-

Table 7

Calculated data of the first chromatographic fractions of Samples 1 and 2

No. of fraction	M	Av	Rv	Sv
1—1	355	2	1.5	3.5
1—2	355	2	1.5	3.5
1—3	355	2	1.5	3.5
1—4	355	2	1.5	3.5
2—1	—	—	—	—
2—2	—	—	—	—
2—3	392	0.5	4.0	4.5
2—4	392	0.5	4.0	4.5
2—5	392	0.5	4.0	4.5
2—6	392	0.5	4.0	4.5

Av = asymmetry value
Rv = ring value
Sv = sum value

forming the tests, while others did not give enough even for refraction measurements. The recovered substance fractions of sufficient quantity were tested for refraction, molecular weight, and other characteristics, and values thus found agreed within limits of experimental error with the data of the initial substance.

Ultra violet spectra showed the aromatic contents of the sample to be composed mainly of hydrocarbons with the benzene ring. Percentage by weight of carbon in benzene ring bond was 0.07%, that in naphthalene bond 0.01%. Neither phenanthrene, nor anthracene were detected.

With molecular sieves, 9.4 per cent by weight of not adsorbed, branched and cyclic compounds could be separated from the normal paraffins. The

Table 8

Experimental and calculated data of fractions separated with molecular sieves from Sample 1

	n_D^{50}	Rotat. setting point, °C	M	Av	Rv	Sv
Initial substance	1.4265	52.5	355	2	1.5	3.5
Normal hydrocarbon fraction	1.4256	52.5	353	0.5	0.5	1
Other than normal hydrocarbon fraction	1.4320	40	375	14	10	24

amount of absorbed normal paraffins was 90.6 per cent by weight, of which, however, only a part (98.5 per cent) could be recovered by desorption with n-hexane (cf. Table 6). Measured and calculated characteristics of the fractions are listed in Table 8. On the basis of refraction, setting, molecular weight, asymmetry-, ring-, and sum values it can be said that separation of normal from other paraffins was effective and that these groups of hydrocarbons were distinctly isolated.

According to chromatographic and molecular sieve separation of Sample 1, the distribution by weight of its main hydrocarbon groups is shown in Table 13.

Sample 2

Desorption from the silica gel yielded 24 fractions. Similarly to the previous sample, the first 1.5 litre of the solution contained 98 per cent of the total yield. Referred to the yield, the amount of the saturated hydrocarbons was 98.57 per cent, that of the unsaturated was 1.43 per cent. Chromatogram is shown in Fig. 2, yields of fractions, measured and calculated characteristics are listed in Tables 3 and 7. Curves of refraction and setting values are shown in Fig. 5.

According to UV spectra, carbon content of the sample bond on benzene rings was 0.11 per cent by weight, naphthalene was present in traces, and no phenanthrene or anthracene could be detected. Distribution by weight of the main hydrocarbon groups in the sample is shown in Table 13.

With the molecular sieve, 17.3 per cent of branched chain and cyclic hydrocarbons were separated from the normal paraffins, 94.2 per cent of which were only recovered from the molecular sieve (Table 6). Measured and calculated characteristics are shown in Table 9, according to which the separation of the normal components was successful, the changes in the individual characteristics were as expected.

Table 9

Experimental and calculated data of fractions separated with molecular sieves from Sample 2

	n_D^{50}	Rotat. setting point, °C	M	Av	Rv	Sv
Initial substance	1.4295	58	390	0.5	4	4.5
Normal hydrocarbon fraction	1.4283	61	392	0	0	0
Other than normal hydrocarbon fraction	1.4340	46	396	11.5	9.5	21

In the case of this sample the selectivity of separation was also checked by mass spectrometry. Under the conditions of testing the branches hydrocarbons are broken at their tertiary carbon atom to give fragments, while some normal paraffins are fragmented, and some give molecule ions $C_nH_{2\,n+2}$. Thereby it is principally the fraction containing the iso-paraffins that is suitable for an evaluation of selectivity in so far as in a mixture free of normal paraffins molecular ions do not appear at all whereas pure normal paraffins exhibit both fragment and molecule-ion peaks.

The mass spectrograph used was an MN-1303 type instrument.

Testing conditions were as follows. Temperature 200 °C; ionization voltage 50 eV; emission current 1.5 mA.

In the mass spectrum no peak characteristic of C_nH_{2n+2} molecule ions was in evidence, thus normal paraffins were missing. The peaks corresponded mainly to mass number C_nH_{2n+1}; this is characteristic of the fragments produced by ionization effect from branched molecules. The spectrum suggests the presence of hydrocarbons of the series C_nH_{2n} and C_nH_{2n-6}. This is due to the presence of naphthenic and aromatic compounds.

Sample 3

In the course of chromatography, desorption of the ceresin was carried out with 14 litres of light naphtha free of aromatics, in 22 fractions, then with 6 litres of chloroform—ethanol mixture in 6 fractions. 89.55 per cent of the total yield consisted of the saturated fractions desorbed with aromatic free light naphtha, and 10.45 per cent of unsaturated fractions desorbed with the chloroform—ethanol mixture. In contrast to experiences with paraffins, here the first 1.5 litre of the eluate gave only 49 per cent of the total yield. The colour of the saturated fraction was white instead of ochre like that of the initial sample. The colour of the unsaturated compounds, both here and for the paraffinic sample, was dark brown. The chromatogram of ceresin is shown in Fig. 3, for characteristics of the several fractions see Tables 4 and 10, and Fig. 6, respectively.

As compared with the chromatography of paraffins, a characteristic difference was that in the course of desorption with aromatic free light naphtha the saturated type compounds separated also according to their molecular weight (cf. Table 10).

The asymmetry-, ring-, and symmetry values, as defined by GROSZ and GRODDE [19], show that also the quantity of branched and saturated rings is greater than that of saturated and cyclic compounds in paraffins. This statement is in accordance with the generally accepted view about the composition of paraffins, and with observations made with molecular sieve separations. Figs 4, 5 and 6 show the changes that occur in the refraction in-

Table 10

Calculated data for ceresin, Sample 3

No. of fraction	M	Av	Rv	Sv
3— 1	—	—	—	—
3— 2	—	—	—	—
3— 3	504	10	10	20
3— 4	510	8	12.5	20.5
3— 5	515	9.5	10.5	20
3— 6	525	9.5	3.5	13
3— 7	536	9.0	7.0	16
3— 8	558	9.0	13.0	22
3— 9	580	10.0	8.5	18.5
3—10	658	11.5	16.5	28

dices measured at 80 °C, or calculated, and in rotational setting point values, as elution proceeds. Especially with ceresin chromatography it is interesting to see, with the progress of desorption, the refractive index to diminish after a certain "desorption yield". This can be attributed in part to the fact that the last fractions of the elution with naphtha become enriched in hetero-compounds. In this domain also the course of the refractive index vs. temperature curves changes (cf. Fig. 7). The two refractive indices due to the birefringence of the

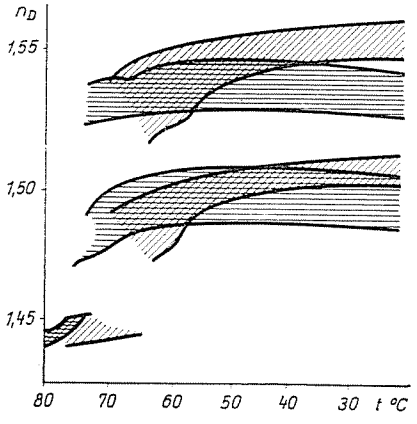

Fig. 7. Refractive indices vs. temperature curves of two principal groups of fractions obtained by the separation on silica gel of Sample 3. Oblique shaded lines show extension of the set of curves relating to fractions between the first and tenth, horizontal shaded lines show that of the set of curves relating to fractions between the eleventh and fifteenth fraction

solid phase of the first fraction in naphtha increase monotonously with the decrease of temperature, whereas the solid phase refractive indices of the solid hydrocarbons in the tenth to fifteenth fractions became practically independent of temperature at about 15 °C below the setting point. Considering the fact that temperature dependence of optical birefringence and refractive indices is governed by the crystalline structure [22], it may be supposed that compounds differing in crystalline structures from that of the initial substance can be separated by elution chromatography on silica gel.

Separation with molecular sieves showed that no significant change of the refraction of the separated fractions occurred. Changes of setting points were as expected (cf. Table 11).

According to UV spectra, the percentage distribution of carbons in aromatic bonding was considerably higher as compared with that of macrocrystalline paraffins; quantitative proportions are shown in Table 12.

A comparison of separations with molecular sieve, and by chromatography, of the samples studied, show the weight ratios between the main hydrocarbon groups as presented in Table 13.

Table 11

Experimental and calculated data of fractions separated with molecular sieves from Sample 3

	n_D^{50}	Rotat. setting point, °C	M
Initial substance	1.4410	73—75	570
Normal hydrocarbon fraction	1.4414	79	605
Other than normal hydrocarbon fraction	1.4390	71	550

Table 12

Distribution according to ring types, of the carbon contents in aromatic bonding, in Samples 1, 2, and 3

No. of sample	1	2	3
Percentage by weight in benzene	0.07	0.11	0.94
Naphthalene	0.01	traces	0.16
Phenanthrene	—	—	0.03
Anthracene	—	—	0.03

Table 13

Composition of Samples 1, 2, and 3 in percentage by weight of the main hydrocarbon groups

Sample	Normal hydrocarbons	Aromatic hydrocarbons	Branched chains and naphthenic rings
1	90.60	0.84	8.56
2	82.70	1.43	15.87
3	21.70	10.45	67.85

Data of this Table show that the ratios of the individual hydrocarbon groups which play an important role also in the functional behaviour of ceresins changed abruptly. Most conspicuous was the increase of the isoparaffinic + naphthenic fraction to the expense of normal paraffins.

In view of the fact that hydrocarbons of this group offer the greatest possibility of isomerism, further that conditions for changes of crystallization and modification are not favourable because of steric hindrances, it becomes understandable how composition affects the difference between the main functional properties of paraffins and ceresins.

*

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Summary

Paraffins, and ceresins, obtained from Romaskino petroleum, have been separated into pure paraffinic, aromatic, and mixed naphthenic and isoparaffinic hydrocarbons. Separation was effected by chromatography on silica gel and adsorption on molecular sieves. In macro-crystalline paraffin samples 1 per cent by weight and in micro-crystalline paraffin samples 10 per cent by weight of aromatics were found. Macro-crystalline substances contained mainly benzene homologues, and in a lesser degree naphthalene with phenanthrene and aromatic impurities. Branched chains and cyclic structures were separated from n-paraffins with molecular sieves. Selectivity of separations was checked by analytical tests of the fractions, and by mass spectrometry. In macro-crystalline and in micro-crystalline paraffins, 83 to 90 and 20 per cent by weight, respectively, of normal hydrocarbons were found.

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