INVESTIGATION OF MOTOR OILS BY SELECTIVE ADSORPTION

By

L. VAJTA

Department of Chemical Technology, Polytechnical University, Budapest

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It is known that at the evaluation of motor oils the classification of their viscosity and the performance properties serve as main basis.

The most widespread method of classification of viscosity is the SAE system which, in certain cases, takes into account not only the viscosity itself but also the viscosity indexes, e.g. when multigrade oils are evaluated. In these instances, on the basis of the known correlations between the hydrocarbon composition and the viscosity properties, the classification indicates the chemical nature of lubricating oils as well.

The performance depends on the nature of the basic oil only to a smaller extent, being influenced to a much greater extent by the additives applied.

The present experiments were undertaken with the purpose to investigate the variations in the chemical structure of various motor oils with the aid of selective adsorption.

Investigated types of motor oils

For the purposes of investigation, three motor oils of different chemical character were chosen. The data of these oils are presented in Table I. Of these motor oils, No. I is a refined solvent product, identical with the oil used since several years as a motor oil in Hungarian two-cycle gasoline motors. Oils No. II and III are sulfuric acid refined products with smaller and greater contents of naphthenic hydrocarbons.

Motor oil No. I is prepared by blending with residual oil. It can be seen in Table 1 that significant differences exist in the chemical structure of the oils. While motor oil No. I has a viscosity index of 82, the indexes of oil No. II and III are 28 and 14, respectively. As regards Conradson number, oil No. I shows the highest number: 0.49, oils No. II and III having Conradson numbers of 0.39 and 0.45, respectively. The relatively higher Conradson number of oil No. I is not due to unsatisfactory refining but it is to be ascribed to its paraffinic character. Still, this paraffinic character is not reflected by the pour point of the oil (its value of -10 °C could be attained by using a depressing

Table 1

Investigation of the experimental motor oils

Number of motor oil	I	II	III
Density at 20 °C	0.893	0.929	0.932
Refractive index at 20 °C	0.4951	1.5131	1.5150
Kinematic viscosity, cSt at 50 °C	90.40	142	151
at 100 °C	13.97	15.78	15.96
Engler viscosity, °E at 50 °C	11.91	18.69	19.87
at 100 °C	2.11	2.40	2.43
Viscosity index DD	82	28	14
Spec. gravity/viscosity constant	0.8301	0.8677	0.8708
Aniline point, °C	107.7	88.8	87.0
Pour point, °C according to MSz (Hung. stand.)	−10	−24	−20
Flash point, °C (Marcusson)	242	246	241
Conradson number, %	0.49	0.39	0.45
Acid number, mg KOH/g	0.05	0.07	0.12
Ash content, %	0.0185	0.0172	0.0022
Water content, %	ø	ø	ø
Hard asphalt content, %	ø	ø	ø
Free mineral acid and alkali	ø	ø	ø
Mechanical contamination, %	ø	ø	ø
Distillation according to Peterkin—Ferris at an absolute pressure of 10 mm Hg			
Initial b. p., °C	238	250	247
5% by vol. distils to °C	257	263	260
10% by vol. distils to °C	270	279	270
20% by vol. distils to °C	286	292	283
30% by vol. distils to °C	305	300	290
40% by vol. distils to °C	316	307	298
50% by vol. distils to °C	321	315	307
60% by vol. distils to °C	342	323	318
70% by vol. distils to °C	355	330	328
80% by vol. distils to °C	370	337	338
90% by vol. distils to °C	total distillate	346	352
95% by vol. distils to °C	83% by vol.	353	362
Final b. p.		360	372
To 300 °C distilled, % by vol.	28	30	41

additive). The above-mentioned order of properties following from the chemical character can also be supported by other parameters such as aniline point, specific gravity/viscosity constant, refractive index.

The flash point was practically the same with all the three oils tested (241—246 °C). As regards viscosity, oil No. I showed the lowest, while oil No. III the highest viscosity. In respect to the composition of distillate, the following observations were made. The role of residue oil applied for blending oil No. I is clearly visible from the data of the distillation according to Peterkin Ferris. Oils No. II and III show almost identical distillation curves, boiling points pertaining to 50% of distillate are 315 and 307, respectively. However, it must be noted that oil No. II is a narrower fraction, the initial b.p. of which is higher by 3 degrees, while the final b.p. is lower by 12 degrees than those of oil No. III.

Investigation of motor oils by selective adsorption

In order to evaluate in detail the nature of the mentioned three types of motor oil it appeared to be practical to fractionate the oils by selective adsorption, and to investigate the fractions with the purpose of approaching the structure of oils.

By separating the oils to ten fractions each, thirty fractions could be obtained.

Selective adsorption

In the present investigations, an iron tube of 70 mm diameter and 5100 mm height served as adsorption column (Fig. 1).

The column was packed with 15 kg of silicagel adsorbent of a particle size smaller than 0.5 mm, previously dried to constant weight. The absorbent was placed between sieve cloth and cotton as sealing layers. The tested oils were diluted with analytical gasoline in a ratio of 1 : 1, and the diluted solution was poured on the adsorbent column. 1. Analytical gasoline, 2. analytical gasoline containing 10% of benzene, 3. benzene and 4. acetone, previously treated with calcium chloride to remove water traces, served as eluting agents. Prior to beginning the tests, the column was filled up with analytical gasoline from the bottom upwards, in order to remove air bubbles. In each run, 9% of oil (1300 g) referred to silicagel could be fed to the column. On applying a pressure of 1 to 3 atm., an operating rate of one litre per hour could be maintained, both on feeding the oils and at the elution.

The single fractions eluted varied from 100 to 800 ml, depending on the oil content. After the distillation of the solvent, its last traces were removed on the water bath, by introducing a stream of carbon dioxide.

Table 2
Investigation of the fractions of oil No. I.

	1	2	3
Yield, %	10.1	9.8	10.2
Density at 20 °C	0.8601	0.8657	0.8697
Refractive index, n_D at 20 °C	1.4830	1.4837	1.4857
Kinematic viscosity at 20 °C, sCt	342	240	240
,, 50 °C, sCt	69.88	52.83	51.28
Engler viscosity at 50 °C, °E	9.2	7.0	6.8
Kinematic viscosity at 100 °C, cSt	13.7	10.6	10.1
,, 100 °F, cSt	124.4	93.0	90.5
,, 210 °F, cSt	14.05	10.93	10.51
Viscosity index DD	+116	+110	+107
Specific gravity/viscosity constant	0.795	0.810	0.812
Aniline point, °C	132,0	124.6	121.3
Turbidity point, °C	+24	+20	+18
Pour point (Marcusson), °C	+13	+11	+10
Flash point (Marcusson), °C	268	243	234
Conradson number, %	0.02	0.02	0.02
Aromatic cyclics, % by weight	12	10	10
Naphthene aromatics, % by weight	3	8	10

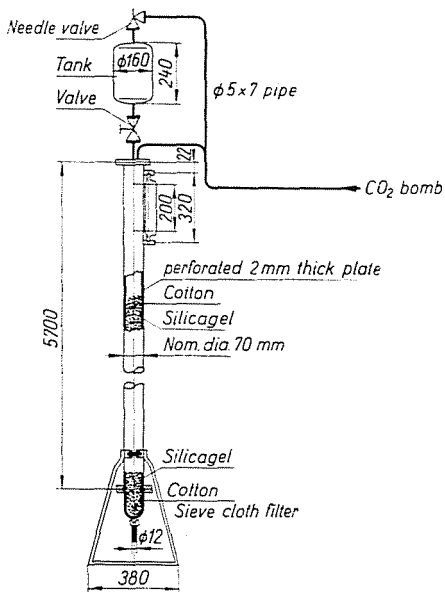

Fig. 1. Laboratory equipment for selective adsorption

obtained by selective adsorption

4	5	6	7	8	9	10
9.6	10.1	9.7	9.9	9.7	10.2	7.8
0.8740	0.8769	0.8809	0.8935	0.9274	0.9614	
1.4872	1.4882	1.4899	1.4970	1.5230	1.5473	
255	292	315	600	2350	6150	
52.40	53.86	56.54	88.85	124.3	359.1	
6.9	7.1	7.5	11.7	16.3	47.2	
10.0	10.1	10.3	13.7	23.5	26.1	48.9
93.5	97.5	103.3	175.5	510.6	990.0	
10.36	10.47	10.62	14.13	24.28	27.15	
+100	+97	+92	+82	+61	−5	
0.822	0.824	0.827	0.832	0.850	0.883	
120.0	117.9	117.8	113.5	82.4	56.6	
+17	+16	+14	+14	+9		
+9	+9	+6	+3	−6	−6	+6
227	218	217	219	262	242	234
0.02	0.02	0.02	0.07	0.75	1.48	5.6
10	10	11	13.5	28.5	41	
14	16	17	21	15	15	

This operation was repeated four times to obtain oil fractions of about 500 g. Thus, during the experiment as many as 12 runs of selective adsorption process were carried out. During these operations, it was necessary to regenerate the silicagel.

Investigation of the fractions obtained by selective adsorption

The data of the fractions obtained from the three basic oils tested are listed in Tables 2, 3 and 4. Changes in the analytical data of the fractions can readily be followed in Figures 2 to 5.

In the various fractions, the quantity of hydrocarbons with a closed carbon chain was determined. This was calculated by the method suggested by Cornelissen and Watermann, on the basis of the density measured at 20 °C, of the refractive index, and of the viscosity measured at 20 °C. The spec. gravity/viscosity constant was calculated by the Zerbe nomogram.

Besides the amounts required for the above-mentioned investigations, the fractions obtained by selective adsorption were also sufficient for the later motor tests of the single fractions.

Table 3
Investigation of the fractions of oil No. II.

	1	2	3
Yield, %	10.0	9.9	9.9
Density at 20 °C	0.8739	0.8828	0.891 5
Refractive index, n_D at 20 °C	1.4855	1.4905	1.4933
Kinematic viscosity at 20 °C, cSt	252	340	415
„ 50 °C, cSt	49.4	58.8	65.8
Engler viscosity at 50 °C, °E	5.6	7.8	8.7
Kinematic viscosity at 100 °C, cSt	9.65	10.4	10.8
„ 100 °F cSt	87.9	111.0	127.5
„ 210 °F cSt	9.89	10.6	11.1
Viscosity index DD	+99	+83	+74
Specific gravity/viscosity constant	0.823	0.830	0.838
Aniline point, °C	120.6	115.7	112.8
Turbidity point, °C	+5	+2	+2
Pour point (Marcusson), °C	−17	−28	−30
Flash point (Marcusson), °C	249	239	238
Conradson number, %	0.01	0.01	0.01
Aromatic cyclics, % by weight	8	9	9
Naphthene aromatics, % by weight	17	17.5	27

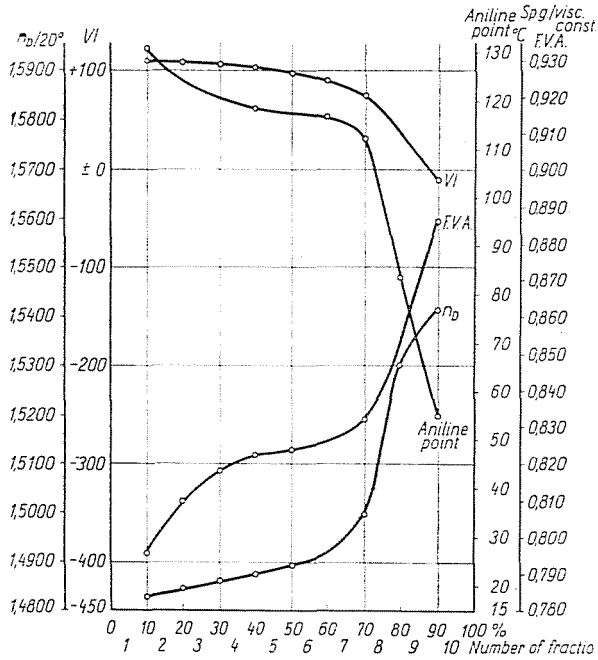

Fig. 2. Main characteristics of the fractions obtained by selective adsorption from oil No. I

obtained by selective adsorption

4	5	6	7	8	9	10
9.9	9.9	9.9	10.0	9.8	10.2	8.8
0.8945	0.9024	0.9172	0.9537	0.9760	1.0092	
1.4951	1.4972	1.5094	1.5359	1.5518	1.5830	
480	570	1060	4500	13 000	150 000	
70.6	78.5	121.5	275	478	1813	
9.3	10.4	16.0	36.2	62.9		
11.1	11.8	15.0	21.8	26.7	44.8	115.3
139.7	159.0	259.5	723.0	1496	8460	
11.4	12.1	15.5	22.5	27.8	47.3	
+67	+62	+50	−11	−83	−450	
0.840	0.846	0.854	0.881	0.898	0.918	
111.8	110.9	93.8	61.3	47.7	25.0	
+2	0	−6				
−32	−30	−22	−11	+4	+16	+30
232	233	242	248	242	249	258
0.01	0.02	0.13	0.31	0.46	1.7	5.4
11	10	18	32	48		
27	33	30	28	30		

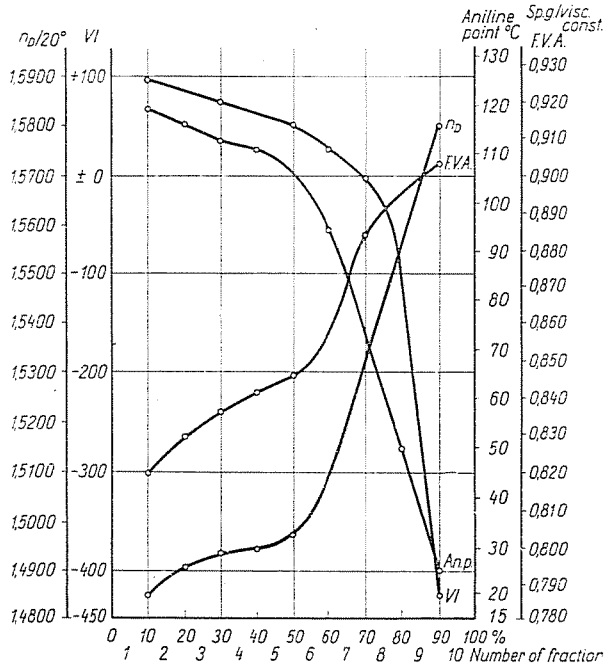

Fig. 3. Main characteristics of the fractions obtained by selective adsorption from oil No. II

Table 4

Investigation of the fractions of oil No. III.

	1	2	3
Yield, %	9.8	9.9	9.9
Density at 20 °C	0.8712	0.8904	0.9004
Refractive index, n_D at 20 °C	1.4869	1.4941	1.4975
Kinematic viscosity at 20 °C, cSt	300	480	610
„ 50 °C, cSt	55.4	72.5	85.7
Engler viscosity at 50 °C, °E	7.3	9.6	11.3
Kinematic viscosity at 100 °C, cSt	10.5	11.4	12.1
„ 100 °F, cSt	102.1	142	176
„ 210 °F, cSt	10.7	11.7	12.4
Viscosity index DD	+95	+70	+53
Specific gravity/viscosity constant	0.816	0.835	0.843
Aniline point, °C	120.2	113.6	110.3
Turbidity point, °C	+13	−4	−4
Pour point (Marcusson), °C	−7	−15	−16
Flash point (Marcusson), °C	242	238	234
Conradson number, %	0.01	0.01	0.01
Aromatic cyclics, % by weight	10	9	9
Naphthene aromatics, % by weight	12	24	30

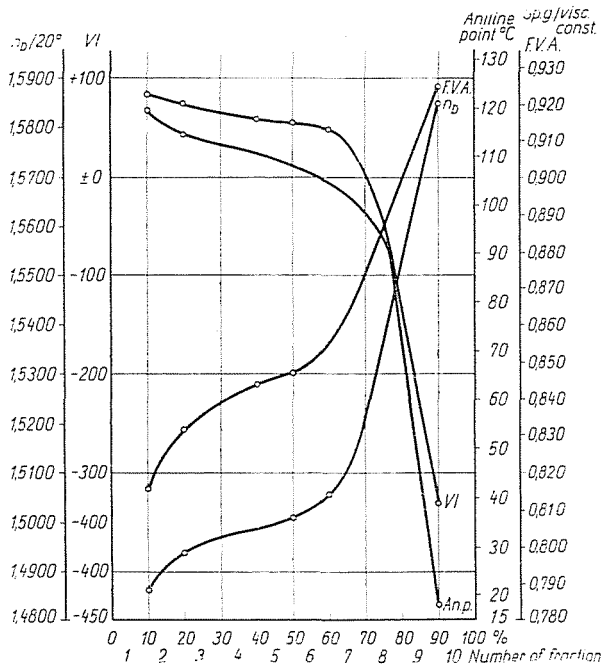

Fig. 4. Main characteristics of the fractions obtained by selective adsorption from oil No. III

obtained by selective adsorption

4	5	6	7	8	9	10
9.8	9.8	9.8	9.9	9.9	9.8	9.9
0.9024	0.9048	0.9115	0.9422	0.9709	1.0098	
1.4985	1.4994	1.5049	1.5310	1.5524	1.5862	
720	800	1180	3000	9500	85 000	
89.8	95.9	124.3	215	373	1214	
11.8	12.6	16.4	28.3	49.3		
12.4	12.7	14.8	19.0	22.5	34.8	83.5
189	203	273	543	1560	5220	
12.7	13.1	15.3	19.7	23.5	37.0	
+49	+44	+40	−29	−101	−330	
0.845	0.847	0.849	0.872	0.898	0.925	
110.0	109.1	102.7	64.0	51.0	17.8	
−4	−4	−6				
−17	−18	−21	−13	+2	+13	+33
228	226	238	240	243	235	249
0.01	0.01	0.04	0.24	0.50	1.84	5.1
9	9	14	31	42		
32	34	32	21	20		

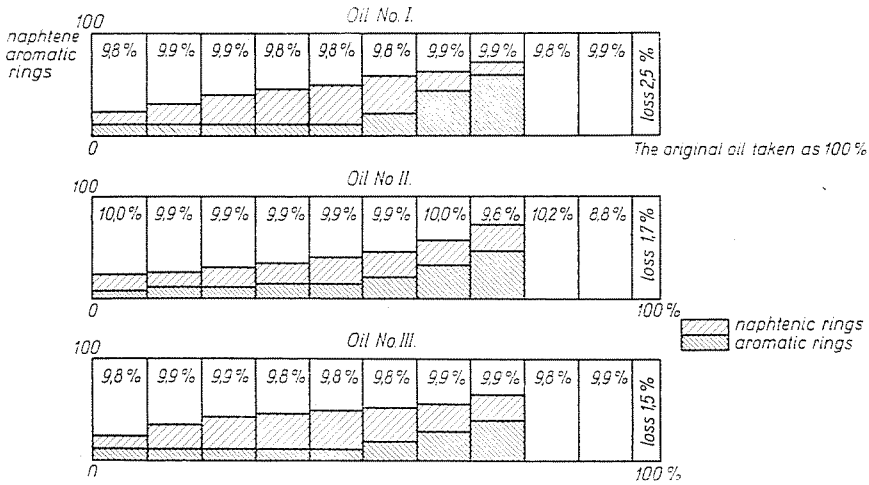

Fig. 5. Distribution and naphthene aromatic ring content of fractions obtained by selective adsorption from oils No. I—III

On investigating the fractions of oil No. I it was found that the content of naphthene aromatics increased from 15% in fraction 1 to 56% in fraction 9. The aniline points of these fractions are 132 and 56.6 °C, respectively. The amount of the fractions mentioned is nearly the same. The last fraction is not an oil-like substance any more. The variation of the viscosity indexes is as follows. The value of the viscosity index of three fractions is higher than 100, that of one fraction is 100, the viscosity index of three fractions ranges from 80 to 100, that of one fraction ranges from 80 to 0, while the viscosity index of two fractions is below 0. One fraction of the oil with an original Conradson number of 0.49 had Conradson number 0.02, while the Conradson numbers of fractions 8, 9 and 10 were 0.75, 1.48 and 5.6, respectively.

Investigation of the fractions of motor oil No. II proved that the content of naphthene aromatics of the fractions increased from 25% in fraction 1 to 78 in fraction 8. The aniline points of these fractions decreased from 120.6 °C to 47.7 °C.

The amount of the fractions was nearly the same. The last two fractions were not oil-like substances anymore. The specific gravity of fraction 9 has been higher than 1.0. The variations in the viscosity index were as follows. The viscosity index of two fractions was over 80, that of four fractions ranged from 80 to 0, that of fraction 7 was −11, while that of fraction 8 was −83. Fraction 1 obtained from the oil of the original Conradson number of 0.39 had Conradson number 0.01, fraction 8 that of 0.46, while fractions 9 and 10 showed Conradson numbers of 1.7 and 5.4, respectively. The pour points of the single fractions decreased at first from −17 to −32 to show later an increasing trend. Fraction 8 had a pour point of +4. However, this increase of pour point cannot be ascribed to the formation of a paraffin skeleton but rather to solidification due to increased viscosity.

On investigating the fractions of motor oil No. III it was found that the content of naphthene aromatics of the fractions increased from 22% in fraction 1 to 62% in fraction 8. The aniline points of the same fractions were 120.2 and 51 °C, respectively. The amounts of the fractions were almost the same. The last two fractions were not oil-like substances anymore. The specific gravity of fraction 8 is already higher than unit. The variations in viscosity in the single fractions were as follows. Three fractions, obtained from the original oil having a viscosity index of 14, showed viscosity indexes ranging from 100 to 50, three fractions had viscosity indexes ranging from 50 to 0, while fraction 7 and 8 showed viscosity indexes of −29 and −101, respectively. Fraction 1, obtained from the oil having an original Conradson number of 0.45, possessed a Conradson number of 0.01, while fractions 8, 9 and 10 showed Conradson numbers of 0.50, 1.84 and 5.1, respectively.

The results of investigations prove the existence of certain similarity between certain fractions of the three tested lubricating oils of different

character. Thus e.g. from the point of view of naphthene aromatics contents, of fractions 3 and 4 of oil No. I, fraction 1 of oil No. II and fraction 1 of oil No. III disclosed contents of hydrocarbons of closed carbon chain resembling each other.

As regards aniline points, a striking similarity was observed between fractions 3 and 4 of oil No. I, fraction 1 of oil No. II, and fraction 1 of oil No. III. From the aspect of viscosity indexes, in turn, fractions 5 and 6 of oil No. I, fraction 1 of oil No. II and fraction 1 of oil No. III resembled each other.

It appears from the above-given results that certain structural elements of the three basic oils of different structure are similar to or even identical with each other. However, it can clearly be seen at the same time that the basic oils were separated to fractions of very different nature by means of the fractionation process.

Striking results were obtained when the colour of the single fraction was examined. The first seven fractions of oil No. I were colourless, fraction 8 and 9 showed colour No. 3 and 4, respectively, while fraction 10 was black. The first six fractions of oil No. II were colourless, fractions 7, 8 and 9 showed colour No. 2, No. 3 and No. 5, respectively, while fraction 10 was black. The first six fractions of oil No. III were colourless, while fractions 7, 8 and 9 showed colour No. 3, No. 4 and No. 5, respectively, fraction 10 being black.

Investigation by circulating oxidation of the fractions obtained by selective adsorption

In addition to the descriptive evaluation of the fractions obtained by selective adsorption, very interesting data are afforded by their investigation by circulating oxidation.

The laboratory assay of lubricating oils with the aid of the circulation method furnishes informations on the nature of oils from three main aspects: thermal stability, resistance to oxidizing effects, and trend to form lacquers.

In order to determine thermal stability, the percentage of loss on evaporation during the test period is measured. Resistance to oxidation effects is estimated on the basis of the changes observed in certain parameters such as viscosity ratio, differences in Conradson numbers and acid numbers as compared with the corresponding original, unused oils.

The trend to form lacquers manifests itself in form of deposits which separate from the oil. Namely, when motor oils are intensively oxidized on metal surfaces, various oxyacids, resin and asphalt compounds are formed which adhere to the metal surface.

Under the conditions prevailing in spark ignition engines, the behaviour of oils in this respect is obviously unequivocal to lacquer formation, when

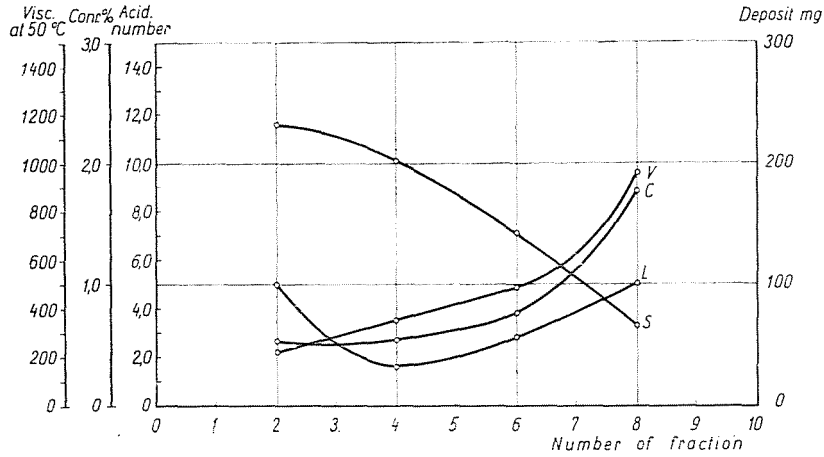

Fig. 6. Circulating oxidation of the fractions of oil No. I. Change of the main characteristics

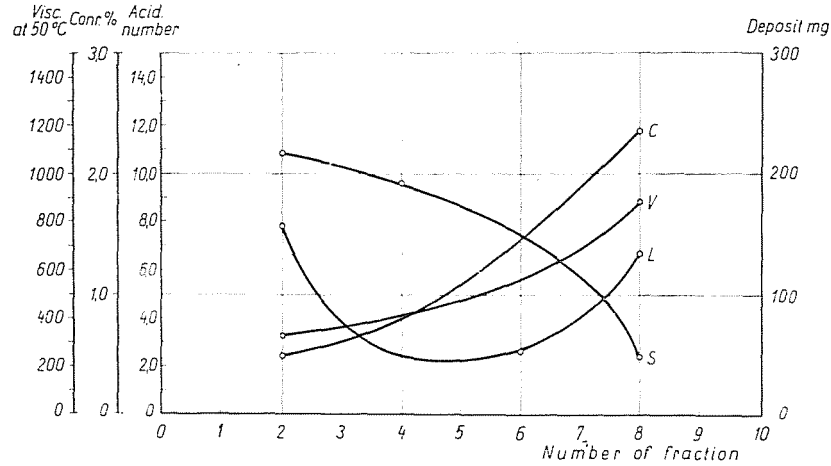

Fig. 7. Circulating oxidation of the fractions of oil No. II. Change of the main characteristics

piston rings gum up. In the case of the present experiments, our investigations were carried out according to the cited standard test, point I, at 250 °C, though in six-hour periods thus deviating from the prescriptions of this standard. The results obtained in these investigations as regards resistance to oxidizing effects and inhibition to lacquer formation are shown in Table 5 and in Figures 6 to 9, respectively.

From these data, the following conclusions can be drawn.

1. The oxidized fractions of all the three oils are characterized by the fact that with the increase of the numbering of the fractions, viscosity and Conradson numbers increase while acid numbers decrease. The increase of viscosity and Conradson number was the highest in case of oil No. III.

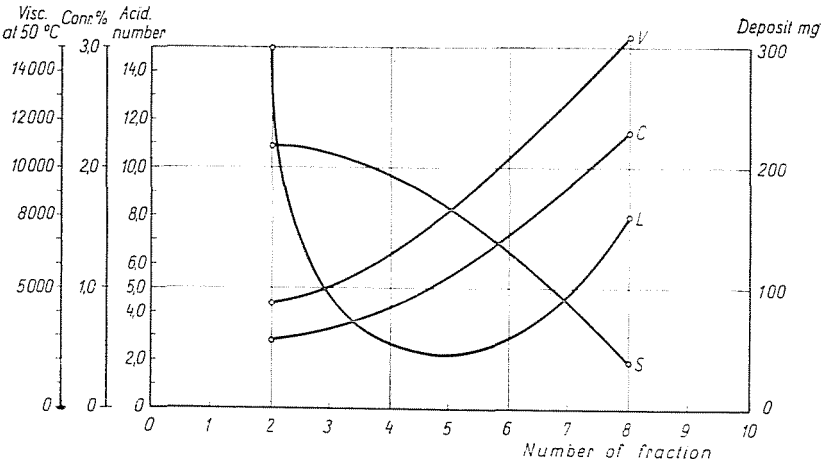

Fig. 8. Circulating oxidation of the fractions of oil No. III. Change of the main characteristics

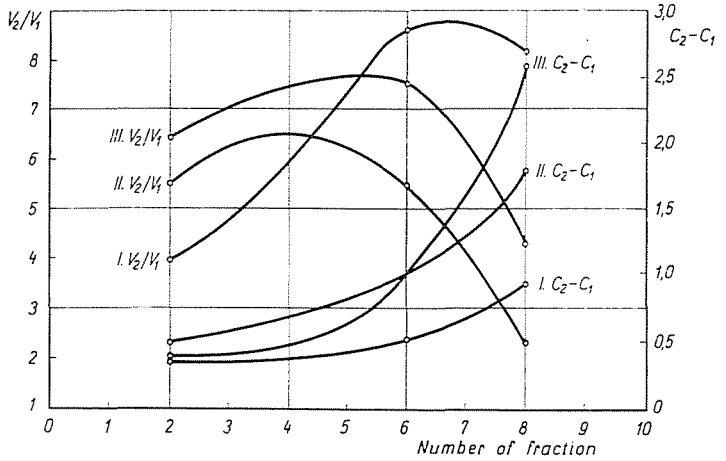

Fig. 9. Circulating oxidation of the fractions of oils No. I—III. Change of viscosity ratios and Conradson carbon differences

2. All the three oils are characterized by the fact that the minimum values of the curve representing the amount of deposits formed appear always in fractions No. 4 and 5. Deposits formed in the first fractions are essentially greater than those separated from the later fractions. However, fractions 6 and 8 are characterized again by larger values of deposits. The formation of deposits given above can be ascribed in the first fractions to the absence of inhibitors, while in the later fractions to higher resin contents.

3. Viscosity ratios ($V_2 : V_1$) disclose maximum values in fractions No. 4 and 5. From this aspect, the optimum behaviour was shown by the fractions of oil No. II. Increases in Conradson numbers ($C_2 - C_1$) proved to rise with

Table 5

Data of circulating oxidation tests of oil fractions obtained by selective adsorption

Number of oil type	Number of fraction	Kinematic viscosity at 50 °C prior to oxidation V_1	Kinematic viscosity at 50 °C after oxidation V_2	$V_2 : V_1$	Conradson number, % prior to oxidation C_1	Conradson number, % after oxidation C_2	$C_2 - C_1$	Acid number mg KOH/g after oxidation	Amount of deposit mg
I	2	52.8	207	3.92	0.02	0.42	0.40	—	100
	4	52.4	320	6.12	0.02	0.45	0.43	10.01	20
	6	56.5	460	8.15	0.02	0.68	0.66	8.23	50
	8	124.3	340	2.74	0.75	1.72	0.97	3.22	100
II	2	58.8	314	5.35	0.01	0.50	0.49	10.56	150
	4	70.6	430	6.13	0.01	0.64	0.63	9.78	40
	6	121.5	640	5.28	0.13	1.57	1.44	6.66	50
	8	478	1006	2.10	0.46	2.32	1.86	2.56	150
III	2	72.5	470	6.48	0.01	0.44	0.43	11.12	300
	4	89.8	630	7.02	0.01	0.49	0.48	8.34	40
	6	124.3	900	7.26	0.04	0.99	0.95	4.45	50
	8	375	1566	4.16	0.50	3.15	2.65	1.89	150

the numbering of fractions. Maximum increase was observed in the case o oil No. III.

By investigating the three motor oils of different chemical character it was possible to detect changes in the chemical character by fractionation with selective adsorption. Correlations were found with the character of fractions obtained by selective adsorption, disclosed in the ageing tests of these fractions. The present investigations yielded valuable data for the development of lubricating oils for two-stroke pump-spark-ignition explosion engines operated with gasoline.

Summary

Three motor oils having different chemical characters have been separated into 10 fractions each, by means of selective adsorption. The viscosity indexes of the oils have been +82, +28 and +14, respectively. From the main characteristics of the fractions it could be established, that the individual fractions (structural elements) of the oils having different structures resembled each other.

The results obtained by the oxidation test of the fractions showed that:

1. The viscosity and Conradson number increased with increasing serial number of the fractions.

2. The curve representing the amount of the deposit formed reached a minimum at the fractions No. 4 and 5.

3. The greatest viscosity ratio (V_2/V_1 after oxidation test) values were found in fractions No. 4 and 5.

László VAJTA, Budapest XI. Stoczek u. 2—4, Hungary