CHROMATOGRAPHY OF MINERAL OILS

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Translation

INTRODUCTION

2854

Through Professor Zerbe we obtained a description of the way in which the Rhenania used the chromatographic analytical method in determining the resin content.

In order to become acquainted with the procedure of the Rhenania, the resin content of a Balik Papan oil (TMC 6996) was determined precisely according to directions.

A sample of Freital Endvolt oil was also investigated in the hope that differences between Endvolt oils could be established by means of these experiments.

SUMMARY OF THE INVESTIGATION

A medium heavy machine oil from Balik Papan (TMC 6996) was treated according to the directions of the Rhenania: 10.00 g of oil dissolved in 20 cc aromatic-free benzine 60/80 was filtered through a column of 60 g Fuller's earth covered with 20 g of alumina. According to directions, the earth was rinsed with pure petroleum ether until the first of the colored zones which moved downward had nearly reached the bottom of the column. However, the column of Fuller's earth showed no rings. Therefore, we decided to rinse with 500 cc aromatic-free benzine 60/80, and to determine the oil content of the last rinsings. The yield was 440 cc filtrate of which the last 100 cc contained 0.015 g oil and the next to the last 0.031 g oil. The alumina was extracted twice with 100 cc methanol-chloroform (30:70 by volume) and the Fuller's earth six times. The total extracts yielded 0.355 g resins.

Two experiments were undertaken with Freital Endvolt oil to determine what possibilities chromatographic analysis offered in the investiga-

tion of lube oils.

In the first test 10.00 g Freital Endvolt oil was filtered through a column of 60 g Fuller's earth covered with 20 g alumina after it had been dissolved in 20 cc aromatic-free benzine 60/80.

At a pressure of 10 cm Hg about seven hours were required to infiltrate the column. In view of this slow flow only 100 cc of aromatic-free benzine 60/80 was used for rinsing. 4.94 g of oil was recovered from the small amount of filtrate. The oil analyzed 95.5 per cent as unsaponifiable according to the method of Spitz and Hönig. The column of Fuller's earth showed no rings. The alumina was extracted twice with 100 cc methanol chloroform (30:70 by volume) and yielded 0.15 g viscous oil. The column of Fuller's earth was divided into two equal parts. The halves were extracted three times with 100 cc methanol-chloroform. The upper part yielded 1.47 g oil of which 33.5 per cent was not saponifiable, and the bottom part 2.20 g oil which 56.6 per cent was not saponifiable.

In the second test 9.99 g Freital Endvolt oil was dissolved in 50 cc aromatic-free benzine 60/80 and filtered through a column of 60 g Fuller's earth covered with 20 g alumina. Two and a half hours were required to infiltrate the column; the solution then just filled the pore space. This was washed out with 500 cc aromatic-free benzine 60/80. From the filtrate 7.44 g oil were obtained of which 82.3 per cent was not saponifiable. The column showed no rings. The quartz lamp made by Hanau and used for this analysis showed no differences. The upper 38 mm of the Fuller's earth fluoresced less than the remaining 103 mm. These two portions of the Fuller's earth and the layer of alumina were treated individually by Soxlet extraction with methanol-chloroform (30:70 parts by volume).

0.10 g of very viscous oil were recovered from the alumina; from the dark part of the column of Fuller's earth 0.40 g oil and 1.74 g oil from the part which fluoresced. The non-saponifiable part of the latter oil was found to be 8.8 per cent. By drawing fibers with the help of a pencil the impression was obtained that the oil from the upper darker part of the column was more viscous and the oil from the fluorescing part more gumlike. It was observed by evaporating the oils that the product from the dark part of the column would gelatinize.

CONCLUSIONS

Neither Balik Papan or Freital Endvolt oil showed any rings in the column in daylight. Upon illuminating with ultraviolet light Freital Endvolt oil showed a clearly distinguishable dark and fluorescing part in the column of Fuller's earth.

It is difficult to determine how long to continue washing out the column when no rings appear. One may, of course, continue washing out until

the filtrate contains less than a certain percentage of oil. However, the determination of resin content then depends very much on circumstances. It is simpler to prescribe a definite amount of washing fluid.

PLANS FOR FURTHER INVESTIGATION

In view of the importance of measuring immediately the synthetic Bright Stocks it will be determined whether differences between these Bright Stocks and Penna Bright Stocks will be revealed in chromatographical analysis.

January 1943

2870

INTRODUCTION

The previous report described how the Fuller's earth column showed a dark and fluorescing part when irradiated with ultraviolet light in the experiments with Freital Endvolt oil. The extract of the dark (upper) part of the column, which was supposed to contain the most strongly adsorbed components, was examined more closely.

In two tests Penna Bright Stock (TMC 364) was chromatographized with the purpose to compare a synthetic Bright Stock with this later.

SUMMARY OF THE INVESTIGATION

Dr. Leendertse was asked to make an elementary analysis of the fraction of Freital Endvolt oil extracted from the dark part of the column of Fuller's earth.

In view of the small sample available (320 mg) he made a determination of the C, H, S, and N content by microanalytical methods. He followed the method of Pregl for C and H, the micro-method of Carius for S, and the micro-method of Dumas for N. Enough material remained after this to determine C and H by our "precise" macro method.

The following results were obtained:

	% C	% H	% S	% N
micro-method	(77.7	11.6	0.3	0.9
	(77.6	11.5	0.4	
macro-method	77.2	11.5	-	-

After the macro analysis was made, it was found that a white residue remained after combustion and that the combustion tube also showed a white deposit. The residue in the combustion crucible was about 0.6 per cent of the initial material and the deposit estimated at least twice this amount. However, the deposit in the tube could not be determined due to the construction of the apparatus. The part not burned is doubtless of inorganic origin.

C, H, N, and S together account for more than 90 per cent. The remaining 10 per cent is mostly O with smaller amounts of other elements, for example

P and K. In the preparation of Endvolt oil, one-third rape seed oil is used, which contains about 10 per cent oxygen. The sulfur content of a sample of rape seed oil for Freital was 0.05 per cent, and of the mineral oil used in the preparation of Endvolt oil 0.20 per cent.

The nitrogen content of the extract particularly shows that 2871
impurities of the rape seed oil were concentrated in the dark upper part of the column. The impurites are, in part, proteins, mucins, phosphates.

In two experiments 10.00 g Penna Bright Stock (TMC 364) were dissolved in 20 cc aromatic-free benzine, and filtered through a column of 60 g Fuller's earth covered with 20 g alumina. In both cases it was rinsed with 500 cc of aromatic-free benzine 60/80. The Fuller's earth column became brighter on top during this washing out process. The grey ring separated into a reddish-brown slow-moving part and a grey more rapidly moving part as it proceeded downward.

In the first trial when all the washing fluid was used about 38 mm of the Fuller's earth regained its bright color, below which about 10 mm was reddish-brown which again merged into the grey ring below that.

In the second trial only about 8 mm of the Fuller's earth became bright again and about 4 mm reddish brown. Thus, the rings separated more slowly in the second trial.

However, the per cent resins was nearly the same in the two cases, namely 2.39 and 2.22 per cent.

It should be noted that the washing fluid remained colored for a long time in contrast to that observed with Balik Papan oil. In the case of the medium heavy machine oil from Balik Papan previously used the filtrate soon became colorless, and at the same time retained very little oil, as was shown by evaporating. It would be desirable to collect fractions of a Bright Stock filtrate and to test whether the oil would be washed out of the Fuller's earth column less rapidly than with Balik Papan oil.

CONCLUSIONS

Medium weight machine oil from Balik Papan and L.C.T. Penna Bright Stock behave decidedly differently in chromatographical analysis. The resinous components appear to be adsorbed much more strongly in the case of Balik Papan oil.

PLANS FOR FURTHER WORK

A synthetic Bright Stock will be investigated for comparison with Penna Bright Stock. The separation of the oils in successively collected filtrates will be investigated.

February 1943

2885

INTRODUCTION

When chromatographical investigation of mineral oils is made according to the specifications of Rhenania, 10 g of oil dissolved in 20 cc aromatic-free benzine is filtered through a column of 60 g Fuller's earth over which is placed 20 g of Al_2O_3. This is followed by washing with aromatic-free benzine. In the tests described below the filtrate was collected in small fractions and the solvent boiled off, after which the index of refraction was determined. In this way one Penna Bright Stock and one synthetic Bright Stock were investigated.

SUMMARY OF THE INVESTIGATION

10.02 g of Penna Bright Stock (TMC 364) dissolved in 20 cc aromatic-free benzine 60/80 was filtered through a column of 60 g Fuller's earth covered with 20 g of Al_2O_3. Following this 500 cc of aromatic-free benzine 60/80 was used for washing. Oils which showed a blue fluorescence under ultraviolet radiation in solution also showed blue fluorescence in the Fuller's earth column. This fluorescence vanished rather rapidly upon washing with aromatic-free benzine. The fluorescence had practically disappeared after 130 cc filtrate was collected. The upper layer ($\leq$ 1 cm) of Fuller's earth was bright again and underneath that the column was more greyish. However, various rings were not formed as was the case in a previous test on this base material.

The filtrate was collected in various fractions given in the table below. The weight of the oil left upon boiling down the filtrate is in the second, and the index of refraction of this oil in the third column.

Penna Bright Stock (TMC 364)

Filtrate	Oil	n_D^{20}
10 cc	0.83 g	1.4891
10	1.19	1.4913
10	1.69	1.4897
20	2.81	1.4908
20	1.57	1.4940
30	1.23	1.4967
50	0.43	1.5030
100	0.026	
250	0.023	
Extract (Chloroform-methanol)	0.238	

The index of refraction of the consecutive fractions does not increase regularly but shows a maximum in the second fraction. This maximum was found again upon repeating the test. 2886

Penna Bright Stock (TMC 364)

Filtrate	Oil	n_D^{20}
10	1.14	1.4891
10	1.32	1.4915
10	1.58	1.4907
10	1.77	1.4909
10	1.45	1.4911
10	1.01	1.4926
20	1.10	1.4962
20	0.28	1.5001

Synthetic Bright Stock was then tested for comparison with Penna Bright Stock (TMC 8225). 10.00 g of this oil was dissolved in 20 cc aromatic-free benzine 60/80 and filtered through 60 g Fuller's earth and 20 g Al_2O_3. Then the column was washed with 500 cc aromatic-free benzine, due to which the column soon regained its bright color. The fluorescence was much weaker than with Penna Bright Stock.

Synthetic Bright Stock (TMC 8225)

Filtrate	Oil	n_D^{20}
10	1.23	1.4788
10	1.52	1.4790
10	1.50	1.4791
10	1.25	1.4791
10	1.04	1.4793
10	0.71	1.4795
20	1.11	1.4799
20	0.57	1.4804
100	0.13	1.4876
Remainder	0.08	
Extract (Chloro-form-methanol)	0.87	1.4926

In the accompanying diagram (5730-B4) the index of refraction of oil from the collected fractions of filtrate is given as a function of the weight for Penna Bright Stock and synthetic Bright Stock. The index of refraction of the fractions of synthetic oil are much lower and do not increase as rapidly as that of the fractions of Penna oil. The part of the oil remaining in the column after washing with aromatic-free benzine is appreciably greater with synthetic oil than with Penna Bright Stock.

CONCLUSIONS

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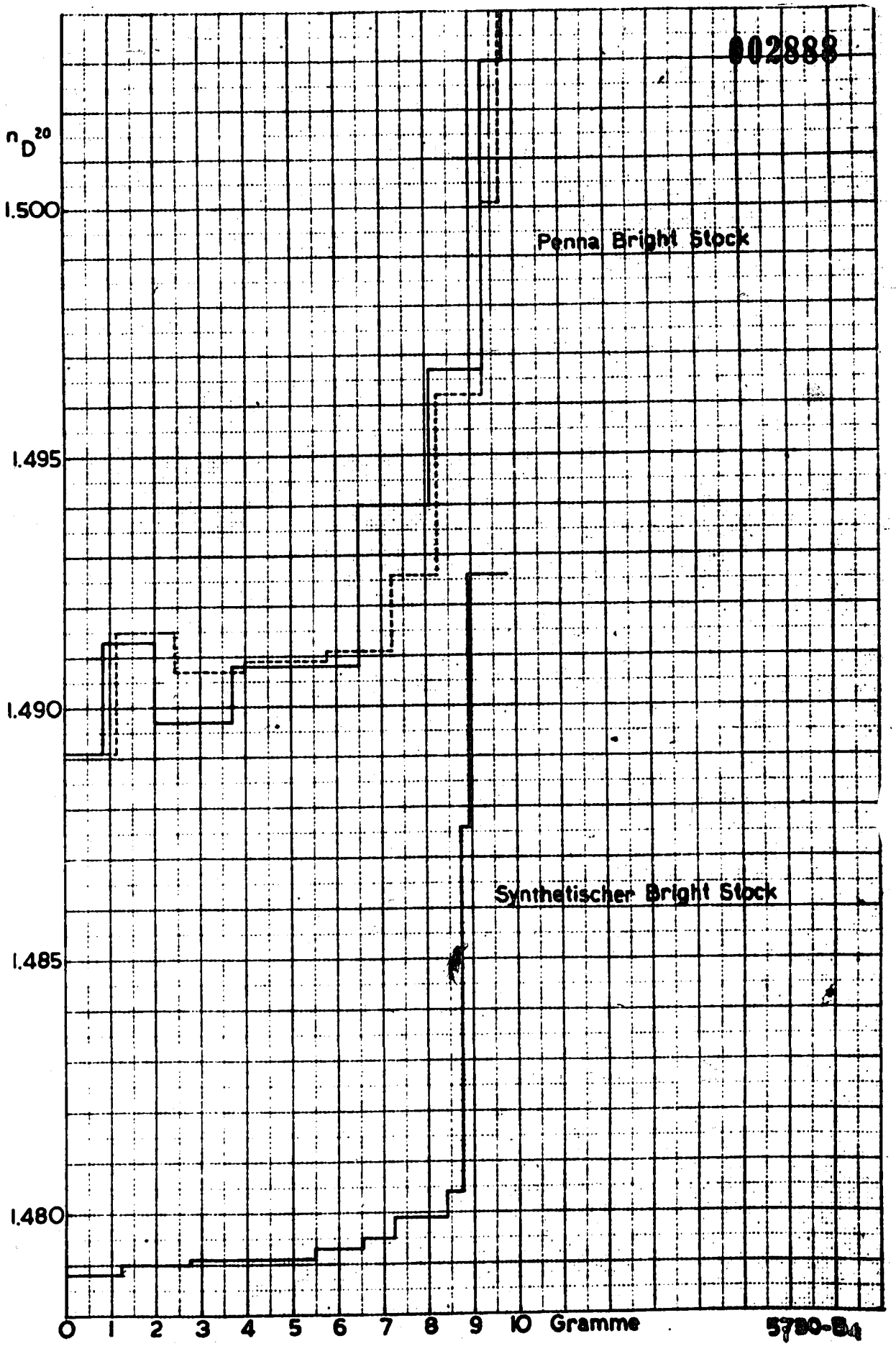
The index of refraction was determined for successive fractions of filtrate of two oils. With Penna Bright Stock the index of refraction showed


n_D^{20}
1.500
1.495
1.490
1.485
1.480
Penna Bright Stock
Synthetischer Bright Stock
0 1 2 3 4 5 6 7 8 9 10 Gramme
5780-B4

a maximum value in the second fraction, whereas it increased gradually when synthetic Bright Stock was used.

PLANS FOR FURTHER INVESTIGATION

An investigation will be made to see if the maxima in Penna Bright Stock also occurs when conditions are changed, for example, when more Fuller's earth $\not$ Al_2O_3 or a more dilute solution is used.

March 1943

INTRODUCTION

2901

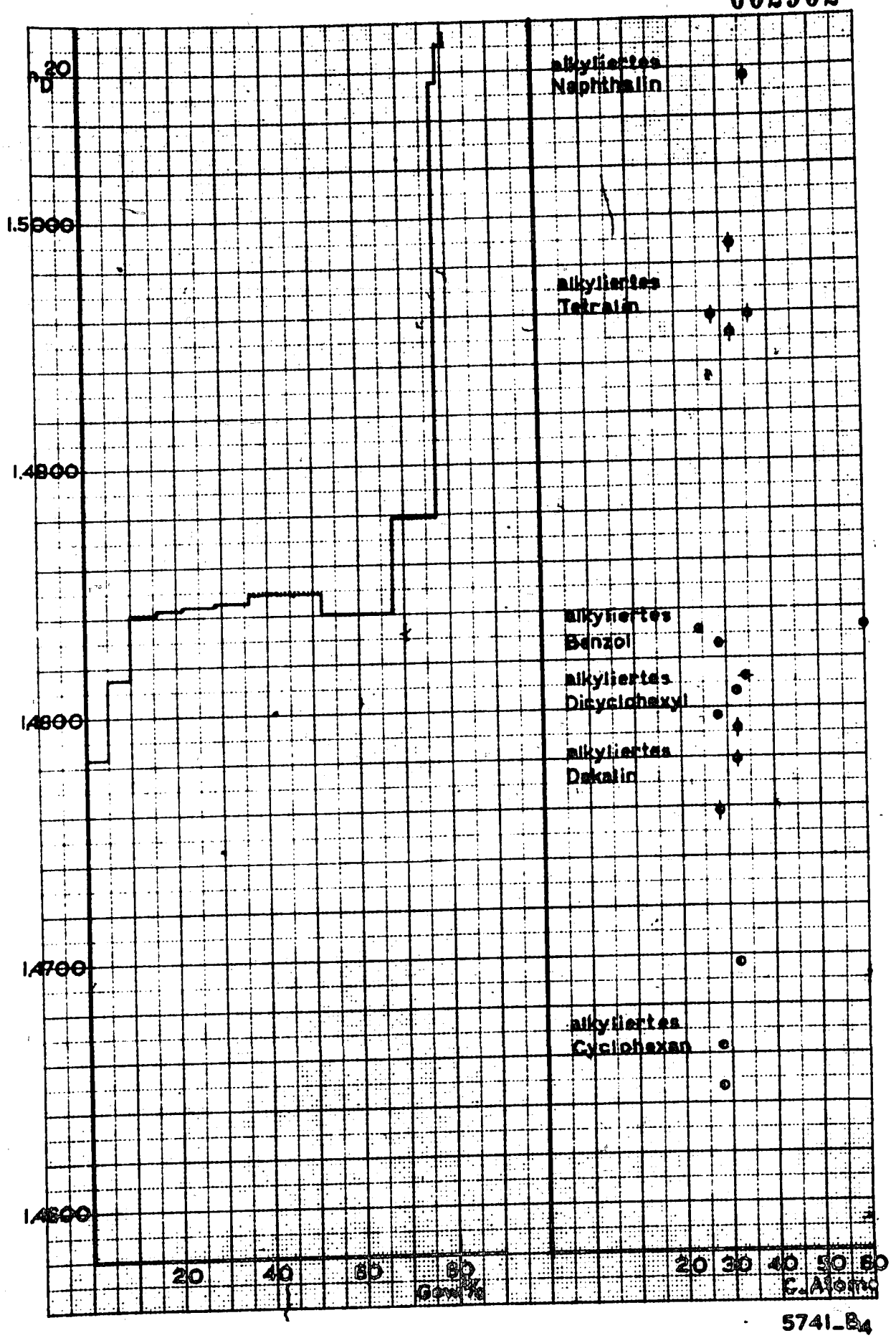
In the previous report was described how Penna Bright Stock was separated into a number of fractions when the oil was diluted with benzine and filtered through a column of Fuller's earth LL which was washed with benzine. The index of refraction was determined for the oil remaining after the solvent was evaporated in each fraction collected. For further work it was recommended to take enough oil so that more properties could be determined from the fractions, i.e. ring analyses could be carried out. Before initiating this inclusive work one must know whether the separation into fractions is accomplished in the most effective manner. For this purpose a comparison of various earths is necessary; thus this was started at this time.

SUMMARY OF THE INVESTIGATION

For a rapid preliminary estimate of adsorbing earths, the amount of higher hydrocarbons adsorbed from benzine solution was taken as a measure of its effectiveness. Enough octadecylbenzene was dissolved in aromatic-free benzine until the solution contained 0.020 g per cc. 80 cc of this solution was added to 40 g of earth. After shaking, this mixture was filtered over glass and the concentration of the filtered solution determined by weighing after it was boiled down.

Fuller's earth LL and a Florida earth were compared both directly and after heating to 300 C for half an hour. The Florida earth was powdered by the heat treatment.

	Octadecylbenzene in solution	
	before adding to earth g/cc	after adding to earth g/cc
Fuller's earth LL	0.0200	0.0193
after 1/2 hr. heating at 300 C	0.0200	0.0184
Florida earth TMC 267	0.0200	0.0196
powdered and after 1/2 hr. heating at 300 C	0.0200	0.0139


n_D^{20}
1.5000
1.4900
1.4800
1.4700
1.4600
alkyliertes Naphthalin
alkyliertes Tetralin
alkyliertes Benzol
alkyliertes Dicyclohexyl
alkyliertes Dekalin
alkyliertes Cyclohexan
20
40
60
80
Gew.%
20
30
40
50
60
C-Atome

5741-B4

The Fuller's earth LL from Rhenania and the powdered Florida earth TMC 267 heated for half an hour at 500 C were compared further by filtering Penna Bright Stock TMC 364 through them. Instead of 10 g oil, as was used in previous tests, 5 g oil in 20 cc aromatic-free benzine 60/80 was filtered through 60 g of earth. In the test with Fuller's earth 20 g Al_2O_3 was also placed above the earth.

Penna Bright Stock filtered through Fuller's earth LL

Filtrate	Oil	n_D^{20}
10	1.119 g	1.4861
10	1.069	1.4888
10	1.002	1.4918
10	0.889	1.4941
10	0.543	1.4971
10	0.241	1.5042
20	0.066	1.5340
20	0.016	-

Penna Bright Stock filtered through Florida earth

Filtrate	Oil	n_D^{20}
10	0.256 g	1.4783
10	0.251	1.4815
10	0.274	1.4841
10	0.299	1.4843
10	0.351	1.4844
10	0.377	1.4845
20	0.801	1.4849
20	0.779	1.4840
50	0.472	1.4879
100	0.086	1.5056
250	0.078	1.5072
Filtrate (Chloroform-methanol)	-	

The index of refraction is plotted against the yield in the diagram. The index of refraction, n_D^{20}, of several aromatics and naphthenes* are shown in the same diagram as a function of the number of C atoms.

CONCLUSIONS

It is concluded from the tests with octadecylbenzene that the

* Mikeska, Ind. Eng. Chem. 28, 970, (1936).

effect of Florida earth as adsorbent is many times greater than that of Fuller's earth LL. The effectiveness of the Florida earth is also seen from the measurements on Penna Bright Stock. It is observed in the latter measurements that the index of refraction remains approximately the same for the third to eighth fraction so that a sort of plateau is formed.

PLANS FOR FURTHER WORK

To use Florida earth as adsorbent for a narrow fraction of Penna so that differences in molecular weight plays practically no part.

May 1943 2938

A. DETERMINATION OF THE ACTIVITY OF TERRANA AND ALUMINA

INTRODUCTION

To judge the activity of Terrana and of alumina the amount of octadecylbenzene which was adsorbed by these powders from solution in aromatic-free 60/80 benzine was determined, as was done previously for Fuller's earth LL and Florida earth.

SUMMARY OF THE INVESTIGATION

In order to determine the activity of Terrana and alumina enough octadecylbenzene was dissolved aromatic-free benzine to make 0.020 g/cc solution. 80 cc of this solution was added to 40 g of powder. After shaking, it was filtered over glass and the concentration of the filtrate determined by weighing the boiled off residue.

The following were tested: Terrana untreated, Terrana after heating to 300 C for half an hour, and alumina after heating to 800 C for half an hour. The results are shown in the table below together with previous measurements when Fuller's earth LL and Florida earth were used.

	Octadecylbenzene in solution		
	Before treatment g/cc	After treatment with earth g/cc	Adsorbed per gram earth
Fuller's earth LL	0.0200	0.0193	0.0014
after 1/2 hr. at 300 C	"	0.0184	0.0032
Florida earth TMC 267	"	0.0196	0.0008
powdered after 1/2 hr. at 300 C	"	0.0139	0.0122
Terrana TMC 5511	"	0.0146	0.0108
after 1/2 hr. at 300 C	"	0.0116	0.0168
Alumina after 1/2 hr. at 800 C	"	0.0166	0.0068

The water content of Fuller's earth LL was found to be 8.9 per cent after heating at 120 C until it reached a constant weight. In the same way the water content of Terrana (TMC 5511) was found to be 12.6 per cent.

The surface of the powder after heating to 300 C was determined by Mr. W. P. van Oort by means of gas adsorption. For Fuller's earth LL it was found to be 32 x 10^4 cm^2 per gram, for Florida earth 90 x 10^4 cm^2 per gram, whereas previously a value of 189 x 10^4 cm^2 per gram for Terrana and 80 x 10^4 per gram for alumina which had been treated in about the same way had been established. 2939

CONCLUSIONS

The quantity of adsorbed octadecylbenzene per gram is approximately proportional to the surface.

B. SEPARATION OF MINERAL OILS INTO FRACTIONS

INTRODUCTION

We have applied the tests with activated Florida earth TMC 267, as mentioned in the report of March 1943, to the further separation of the fractions of mineral oils. One Penna fraction and the same oil after hydrogenation were investigated with a view toward getting an idea on the selectivity with reference to aromatics, and naphthenes respectively.

SUMMARY OF THE INVESTIGATION

Two oils were used in the experiment which belonged to the collection of characteristic oil fractions of Dr. J. J. Leendertse, namely the narrow Penna fraction P IV (10.16 cS at 100 F and 2.62 cS at 210 F) and the same oil after hydrogenation.

In these tests 4.99 and 5.00 g oil respectively were dissolved in 20 cc pentane and percolated through a column of 60 g of powder. The Florida earth had been heated for half an hour at 300 C. The column was washed out afterwards with pentane.

Penna IV filtered through Florida earth

Filtrate	Oil	n_D^{20}	Time of rise in paper
10	0.845 g	1.4540	2000 sec.
10	1.113	1.4550	2140
10	0.822	1.4556	2420
10	0.461	1.4578	2460
10	0.328	1.4593	2485
10	0.287	1.4613	2500
10	0.275	1.4636	2540
10	0.157	1.4718	3060
10	0.204	1.4834	
10	0.046	1.5124	4530

(Continued)

Penna IV filtered through Florida earth (Continued)

Filtrate	Oil	n_D^{20}	Time of rise in paper
25	0.079	1.5248	12,200
75	0.067	1.5364	
100	0.048	1.5426	
Extract (Chloro-form-methanol)	0.257	1.586	

Hydrogenated Penna VI, filtered through Florida earth 2940

Filtrate	Oil	n_D^{20}	Time of rise in paper
10	1.305 g.	1.4594	2150
10	1.121	1.4603	2340
10	1.16	1.4602	2180
10	0.514	1.4602	2060
10	0.283	1.4602	2340
10	0.221	1.4600	2350
10	0.178	1.4600	2250
10	0.165	1.4610	2700
20	0.034	Solid	
200	1.005		
Extract (Chloro-form-methanol)	Traces		

In the accompanying diagram No. 5776-B4 the index of refraction of both oils is plotted as a function of the yield. The index of refraction changes rapidly for the non-hydrogenated, but hardly at all for the hydrogenated Penna IV, which indicates low selectivity of the Florida earth used for naphthenes. This is also seen clearly when one considers the visocisty.

In the above table is given the time required for the oil to rise from 2 to 4 cm mark (above the surface) in a filter paper SS 595 strip 1 cm wide when the bottom of the strip is in the oil. This time is proportional to the viscosity and obviously in addition dependent on the surface tension. Great differences in the time of rise, as is the case of non-hydrogenated Penna IV, indicate great differences in viscosity. Such order of differences do not occur in the case of the hydrogenated Penna IV whereas the great differences in viscosity between mono- and polycylcic aromatics upon hydrogenation is established.

The fractions 1, 2 and 3 obtained from Penna IV were combined, after the index of refraction and time of rise had been determined, to make sample 43/1645; the fractions 4, 5, 6 and 7 to make sample 43/1646. The two samples were delivered to Dr. J. J. Leendertse for analyses. The report

on these analyses follow:

Analysis

Since we were dealing with small samples (3 and 1 cc respectively) we considered it necessary to develop special analytical techniques for some determinations.

Besides the ring analysis according to Sundry Methods Book E 18 (determination of n_D, the specific gravity, molecular weight and aniline point) measurements were also carried out on dispersion and a precise elementary analysis made.

Greater certainty on the aromatic content could be obtained by carrying out the latter two measurements mentioned than could be obtained alone with ring analysis.

2941

Procedure

The index of refraction and dispersion are determined by means of a Pulfrich refractometer (20 C). For determining the specific gravity, we used a pycnometer of 1 cc capacity specially constructed for this purpose; the precision attainable with this apparatus was about 0.0003.

For determining the aniline point an apparatus was used which gave satisfactory results when filled with 0.2-0.3 cc of the test oil.

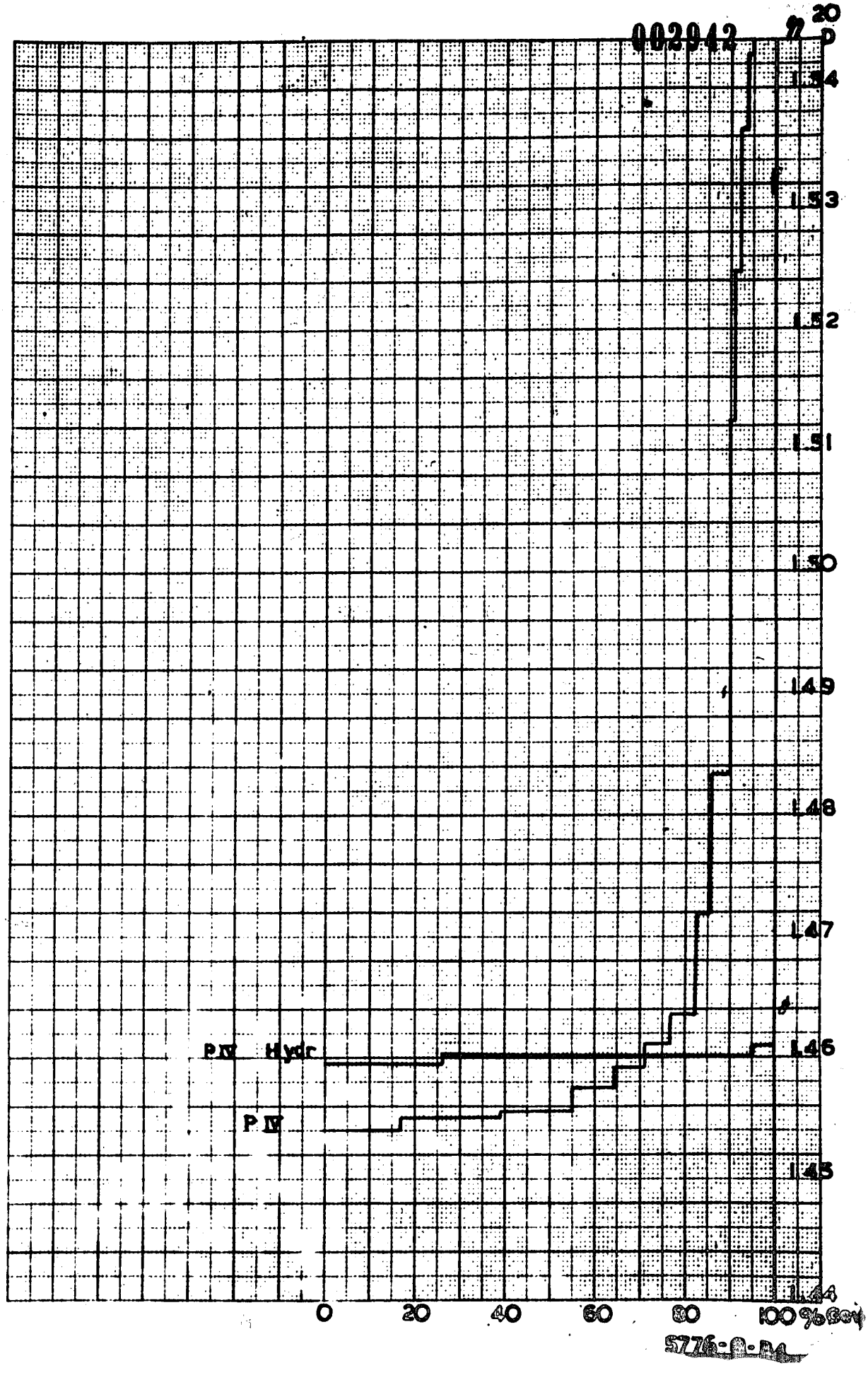
The molecular weight was determined ebullioscopically with benzene as solvent. Deviating from the usual procedure, however, only one point was determined on the concentration-molecular weight curve because of the amount of substance available, and that at low concentrations (rise in boiling point about 0.1 C). Experience showed that the values obtained in this way in general agreed with the molecular weights determined in the usual way by infinite dilution to within 1-2 per cent.

The precise elementary analysis was carried out in the manner usual for this case (hydrogen dependable to about 0.03 per cent). Before the actual investigation both samples were treated with sulphuric acid and formaldehyde to test for aromatics.

Experimental Conditions

The experimental conditions for the determinations and the combined results obtained are recorded in Table I. The data on the P IV fraction used in the chromatographical tests can also be found in this table, the data on "P IV after hydrogenation" obtained after weak prehydrogenation, and the data after hydrogenation on the products of complete hydrogenation of P IV.

Mention should be made in this connection that the manner in which the ring is combined was calculated according to Method E 18 in two ways, in the first place with the molecular weight obtained in the determinations, and further with a molecular weight 15-18 units greater


002042
20
1.54
1.53
1.52
1.51
1.50
1.49
1.48
1.47
1.46
1.45
1.44
P IV Hydr
P IV
0
20
40
60
80
100 % Hg
5776-B-D

(given in parenthesis in the table). This is based on the fact that the diagram of Method E 18 is based on the cryoscopic molecular weight determination by the depression of the freezing point of naphthalene by 1.0 C. The results of these determinations are higher for paraffin oils such as Penna oil than those determined by infinite dilution found by the ebullioscopic method. A difference of 15-18 points is acceptable for this P IV fraction. As can be seen from the table this means a difference of 1-2 per cent in the results of the percentage of C in aromatic, naphthlenic and paraffinic structure and a difference of 0.1 in the number of rings per molecule. As a result of these facts and the uncertainty of the ring analysis it is difficult to know for sure whether or not one can say that aromatics are present in sample 43/1645, and whether there are any differences in samples 43/1646 and the original P IV fraction, especially since one is dealing with comparatively small aromatic contents.

The data for the specific dispersion and the hydrogen content 2943
are more certain on this point. The specific dispersions ($\times 10^4$) are 99 and 102 respectively for samples 43/1645 and 1646, and therefore definitely higher than the completely saturated Penna fraction (97). This points toward the presence of aromatics in sample 43/1645 also. Since Penna IV shows a specific dispersion 110 after pre-hydrogenation with a real percentage of 7 per cent of C atoms in the aromatic structure (deduced from the hydrogen content before and after hydrogenation) the aromatic content of the sample can be established at 1 and 3 per cent C respectively in the aromatic structure. These figures will be verified by comparison of the hydrogen content and the specific refraction with the available data showing the relation between hydrogen content and specific refraction of saturated mineral oil fractions. That this comparison leads to real results is shown from the result of P IV after pre-hydrogenation where the aromatic content was evaluated at 6 to 7 per cent when it actually had 7 per cent (from hydrogen content before and after hydrogenation).

CONCLUSIONS

The sample 43/1645, obtained in the chromatographical investigation of Penna fraction P IV, contains 1 to 2 per cent C atoms in aromatic structure, and is as a whole somewhat less cyclic than the original substance.

The second sample (43/1646) contains 3-4 per cent C atoms in aromatic structure and agrees in the overall cyclic character with the original substance. Neither of the two products otherwise varies radically from a medium monocyclic combiantion.

PLANNED FURTHER INVESTIGATION

We shall check how much octadecylbenzene is adsorbed by a powder from solutions of various concentrations.

Table

	Sample 43/1645 (Fractions 1 / 2 / 3)	Sample 43/1646 (Fractions 4 / 5 / 6 / 7)	P IV	P IV after pre-hydrogenation	P IV after hydrogenation
n_D^{20}	1.4577	1.4628	1.4694	1.4683	1.4596
$d\ ^{20}/_4$	0.8245	0.8335	0.8425	0.8411	0.8309
$\frac{n^2-1}{n^2+2} \cdot \frac{1}{d}$ (20 C)	0.3308	0.3304	0.3308	0.3307	0.3294
$\frac{n_F - n_C}{d} \times 10^4$	99	102	-	110	97
Molecular weight (ebull. in C_6H_6)	305 (305 assumed in calculation)		297 (297 assumed in calculation)		297
Aniline point C	102.5	95.9	93.2	94.2	101.4
% H	14.34	14.08	-	13.84	14.29
% C	84.58	85.80	-	86.02	85.71
Method E 18:					
% C in paraffin structure	80 (79)	76 (75)	75 (74)	76 (74)	73
in naphthene structure	20 (19)	20 (19)	19 (19)	19 (20)	27
in aromatic structure	0 (2)	4 (6)	6 (7)	5 (6)	0
No. rings per molecule	0.7 (0.8)	0.9 (1.0)	0.9 (1.0)	0.9 (1.0)	1.0
Formaldehyde-sulfuric acid reaction for aromatics	definitely positive	strongly positive	-	strongly positive	nearly negative
% C in aromatic structure determined from:					
H_2 content after hydrogenation	-	-	-	7	-
Specific dispersion	1	3	-	-	-
(not clear on film)					
Specific refraction (?) % H in comparison to sp. ref. and % H in saturated product.	1-2	4	-	6-7	-

September 1943 2983

INTRODUCTION

In previous investigations the activity of various earths were compared by finding the amount of octadecylbenzene the earths would adsorb out of a solution in aromatic-free benzine. In addition the original solution used always contained 0.020 g octadecylbenzene per cc. Now one earth, namely Floride earth, was tested to determine how the amount of adsorbed octadecylbenzene varied with its concentration in solution, i.e. several points were determined on the adsorption isotherm at 20 C. However, it was necessary first to recover the octadecylbenzene used in previous tests from the earths and to purify it.

SUMMARY OF THE INVESTIGATION

By the Soxlet extraction from the earth with aromatic-free benzine the octadecylbenzene was contaminated to some extent. It is possible that the contamination takes place by polymerization. By repeated recrystallization from benzene-butanone at about -30 C a purified product was obtained. With this some points were obtained on the adsorption isotherm at 20 C. Isooctane was used as solvent. The concentrations of solutions made are given in the first column of the table below. For the first two a 20 cc solution was shaken with 5 g earth and 40 cc of the other solutions with 10 g earth. Florida earth was used after it was activated at 300 C.

The octadecylbenzene concentration was determined by boiling down the solution which was filtered from the earth after shaking.

That the concentration found in this way was correct was shown in the test of two solutions before treatment with earth; 0.0398 g per cc was found for the solution originally containing 0.0400 g, and 0.0050 g per cc for the original containing 0.0050 g per cc.

2984

Octadecylbenzene in soltuion		Octadecylbenzene
before earth treatment g/cc	after earth treatment g/cc	adsorbed per gram earth
0.0800	0.0700	0.040
0.0400	0.0308	0.037
0.0200	0.0102	0.039
0.0100	0.0045	0.022
0.0050	0.0008	0.017

The amount of octadecylbenzene adsorbed by the earth can be calculated from the concentrations before and after the earth treatment. These results

were determined by recovering the octadecylbenzene after the test. Not nearly all of the octadecylbenzene was recovered. Part of it seems to be held obstinately by the earth.

PLANNED FURTHER INVESTIGATION

The amount of octadecylbenzene which undergoes a transformation when adsorbed on an activated earth as Florida earth will be tested more closely.

INVESTIGATIONS AND ANALYTICAL METHODS CONCERNED WITH SYNTHETIC LUBE OILS

Frames:
2889-93
2896-98
2918-20
2934-37
2945-46
2968-71

Abstract

2889-93

Cracked distillate was polymerized with $AlCl_3$. The catalyst-free polymer was washed with 25 per cent NaOH, steam distilled with 4 per cent "Terrana" to 250 C, filtered and again steam-distilled to 280 C. The resulting lube-oils had only barely detectable traces of chlorine, even when the caustic wash was omitted.

Five methods were used for rendering water-soluble the chlorine in the synthetic oils:

a. Burning (lamp-method);

b. Steam-distillation at 350 C; with or without "Terrana";

c. Heating the oil with sodium;

d. Heating the oil with a large excess of calcium oxide;

e. Burning by the Carius method.

The chloride was then determined by the Volhard method.

Methods a and b gave low results.

The reproducibility of methods a and d was not more than 0.01 per cent.

The reproducibility of methods b and c was not more than 0.005 per cent.

Method e used too small a sample to be very exact, while method c permitted convenient use of a very large sample.

2896-8

The sodium method and the lime method for the determination

of chlorine in synthetic oils were tested with knowns prepared by dissolving hexachlorobenzene in chlorine-free oil at chlorine concentrations of 0.022 to 0.5? per cent. It was concluded that these methods are useful for the qualitative detection of small amounts of chlorine (e.g. 0.01 per cent), but that they give results too low for the exact quantitative determination of more than traces.

The use of nitrobenzene during the Volhard titration sharpened the end point. (c. Caldwell and Moyer, Ind. Eng. Chem., Anal. Ed. 10, 530 (1938))

2918-20

The sodium method and the lime method were used for the determination of chlorine in several oil samples obtained by the polymerization of cracked distillates with aluminum chloride.

2954-57

The sodium method and the lime method were both used for the determination of chlorine in oil samples prepared by the polymerization of cracked distillates with aluminum chloride activated with HCl.

Two samples previously analyzed by the above named methods were analyzed for "labile" chlorine by distillation at 300 C with super-heated steam in the presence of 10 per cent "Terrana". The "labile" chlorine thus found approximated the total chlorine found earlier by the sodium method and the lime method.

2945-46

An attempt was made to increase the sensitivity of the lime method for determination of chlorine in synthetic oils, by increasing the amount of oil burnt. The oil was admitted dropwise to the reaction zone and a current of air was simultaneously passed in order to prevent the deposition of products of decomposition on the lime. Using a synthetic oil sample, a result was obtained in agreement with a result obtained earlier by the unmodified method. But results with a known prepared by dissolving hexachlorobenzene in chlorine-free oil were erratic; only about half the chlorine known to be present was found.

The avoidance of a deposit on the lime, accomplished by the use of air, was an advantage.

2963-71

The "Rheanfa" hydrogenation method was used for the determination of chlorine in synthetic oil samples which had previously been analyzed for chlorine by the sodium and/or the lime method. The earlier results were confirmed.

It was found that the hydrogenation method can easily lead to very high values for chlorine, especially if cyanogen compounds are incompletely boiled out, as a result of insufficient acidity of the solution. This source of error could probably be eliminated by omission of the NH_3 from the hydrogen stream.