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On Identification and Determination of Polycyclic Hydrocarbons by Ultraviolet Absorption and Chromatographic Adsorption

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In a previous investigation of fir-stump tars and oils originating from them, a chromatographic method was worked out which, combined with treatment with solvents, made it possible to separate a mixture of pure hydrocarbons from these raw materials [1]. One of the greatest difficulties to overcome was to purify the neutral oils, which were obtained as the intermediate products, from a neutral material containing oxygen. The chromatographic separation was used as the only means by which the separation could be achieved. For this purpose the following adsorbents were employed: Frankonit KL, Tonsil ACA with hexane as a solvent. The purification was carried out by pouring a certain amount of the material dissolved in hexane through the column and then eluting with hexane. Several different fractions were taken out, and after the solvent had been driven off, the residual substances obtained were examined by means of ultraviolet spectra. It was thus found that a certain separation of hydrocarbon occured, and retene, dihydroretene and octahydroretene were likely to be present. In this experiment, however, the solutions used were rather concentrated and the number of fractions taken out was relatively low. Only a »continuous» curve for the amount of the eluated material versus the amount of used solvent was obtained. It was expected that experiments with more diluted solutions and improved methods of measurement would yield more information about the composition of the material from a qualitative as well as a quantitative point of view.

The earlier experiments undertaken by Drumond and co-workers [2] with marine oils showed that circumstances in chromatographic analysis may be very complicated, they may for instance, depend upon relative concentrations.

They showed, however, that more saturated hydrocarbons passed through more easily than less saturated ones. However, it proved to be possible to separate closely related hydrocarbons from one another[3]. Mair and Forziati[4] separated aromatics, benzene etc., from low boiling paraffins and naphthalenes, at about the same time as the present author carried out the above-mentioned investigations. It should also be mentioned that Willingham[5] succeeded in separating one higher cycloparaffin hydrocarbon from the corresponding aromatic compounds, as well as a paraffin from an aromatic hydrocarbon with about the same molecular weight as that of the paraffin. Further, Walker and Mills[6] found during their investigation of linseed oil that is was possible to separate the oils in fractions with 7, 6, 5 and 4 double bonds in the molecule, when hexane and aluminum oxide were used.

As our knowledge of the adsorption of hydrocarbons is far from perfect and information regarding the properties of various solvents is unsatisfactory, it was necessary for the planned investigation of the hydrocarbons contained in tars and oils to make some test experiments with authentic hydrocarbons and to try out different adsorbents. There are two possible types of adsorption analysis: frontal eluation and displacement analysis. An account is given below of experiments using frontal analysis.

The study was carried out in an apparatus constructed after Claeson's design[7] by *LKB-Produkter AB*, in Stockholm.

EXPERIMENTAL SECTION

Adsorbent, solvent and hydrocarbons investigated

The following adsorbents were used: Tonsil ACA obtained with the help of Dr Guy S:son Frey, Super Filtrol, activated clays (BW), Terrana D F, Hyflo Super Cel., obtained by Eng. Bertil Knutsson, Silikagel commercial from AB Eka. The solvent used for the experiments was heptane.

Hydrocarbons used for the test experiments were naphthalene pro analysi[8], and phenanthrene pro analysi[9], which have hitherto shown all signs of homogeneity. In another connection the present author has pointed out that the purification of retene from some impyrity * presents a hard task which can, however, be overcome by recrystallization combined with formation of pictrate or styfnate etc.[1] Only pure retene m. p. 100.5° was used. Dihydroretene was prepared according to Virtanen[10] and had m. p. 62—63° C.

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* Add. to the corr. The presence of dihydroretene is lately denied by *K. J. Karrman* (*Svensk Kem. Tid.* **60** (1948) 18), but the reasons which led the present author to assume dihydroretene to be the »impurity» are only partly published[1] and further discussion will be given later.

Moreover a few fractions of intensely refined tar lubricating oils, were investigated.

The intensely refined tar lubricating oil formerly described by the name R L[1] was distilled in Klitt's apparatus [12], and the following fractions were obtained at 1.7 mm: up to 130°, 8 %; from 130—140°, 11 %; from 140—147', 5 %, and from 147—151°, 53 % yield. The latter fraction contained 89.5 % C and 10.8 % H and had n_D^{20} 1.5500. The residue partly crystallized after distillation.

The specific rotation of the original oil was found to be $[\alpha] = + 30.4°$ in benzene and + 31.8° in abs. alcohol. The corresponding values for the above mentioned main fraction were: 40.0 and 41.0° respectively.

In the same way as in the earlier experiments with rosin acids, the oil was isomerised with Pd-charcoal according to the method of Diels [14], for 3 h at 190°. After the catalyst had been removed by successive washing with ether and filtering, the main fraction was distilled at 138—148° and 0.3 mm pressure. The product obtained contained 89.2 % C, 10.7 % H and had n_D^{20} 1.5490 and D_4^{20} 0.9802. The ultraviolet spectrum of the original oil gives very little information. This is also true of the spectrum of the main fraction. The absorption curve of the latter is shown in Fig. 1. The shape of the curve indicates napththalene structure and that the concentration of the corresponding hydrocarbon may be 10—20 %[16]. Fig. 1 gives the curve of the isomerized oil fraction, which is not essentially different from the curve of the non-isomerized oil. The dien number of the oil was investigated in the same manner as was worked out and used on the crystallized rosin acids from fir-stump tar, but the percentage of dien content proved to be very low. According to one experiment at 130° less than 1 % is present. Evidently the treatment with Pd-charcoal does not have any particularly significant influence on the hydrocarbons.

The main fraction from the distillation of the original oil was sulphonated with conc. sulfuric acid at 70° C. By salting out, a dark-green sticky mass was obtained, which was then dried at high temperature. Extraction with ether resulted in a rather manageable product, containing 5.7 % Na. Next, the product was treated with acetone containing some water and the undissolved part was crystallized from acetone-water solution. The crystals were then washed with ether and dried in the air. Two different crystallized fractions were then worked up, dissolved in 50 % alcohol and their respective ultraviolet spectra determined. As it is evident from Fig. 1, the benzene structure is present. The above results indicate that the hydrocarbons possess naphthalene as well as benzene structure. On the other hand, the diene, styrene an phenanthrene structures are missing, at least to a measureable extent, so as

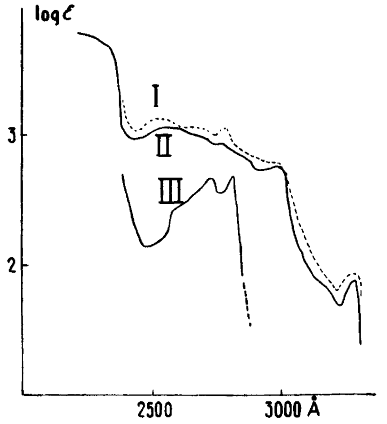


Fig. 1. Ultraviolet absorption of oil before (I) and after isomerization (II) and the sulphonate with benzene structure (III).

their corresponding and very characteristic maxima and typical curve shape are not seen in the absorption curves obtained[15, 16]. The elementary analyses of the hydrocarbon most closely approximates the formulas $C_{18}H_{26}$- or $C_{19}H_{28}$ and, presumably, this hydrocarbon dominates and has benzene structure.

The above mentioned sulphonated salt with benzene structure is not identical with a sulphonated salt with benzene structure from a hydrogenated retene. For instance the corresponding *p*-toluidine salts have been prepared. They have approximately the same melting points: 225—228° and 223—225° respectively, their mixture, however, has a melting point. 15—20° lower. Since the C_{18} hydrocarbon is present in the hydrogenated retene, then the C_{19} hydrocarbon ought to be present in the latter case. The sodium sulphonate was, however, practically inactive and the yield was rather poor.

It has previously[1] been pointed out, that the partially refined lubricating oil contains one or more oxygen compounds which cannot be removed by distillation. It was also stated that they could be removed together with other contaminitants by intense refining, using a special process, *e. g.*, by treatment with stronger H_2SO_4. Thus, it is highly probable that on treating the tar lubricating oil with H_2SO_4, not only the oxygen compounds but also a part of the hydrocarbons are sulphonated. Consequently the working up of the oil involves difficulties and the yields obtained are poor.

Experiments with clays etc.

As an example, an account is given below of some experiments in which a clay, Tonsil A. C. A., was used as adsorbent and heptane as solvent. Frontal analyses were performed using the fraction discussed above. When, for

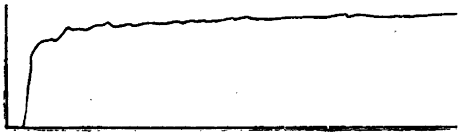


Fig. 2. Frontal analysis of main fraction of intensely refined oil.

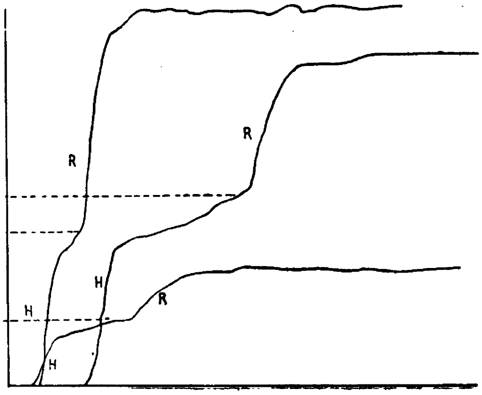


Fig. 3. Frontal analysis of main fraction of intensely refined oil and retene. H head front of oil, R retene step, dotted lines give the calculated values for the oil alone.

instance, 0.60 % solution and filter 1.250 π[7] were used a curve was obtained which is shown in Fig. 2. This curve, as well as a number of others not shown here, indicates that the front is well developed and that the first rise of refractive index is followed by another step. This indicates the presence of smaller amounts of hydrocarbons, being much more strongly adsorbed than those hydrocarbons indicated by the head step. As it was suspected that this hydrocarbon would be replaced by retene, an experiment was undertaken with the fraction of the tar lubricating oil and retene in the same solution. Fig. 3 shows three experiments with various concentrations of tar lubricating oil and filter sizes and of retene. The diagram shows that between the head-front (H) and the retene-front (R) there is a plateau which is flatter at low concentrations of retene. To learn to what extent the separation really occurs between retene and the hydrocarbons of the tar oil, an experiment with this fraction was carried out as follows. The solution 0.765 % of oil and 0.317 % of retene was passed through the apparatus and changes of refractive index were read off direct while the liquid leaving the apparatus was taken out in small fractions and then weighed. From this data a curve was drawn and the fractions were combined as shown in Fig. 4.

The solvent was removed from these fractions over a boiling water bath, and suitable amounts of residues were dissolved in absolute alcohol for examination of their ultraviolet spectra. The results obtained are shown in Fig. 5. The spectra of the hydrocarbons which are represented in Fig. 4, in fractions 1—3, are rather similar and all of them have the typical benzene structure showing double maxima at 2.700—2.800 Å. The hydrocarbons represented by the fourth section in Fig. 4, gave an absorption curve which shows the typical

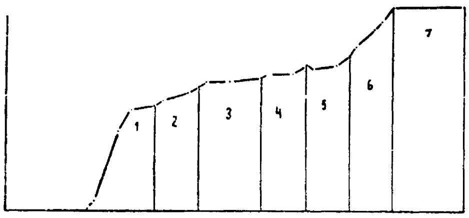


Fig. 4. Frontal analysis of main fraction of intensely refined oil and retene performed to give fractions 1—7.

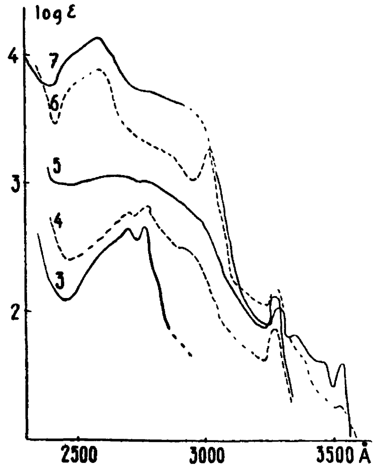


Fig. 5. Ultraviolet absorption of fractions 3—7 from frontal analysis, fig. 4.

naphthalene structure maximum at 3.250 Å. Only the hydrocarbons in fraction 6, show the typical retene maximum at 2.600 Å. However the maximum at 3,000 Å[1] is only slightly apparent. This indicates that sections 1—3 contain hydrocarbons with benzene structure, 4 contains benzene and naphthalene structures, 5 contains these plus an insignificant amount of compounds with phenanthrene structure, and 6 and 7 contain these plus compounds with phenanthrene structure (retene). It suggests that the hydrocarbons are adsorbed in the following order: $3 < 5 < 6$ F. Unfortunately, the separation was not so sharp as was desired. This can be due partly to the presence of smaller amounts of some compounds whose adsorption isotherms are such that a sharper separation is impossible, or because the number of isomerides and homologues is too large, or both. An attempt to obtain more distinct steps in adsorbtion curves by changing the absolute and relative concentrations unfortunately failed.

A number of active clays were tried as adsorbent for the tar lubricating oil. In these experiments, however, the separations obtained were not sharper than the ones described above. The results of some of the experiments, performed in different ways, are collected in Table 1.

In this case the final step height was adjusted to $n = 100$, and concentration 1 %. The table indicates that the oil fraction in question gives the maximal step height about 11.1—11.4 units. The lower values for step heights are caused by the use of more adsorbent than could be saturated with the oil present in the 50 ml of solution pressed through the filter.

Table 1. Frontal analysis of tar oil and different adsorbents.

Adsorbent	Filter π	Conc. %	Corr. step-height cm
Tonsil ACA, non-dried	1250	0.82	11.1
» » dried 105°	250	1.47, 0.58	11.3, 11.4
Frankonit KL	500	0.72, 0.75	10.9, 10.5
Hyflo	1250	0.79	11.4
Terrana	1250	0.78	11.2
Super Filtrol	1250	0.76	10.4
» »	2500	0.75	8.7
Silikagel, EKA	500	0.84	11.2
» »	1250	0.84	10.8

The retention volumes in these cases are so small that they cannot be used accurately for calculating constants etc.

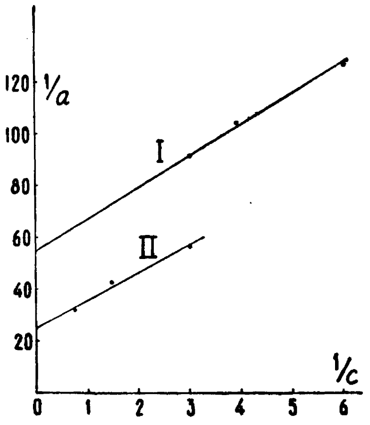
It has been assumed above that retene displaces the hydrocarbons in the oil, and that all the hydrocarbons should be present in the steps preceding the retene step. In a series of experiments, shown in Table 2, it was found possible to calculate the final step height, if the concentrations of oil and retene were known.

Table 2. Frontal analysis of tar oil and retene.

Fraction of tar lubricating oil %	Retene %	Maximum step-height Found cm	 Calc. cm
0.795	0.402	16.0	15.8
0.760	0.750	20.5	21.4
0.765	0.312	14.1	14.1
0.870	0.525	19.6	18.9
0.395	0.208	8.6	8.0
0.770	0.320	13.2	14.2
0.785	0.323	14.3	14.4
1.180	0.284	12.4	18.2
0.800	0.324	8.3	15.1

For the calculations the factors 11.3 for the oil and 17.0 for retene have been used. The latter was obtained in the experiment with retene only. Agreement is quite satisfactory.

It is also possible to estimate from such a curve the amount of oil used, as it is evident from the experiments shown in Fig. 3, where the dotted lines indicate the concentrations of oil in the test solutions used. It is noteworthy



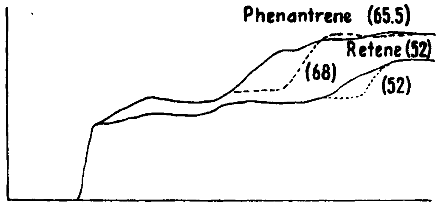


Fig. 7. Frontal analysis (sensitivity given in brackets) of phenantrene and retene (dotted lines) and these hydrocarbons and tar oil.

Fig. 6. Adsorption isotherms for phenantrene (I) and retene (II).

that the step height for the oil is almost independent of the ratio of oil to retene.

As it was of interest to try out phenanthrene in a mixture with the tar lubricating oil, test experiments with retene and phenanthrene were first carried out. Super Filtrol, which had previously been heated in small portions (50 g) to 200°, was used as adsorbent. Comparative test experiments with non-dried Super Filtrol gave about the same results in frontal analysis; for displacement development with certain reagents, it is necessary to use dried Super Filtrol. Thus, for better comparison in the future, the use of dried Super Filtrol has been adopted throughout this investigation. The results are collected in Fig. 6. From these experiments also the value 17.0 has been obtained for the retene step height, calculated for sensitivity $n = 100$ and concentration 1 %.

From Fig. 6 it is evident that the isotherms for retene and phenanthrene are nearly parallel. For frontal analysis with two components the following relationship holds [7]:

$$C_{1,2} - \left(1 - \frac{v_1^0}{v_2^0}\right) C_{1,1} = \frac{k_1}{k_2} \cdot C_{1,2}$$

When $k_1 = k_2$ then $v_1^0 = v_2^0$. That is, retention volumes in frontal analyses are alike, if reversible adsorption occurs between phenenthrene and retene, the separation is not obtained. In the experiment with a mixture of phenanthrene and retene, only one pronounced step was observed in the adsorption curve.

It appeared that dihydroretene and retene are not separated in frontal analysis and therefore the calculated retene may include dihydroretene.

The behavior of a phenanthrene and tar oil mixture is a little different from retene, as is evident from the experiment shown in Fig. 7. It shows that — as was expected — the phenanthrene step lies ahead of the retene step. The figure shows, however, that the step heights of the benzene compounds, are practically the same. It may also be noted that the retene step in the curve from the experiment with the mixture of retene and tar oil, has a retention volume which does not differ much from the one given by retene alone. In this figure the curve for retene alone (the dotted line), was shifted along the concentration axis so that the maximum values of the curves coincide.

From Fig. 8, it is evident that the phenanthrene step comes at definitely smaller retention volume than that for phenanthrene alone. Moreover, the step denoting hydrocarbons of naphthalene structure is missing. Hence, one can conclude that »naphthalenes» do not separate from phenanthrene. It might be possible to determine the hydrocarbons with benzene structure by adding phenanthrene, but it seems to be impossible to aquire any information about the concentration of »naphthalene» in this way.

It is of interest to note that the step heights for the hydrocarbons with benzene and naphthalene structures, respectively, within the limits of experimental error, are unchanged in the presence of retene or phenanthrene (this was shown by numerous experiments in which the relative as well as absolute concentrations were varied, but they can only be mentioned in the present report).

These experiments show clearly that it may be possible to obtain a picture of the quantitative composition of the tar oil by adding the proper amounts of retene or phenanthrene and performing frontal analysis.

Experiments with various tar lubricating oils

The previously described preparation of hydrocarbon (neutral oil fractions [1]) containing oxygen, has been used for the following experiments. It has been found that the oxygen containing contamitants are completely adsorbed on dried Super Filtrol. Some of the neutral oil fractions originated from refined tar lubricating oils and some from unrefined ones. The experiments have been carried out as follows. At first the frontal analysis adsorption curves were determined for the various neutral oils, and then the curves were repeated with admixture of suitable amounts of retene or phenanthrene. The concentration of neutral oil was 0.79 % in all experiments. The results are given in Fig. 8 for oil DL. That added retene is present to a concentration of 16 %, is

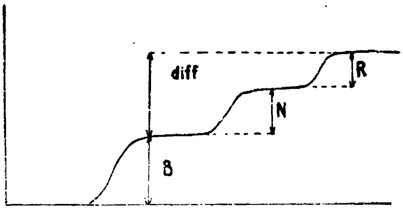


Fig. 9. Principal diagram for frontal analysis. B denotes hydrocarbons with benzene structure N hydrocarbons with naphtalene structure and R retene.

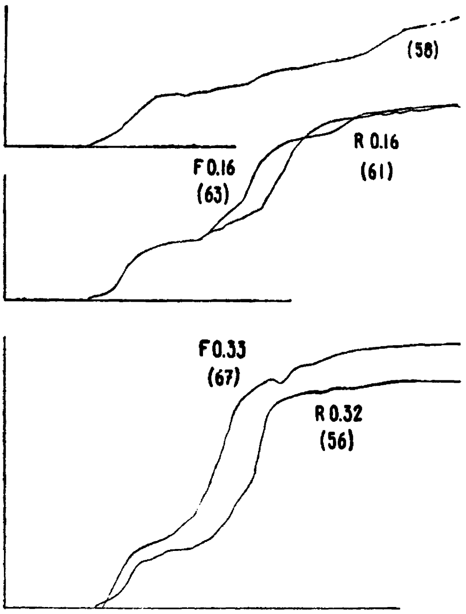


Fig. 8. Frontal analysis (sensitivity given in brackets) of a tar oil, DL, a) alone b) with phenantrene, resp. retene in 0.16 % solution and c) the same but in 0.32 % solution.

denoted by the number 0.16 and that the sensitivity in the experiment was 61 by (61) etc. The results of the experiment with phenanthrene (F) are given in a similar way.

All of the curves from experiments with the oils possess two more pronounced steps and, as a rule, in low retene concentrations, it is possible to estimate retene step height (see Fig. 7, the dotted lines). The curves may be used for quantitative calculation in the following way. The height B in Fig. 9 corresponds to the compound with benzene structure, the step height N to the compound with naphthalene structure, and the step height R to retene. To calculate concentrations of the hydrocarbons from the step heights one must know the refractive index of a standard solution of each. To learn how variations of the values for the factors affect the final results the following values for the factors have been used: benzene-hydrocarbon, 10.0 and 11.0, naphthalene-hydrocarbon and retene, 17.0 and 18.5. From the step heights and these factors, the concentrations of hydrocarbons with benzene structure, naphthalene structure, and retene, have been calculated. Their sum is considerably lower than the weighed quantities of tar oil. The difference F. between these values is due to the presence of impurities. From the table, showing the results of all these calculations, it is seen that the variations in F,

Table 3. Compositions of tar oil according to frontal analysis.

	% B[1])	% R[2]/	% N[3])	% F[4]
RL	75,68	13,14	9,9 8,10	(— 4),8 3,1
RO	37,34	22,24	19,20 17,20	15,24 18,22
RN	38,36	33,36	11,14 9,16	10,20 14,18
DL	47,43	18,19	20,23 19,24	11,19 14,15
DO	39,36	19,20	19,20 18,22	18,24 23,24
DN	33,30	32,34	13,20 17,23	10,19 13,18
T	24,23	15,18	14,14 11,16	38,44 39,42

[1] Calculated from stepheight B
[2] R
[3] Diff — R
[4] 100 — B — Diff.

depending upon different numerical values for factors, are not great. Thus, it may be concluded that it is possible to obtain in this way a fairly accurate picture of the quantitative composition of the oils. Some information concerning the content of impurities in some neutral oils has been previously gained by direct quantitative analyses of larger samples. The comparison of these values and the values obtained by adsorption analysis are shown in the following table.

Table 4. Impurities in tar oil according to frontal analysis.

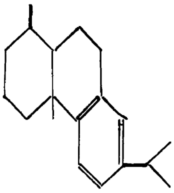
Oil	Previously determined	Present values			
DO	28 %	18,	24,	23,	24 %
DN	20 »	10,	19,	13,	18 »
T	41 »	38,	44,	39,	42 »

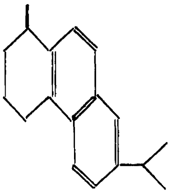
The agreement is remarkably good, particularly when the systematic errors appear in the values for precentage of impurities. It may be possible to regard these results as accurate to at least to 4—5 units.

SUMMARY AND DISCUSSION

Measurement of hydrocarbons in neutral oil fractions of tar lubricating oils has been studied by means of chromatographic adsorption and ultraviolet absorption. Several clays have been employed as adsorbent and heptane as solvent. The adsorption studies have been performed in Claesson's apparatus [7], and frontal analysis has been used. The results have been checked by control experiments in which phenanthrene and retene have been added to the samples. Ultraviolet absorption spectra of small fractions of the eluate have been measured. From the absorption curves it is concluded that components of the oils possess benzene, naphthalene and phenanthrene structures. Structures with double bonds, as in the case of abietic acid, styrene etc., were not detected. Their presence is not excluded, but is very doubtful whether such double bonds occur, as they should be easily disproportioned into the just mentioned structures under the conditions which predominate in the oils production.

The hydrocarbons contained in these tar lubricating oils originate from resin acids. Hence, the following hydrocarbons seem to be present: dehydroabietene and tetrahydroretene



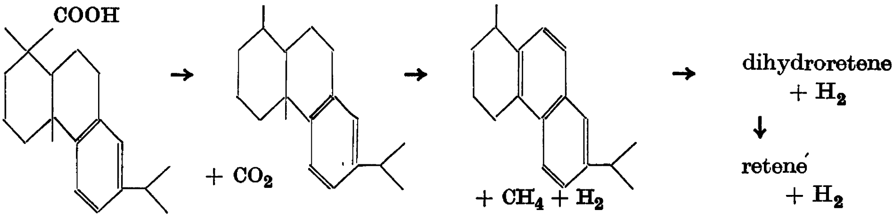


and further retene.

For calculating concentrations of these hydrocarbons the retention volumes could not be used, partly because the adsorption affinity of the hydrocarbon with benzene structure was too weak, when compared with retene adsorption, and partly because the particular step front characterizing the hydrocarbon with naphthalene structure was indistinct. On the other hand, the step heights might be used for calculating concentrations, as it is shown above. With certain reservations, the composition of the neutral oils investigated are given in Table 3.

From the latter it is evident that the intensely refined oil RL, as was to be expected, contains the smallest amounts of impurities (oxygen compounds) and relatively low quantities of retene (dihydroretene) and hydrocarbons with naphthalene structure. On the other hand it is clearly shown that the hard-cracked oils DN and RN respectively, contain great amounts of retene. It is also noteworthy that the content of hydrocarbons with naphthalene structure is not considerably large. This seems to imply that this stage of cracking has passed relatively easily.

It has been stated out earlier that dehydroabietic acid his been the main constituent of the original resin acids, and therefore the following scheme of cracking seems to be most probable:



It is also illuminating that the quantities of impurities in Table 4 are relatively small in these hard-cracked oils. For the significance of the intensity of refining the reader is referred to the paper by Frey.[17]

Frey has determined the retene content of oils not identical with but similar to those investigated here. He got definitly smaller amounts of retene, but further discussion is better postponed until the nature of the »impurity» following retene is elucidated.

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REFERENCES

1. Hellström, N. *Trans. Roy. Inst. Technol. Sweden* (1948) no. 21.
2. Drummund, J. C., *et al. Biochem. J.* **29** (1935) 456; *Analyst* **60** (1935) 23, 382.
3. Strain, H. *Chromatographic adsorption analysis* (1945); *Analyst* **71** (1946) 251.
4. Mair, B. J., and Forziati, A. F. *Nat. Bur. Standards Research J.* **32** (1944) 165; *Cf.* Mair, B. J., and White, J. D. *Ibid.* **15** (1935) 51; Mair, B. J. *Ibid.* **34** (1945) 435.
5. Willingham, Ch. B. *Ibid.* **22** (1939(321.
6. Walker, F. T., and Mills, M. R. *J. Soc. Chem. Ind.* **66** (1942) 125, **62** (1943) 106.

7. Claesson, S. *Dissertation* Uppsala (1946).
8. »Bakers Analyzed».
9. Merck, Darmstadt.
10. Virtanen, A. I. *Ber.* **53** (1920) 1885.
11. Morton, R. A., and de Goureia, A. J. A. *J. Chem. Soc. London* (1934) 911.
12. Schroeter, G. *Ber.* **57** (1924) 2025.
13. Klit, A. *Studier over fractioneret Destillation* Uppsala (1943).
14. Diels, O. *Ber.* **58** (1925) 1231.
15. *Cf. e. g.* Morton, R. A., and de Goureia, A. J. A. (*l. c.*).
16. *Cf. e. g.* Morton, R. A., and de Goureia, A. J. A. (*l. c.*), Mohler, H. *Das Absorptionsspektrum der chemischen Bindung* (1943).
17. Frey, G. S:son *Tek. Tid.* (1945).

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