FOREWORD

This work was conducted by the National Carbon Company, a Division of Union Carbide Corporation under USAF Contract AF 33(616)-6915. This contract was initiated under Project No. 7350 "Refractory Inorganic Non-Metallic Materials", Task No. 735002 "Graphite Materials Development"; Project No. 7381 "Materials Application", Task No. 738102 "Materials Preproduction Process Development"; and Project No. 7-817 "Process Development for Graphite Materials". The work was administered under the direction of the Directorate of Materials and Processes, Deputy Commander/Technology, Aeronautical Systems Division, with Captain R. H. Wilson, L. J. Conlon and W. P. Conrardy acting as Project Engineers.

The work covered in this report was performed by Union Carbide European Research Associates at Brussels, Belgium, under subcontract to National Carbon Company. It covers the period January 1, 1961 through December 31, 1961. This work is still in progress and the information herein is tentative and subject to changes, corrections and modifications.

Prior reports on this Contract have included:

WADD Technical Notes 61-18 and 61-18, Part II, progress reports covering work from the start of the Contract on May 1, 1960 to October 15, 1961.

and the following volumes of WADD Technical Report 61-72 covering various subject phases of the work:

Volume I Observations by Electron Microscopy of Dislocations in Graphite, by Richard Sprague.

Volume II Applications of Anisotropic Elastic Continuum Theory to Dislocations in Graphite, by G. B. Spence.

Volume III Decoration of Dislocations and Low Angle Grain Boundaries in Graphite Single Crystals, by Roger Bacon and Richard Sprague.

Volume IV Adaptation of Radiographic Principles to the Quality Control of Graphite, by R. W. Wallouch.

Volume V Analysis of Creep and Recovery Curves for ATJ Graphite, by E. J. Seldin and R. N. Draper.

Volume VI Creep of Carbons and Graphite in Flexure at High Temperature, by E. J. Seldin.

Volume VII High Density Recrystallized Graphite by Hot Forming, by E. A. Neel, A. A. Kellar, and K. J. Zeitsch.

Volume VIII Electron Spin Resonance in Polycrystalline Graphite, by L. S. Singer and G. Wagoner.

Volume IX Fabrication and Properties of Carbonized Cloth Composites, by W. C. Beasley and E. L. Piper.

Volume X Thermal Reactivity of Aromatic Hydrocarbons, by I. C. Lewis and T. Edstrom.

ABSTRACT

A series of chemical and physical methods, previously developed for use in the study of the constitution of coals, has been applied to the definition of structural parameters for thirteen tar and pitch samples which have a wide range of properties and which are of interest in the fabrication of graphite bodies.

Information obtained on the molecular size and composition indicates the presence of polycyclic compounds with a high degree of aromaticity. Evidence also points to the importance of large aromatic clusters.

This report has been reviewed and is approved.

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I. INTRODUCTION

Studies have been carried out under Subcontract from National Carbon Company by Union Carbide European Research Associates (ERA) in Brussels, Belgium, on coal tars, pitches, and other pyrolysis products of interest in the manufacture of graphite bodies.

Pitches are complex mixtures of molecular species, the chemical and physical behavior of which determine to a large extent their performance as binders in the fabrication of graphite bodies. In an effort to gain a better understanding of binders, a program was undertaken to collect, for a series of pitch samples, a set of data to describe them as well as possible in terms of average chemical structure. This was meant as a first step in a more ambitious project which would attempt to correlate average chemical structure with performance in technological processes. Therefore, a series of chemical and physical methods, previously developed for use in the study of the constitution of coals, has been applied to the definition of structural parameters for thirteen samples having a wide range of properties.

This approach is to be contrasted with other studies under Contract No. AF 33(616)-6915 (see, for example, WADD Technical Report 61-72, Vol. X) on the pyrolysis reactions of pure aromatic hydrocarbons. Knowledge of these is important to an eventual understanding of carbonization using complex commercial mixtures. However, in this present study, the effort is directed toward characterization of these commercially useful tars and pitches by the best analytical means. Such information will be useful both for better application of useful commercial mixtures and for eventual determination of the fundamental chemical reactions.

The materials chosen for study and some of their physical properties are shown in Table 1. These range from tars which are liquid at ordinary temperatures, all the way to semicokes with softening temperatures above 300°C, and finally include a raw petroleum coke having no distinct molten phase. All of the samples in Table 1 except Nos. 1, 12, and 13 were obtained from the Plastics and Coal Chemicals Division (formerly the Barrett Division) of the Allied Chemical Corporation. Sample No. 1 was a tar prepared by National Carbon Company. Sample No. 12 was a semicoke prepared by the Reilly Tar and Chemical Corporation and sample No. 13 was an uncalcined petroleum coke obtained from the Kendall Oil Company. Samples 4 through 7 of 30-medium pitch include material from various commercial lots received over an extended period of time.

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Table 1. Analytical Data for Series of Tar, Pitch, and Semicoke Samples

Sample No.	Description	Results From:	Weight Per Cent							Softening Point(°C)	C V
			C	H	O	N	S	V M	Ash		
1	240 Tar	NCC	90.6	5.15	2.6*	0.99	0.56		0.08	20	36.8
		ERA	91.0	5.1	1.7	1.1	1.1*	76.9	0.1		
2	23 Soft Pitch	NCC	91.5	4.49	2.5*	0.98	0.45		0.18	54	54.6
		ERA	93.2	4.5	1.0	1.1	0.2*	64.7	0.2		
3	15 Vacuum Pitch	NCC	91.1	4.64	2.6*	1.08	0.56		0.08	92	51.0
		ERA	92.1	4.7	1.7	1.3	0.2*	67.6	0.11		
4	30 Medium Pitch	NCC	93.1	4.33	1.1*	1.04	0.50		0.11	99	52.7
		ERA	92.8	4.3	1.3		1.6*	61.3			
5	30 Medium Pitch	NCC	92.1	4.17	2.2*	0.88	0.59		0.28	99	60.7
		ERA	92.9	4.2	1.2	0.7	1.0*	60.2	0.23		
6	30 Medium Pitch	NCC	92.8	4.40	1.0*	1.24	0.57		0.07	100	59.9
		ERA	92.0	4.5	1.4	1.2	0.9*	57.9	0.1		
7	30 Medium Pitch	NCC	92.7	4.43	2.3*	--	0.56		0.07	104	57.4
		ERA	92.2	4.4	1.2		2.2*	61.6			
8	33 Hard Pitch	NCC	92.2	4.16	2.3*	0.85	0.39		0.15	106	63.2
		ERA	93.1	4.2	1.3	0.9	0.5*	54.0	0.16		
9	130°C mp Pitch	NCC	92.0	4.20	2.4*	0.98	0.44		0.15	124	65.8
		ERA	93.1	4.2	1.1	1.1	0.5*	53.4	0.21		
10	175°C mp Pitch	NCC	92.2	3.74	2.7*	0.92	0.46		0.35	167	77.5
		ERA	93.4	3.6	1.0		2.0*	39.3			
11	Barrett Semicoke	NCC	91.6	3.69	3.3*	1.03	0.39		0.47	320	83.5
		ERA	93.6	3.6	1.0		1.8*	23.9			
12	Reilly Semicoke	NCC	87.5	3.66	7.4*	1.10	0.34		0.12	350	83.6
		ERA	94.2	3.7	0.9	1.1	0.1*	20.3	0.1		
13	Raw Kendall Coke	NCC	90.5	4.20	5 2*	0.18	0.26		0.12	--	85.1
		ERA	95.0	4.1	0.6	0.1	0.2*	16.1			

* Calculated by Difference.   V M -- Volatile Matter.   C V -- Coking Value.

2. SUMMARY AND CONCLUSIONS

A series of chemical and physical methods, previously developed for use in the study of the constitution of coals, has been applied to the definition of structural parameters for thirteen tar and pitch samples which have a wide range of properties and which are of interest in the fabrication of graphite bodies. Furthermore, one selected pitch (Sample No. 5) in the middle of the range has been chosen for more intensive investigations, which are still in the preliminary stages.

Solubility characteristics have been determined in pyridine and benzene, and the corresponding extracts have been made available for physical measurements.

Structural parameters including aromaticity, aromatic ring number and number of aromatic carbon and hydrogen atoms per mean molecule have been determined on whole pitches by the graphical densimetric method of statistical structural analysis. Further, this technique has allowed a series of conclusions to be drawn concerning the state of aggregation of pitches (order to disorder ratio, mean interlayer distance) as related to softening point, as well as an estimation of their weight-average molecular weights.

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Light absorption studies have been carried out in the ultraviolet and visible regions on pyridine extracts of pitches, and have allowed estimation of corresponding weight-average molecular weights and average ring numbers. These have been shown to be in good agreement with the parameters derived from the graphical densimetric method, in cases where high extraction yield makes pitch and extract very similar. In other cases, both sets of results can best be reconciled in terms of relatively small aromatic clusters linked together to form molecules of varying degree of polymerization. Number-average molecular weights determined experimentally on pitch extracts by an osmometric (Hill-Baldes) are higher than the calculated weight averages, an observation which has again been interpreted to mean that a fair amount of molecules in pitches are made up of cross-linked aromatic clusters.

Vapor phase chromatography of the pyridine extracts again supports this view. The latter technique has also allowed qualitative identification of a series of polycyclic aromatics among the eluted material from the pyridine extracts. These are naphthalene, substituted naphthalenes, acenaphthene, fluorene, anthracene, phenanthrene, substituted phenanthrenes, fluoranthene, pyrene, substituted pyrene, chrysene, substitued chrysene, 1,2-benzanthracene, benzfluoranthenes, benzpyrenes, substituted benzpyrenes, dibenzanthracene, picene, substituted picene, 3,4,9,10-dibenzpyrene, 1,12-benzperylene, dibenzofluoranthene, coronene. It has been confirmed that qualitatively all pitches are alike in this respect but that the relative amounts of the various polycyclics vary from case to case.

Pitch No. 5 has been fractionated into α, β, and γ fractions which have been investigated spectroscopically and by the graphical densimetric method. The γ fraction has been quantitatively analyzed by vapor-phase chromatography. The pyridine extract has been pyrolyzed under various conditions and the pyrolysis products examined.

Furthermore, pyridine-insoluble residues of pitches have been investigated with respect to electrical conductivity and electron spin resonance. The presence of very large aromatic clusters in the residues is indicated by both methods, although crosslinking of smaller aromatic systems may be partly responsible for the observed phenomena.

Finally, the conclusions which can be drawn in a tentative manner from the first year in this our research program on pitches are that these materials consist of (a) species containing one aromatic cluster per molecule, (b) crosslinked aromatic clusters of small size, (c) large aromatic condensed systems and carbon black.

3. SYSTEMATIC INVESTIGATIONS ON PITCHES AND THEIR EXTRACTS

3.1. Extraction

Pitches vary significantly in their solubility characteristics. Since chemical analysis is limited to their soluble fractions, it became necessary to prepare a series of their extracts. Pyridine and benzene were chosen as suitable solvents which can be obtained with a high degree of purity and which can be

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removed from the extracts with relative ease. Extractions were carried out batchwise at the boiling point of the solvent with a pitch to solvent ratio of 1 g/100 ml, under purified nitrogen. Extraction yields reported in Table 2 show a rough relationship to softening point.

Table 2.   Extraction Yields in Pyridine and Benzene

Sample No. (see Table 1)	Soften- ing Point (°C)	Extraction Yields - Weight Per Cent					
		Pyridine			Benzene		
		Soluble	Insoluble		Soluble	Insoluble	
		ERA	ERA	NCC**	ERA	ERA	NCC
1	20	98	2	2.9	87*	13	9.9
2	54	85	15	12.8	75	26	23.0
3	92	97	2	4.5	83*	17	15.4
4	99	95	8	10.7	68	32	28.5
5	99	82	21	13.4	66	34	28.5
6	100	84	15	10.8	65	35	29.0
7	104	75	25*	11.4	59	36	32.2
8	106	77	23	12.9	61	37	31.9
9	124	83	16	12.4	65	34	29.6
10	167	67	33	23.7	52	48	44.3
11	320	33	67	69.9	26	74	73.8
12	350	29	71*	81.5	22	78*	80.4
13	---	16	84	78.1	15	85*	86.7

*   Weight by difference
**   Insoluble in quinoline as reported by National Carbon Co.

It may be noted that whereas the yields of benzene insoluble residue found both by National Carbon Co. and ERA Laboratory agree quite well, there exist some differences in the yields of pyridine-insoluble residue compared to those reported for quinoline. The behavior is quite irregular, sometimes pyridine and sometimes quinoline seeming to be the better solvent for an individual pitch. Another point which may be of interest is that with increasing softening point temperature the difference in extraction yield between pyridine and benzene first increases but then decreases again.

3.2.   Structural Parameters Derived from Density and Elementary Analysis

The graphical densimetric method of statistical structural analysis [1] allows the determination of important and characteristic parameters which are valid for the mean molecule. It is therefore evident that the results will be the more significant, the more homogeneous the material under investigation. The application of this method in coal research allowed significant progress to be made in the elucidation of its structure and should, therefore, when applied to pitch, yield even more reliable results since (1) a correction of the experimentally determined density for mineral matter can be neglected and (2) pitch can be assumed to be a more homogeneous material than coal.

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3.2.1. Aromaticity

As can be seen from Table 1, the very high percentage of carbon of pitches is accompanied by a very low percentage of hydrogen and an even still lower percentage of foreign elements such as O, N, and S. The aromaticity $(f_a = C_{ar}/C_{tot})$ can be therefore expected to be very high.

The <u>graphical densimetric method</u> allows the determination of f_a for alkyl-aromatic hydrocarbons as well as for mixtures of these materials, and is based on an M_c/d versus H/C diagram (reduced molar volume versus atomic H/C ratio). In principle, each <u>type of condensed aromatics</u> (peri-, angular-, cata-condensed) has its own diagram, [2] but whatever diagram is used f_a for pitches has been found to be very high. Some clear indication of the type of condensation results from the experimentally determined H/C-ratio. Another factor in the determination of the true f_a-value is the <u>stage of aggregation</u> of the sample [3]. In this respect, if use is made of the diagram valid for <u>amorphous</u> materials, f_a for all investigated pitches lies between 0.93 and 0.97, whereas from the diagram based on <u>crystalline</u> models f_a for all pitches would be > 1. Since the f_a-values scatter only in a very small band, an individual characterization of the pitches cannot be made from their f_a-values, considering the inaccuracies of the experimentally determined density and of the elemental analysis.

On the other hand, the extremely high aromaticity of the pitches permits an extension of the graphical densimetric method to the determination of completely new parameters for the mean molecule, such as mean aromatic ring size, number of aromatic C- and H-atoms, an estimation of the state of aggregation of the molecules as well as a calculation of the mean interlayer distance.

3.2.2. State of Aggregation

X-ray investigations [4] have established that pitches possess in any case a higher degree of order than that which would correspond to the M_c/d versus H/C-diagram for <u>completely amorphous</u> material, and therefore this diagram cannot be used.

On the basis of the measured true densities (helium densities), elemental analyses and degree of order derived from X-ray structural analysis, pitches can be assumed to be a mixture of pure aromatic hydrocarbons. The experimentally determined pair of values M_c/d vs. H/C of the different pitches therefor lies on a $f_a = 1$ curve, the position of which depends on the state of aggregation in each pitch sample. The degree of order in the pitches can be derived from the M_c/d vs. H/C relations for pericondensed aromatic systems in the completely ordered and disordered state. With the help of C_{ar}-atomic volumes and molar increments (I) for various degrees of order, a series of $f_a = 1$ curves in the M_c/d vs. H/C diagram can be calculated from the following equation:

$$M_c/d = v_c + v_H \times H/C + \frac{I \times (H/C)^2}{6}$$

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The experimentally determined pair of values M_c/d vs. H/C of the sample lies then on that curve, which has a v_c - and I-value^c corresponding to the degree of order in the sample (cf. Figure 1).

I $V_c = 6.6 \, cm^3/ \, g \, atom$; $I = 31.2 \, cm^3/ \, g \, mol$; $\bar{d} = 4.20 \, Å$
II $V_c = 6.3$; $I = 28.1$; $\bar{d} = 3.95 \, Å$
III $V_c = 6.0$; $I = 25.0$; $\bar{d} = 3.70 \, Å$

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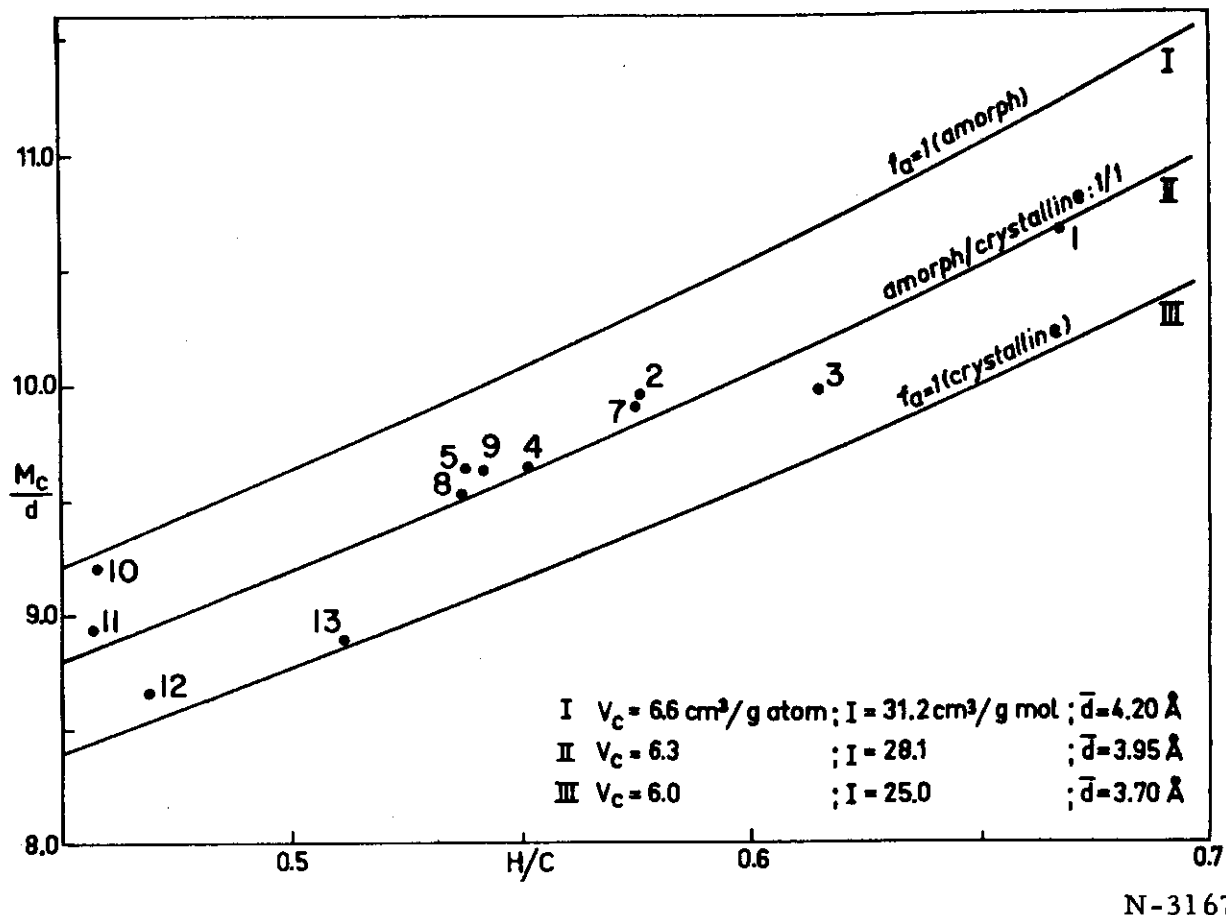
Figure 1.   Graphic Determination of Mean Order in Pitch Samples from Table I

3.2.3.   Results

In Table 3 are summarized all structural parameters which can be derived from the true density (helium density) and elemental analysis. Since it can be assumed that no pore structure is present in pitches, water-densities (pycnometer method) have also been measured. A comparison of these values (Table 3, columns 3 and 4) shows that for pitches the results are in agreement within the experimental errors. Therefore, for pitches, the easily determined water-density is as good as the helium-density which is much more difficult to measure. On the contrary, in the case of semicokes and cokes, there exists an important deviation between water- and helium-densities. This effect can be explained by the development of porosity on account of thermal treatment or by an assumed hydrophobic character for the surface of the coke samples. It should be mentioned that the magnitude of the deviation between helium and water densities runs parallel to the degree of order derived from true density.

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Table 3.   Structural Parameters Derived from Density and Elemental Analysis

Sample No. (see Table I)	Softening Point (°C)	d^{25}_{He}	$d^{25}_{H_2O}$	(H/C) exp.	(H/C) calc.	$\bar{R}_{ar}$	C_{ar}	Order A:K	$\bar{d}(Å)$	$\bar{M}_{calc.}$
1	20		1.212	0.667	0.670	3-4	14-16	1:1	3.95	180
2	54		1.278	0.576	0.578	5	19	2:1	4.00	220
3	92		1.280	0.613	0.613	4-5	16-20	1:2	3.85	220
4	99	1.317	1.321	0.538	0.545	6	22	2:1	4.02	280
5	99	1.320	1.320	0.551	0.545	6	22	1:1	3.95	290
6	100		1.312	0.575	0.573	5-6	20-22	2:1	4.00	250
7	104	1.283		0.575	0.578	5	19	2:1	4.00	250
8	106		1.333	0.538	0.545	6	22	1:1	3.95	270
9	124		1.322	0.538	0.545	6	22	2:1	4.00	260
10	167	1.372	1.363	0.458	0.466	9	30	A	4.14	360
11	320	1.410	1.366	0.457	0.466	9	30	1:1	3.97	390
12	350	1.449	1.379	0.469	0.466	9	30	K	3.70	380
13	---	1.441	1.361	0.512	0.500	7	24	K	3.70	290

$\bar{R}_{ar}$ - and C_{ar} - values for the different samples are given in columns 7 and 8.   The mean molecule in the case of pitches has an $\bar{R}_{ar}$ = 5-6, except for Samples 1 and 3 for which a somewhat lower value   has been found.

The good agreement between the experimentally determined H/C (column 5) and the calculated values (column 6) shows that mainly angular- and/or peri-condensed aromatic systems are present.

The mean order of all samples, derived from true density measurements, is reported in column 9.   Examination of columns 2, 7, and 9 shows that softening temperature depends on $\bar{R}_{ar}$ as well as on state of aggregation.   In-crease in $\bar{R}_{ar}$ from 6 to 9 in Samples 4 and 11, state of aggregation being constant, is accompanied by an increase in softening point from 99°C to 320°C. On the other hand, a change in state of aggregation at constant $\bar{R}_{ar}$ is best illustrated by Samples 10 and 12.   It is seen that improved order is also followed by increase in softening point (from 167°C to 350°C).   Finally, small scatter in softening temperature in samples with roughly the same $\bar{R}_{ar}$ and state of aggregation may possibly be attributed to a change in the distribution of cluster sizes.

In general, the ordering effect has a much greater influence on thermal properties (softening point, thermal expansion coefficient) than the $\bar{R}_{ar}$-value.

Estimation of the mean order can be further refined since it is possible to calculate the mean interlayer distance $\bar{d}$ (results summarized in column 10) by a linear interpolation between $\bar{d}$ = 3.7 Å and $\bar{d}$ = 4.2 Å valid for the com-pletely ordered and disordered states respectively (cf. Figure 1).   The former is calculated from the packing of crystalline aromatic hydrocarbons taking into·

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account the fact that the Van der Waals radius perpendicular to the C_{ar}-layer is $1.85 Å$ [5]. The $\bar{d} = 4.2 Å$ value for the disordered state can be derived from the atomic volume of C_{ar} in the liquid state ($v_C = 6.6 \text{ cm}^3/\text{g atom}$):

$$\bar{d} (Å) = \frac{2 \times 10^{24} \times v_C}{O \times N}$$

where O is the surface of R_{ar} with a mean value of $5.24 Å^2$ from $R_{ar}^{peri} = 4$ onwards, and N is Avogadro's number (6.03×10^{23}).

From the data in Table 3 the weight average <u>molecular weights</u> ($\overline{M}$) can be calculated in two ways: (a) from the $\bar{R}_{ar}$-values and (b) from the atomic volume $v_{C_{ar}}$, the molar increment I and the corresponding interlayer distance $\bar{d}$. The results based on these two methods are in good agreement, as they should be since both methods make use of the same experimental data (density and elemental analysis). The average values for the mean molecular weights are reported in the last column of Table 3. The tar and pitch Samples 1 through 9 have $\overline{M}$ between 200 and 300, the last four samples in Table 3 between 300 and 400.

3.3. Light Absorption in the UV and Visible Region

The UV and visible light absorption of aromatic systems is due to their π-electrons. In general, the long wavelength absorption edge undergoes a red shift with increasing size of the aromatic cluster [6], and as a result an estimation of the size of an unknown aromatic system may be derived from the position of this absorption edge. In the case of a mixture of systems with different ring sizes, only the bigger ones will absorb in the UV. This leads to an absorption spectrum which steadily rises towards the UV, and since many bands corresponding to the different compounds in the mixture will overlap, it may become highly unspecific. Such a spectrum is found for pitches, as well as for their pyridine- and benzene-extracts. In spite of this difficulty, attempts have been made to reconstruct this unspecific absorption with a mixture of 9 condensed aromatic hydrocarbons ($R_{ar} = 2$ to 9) in calculated amounts, and hence to estimate the average size ($\bar{R}_{ar}$) of the aromatic systems in the sample [7]. The reconstruction is carried out in the following way: starting at 650 mμ, where only the model with $R_{ar} = 9$ absorbs, the amount (wt per cent) of this model necessary to match the sample absorption is given by:

$$\frac{100 \times D \text{ sample}}{D \text{ model}}$$

At 600 mμ the next model with $R_{ar} = 7$ absorbs also and its amount can be calculated in the same way, but the contribution of the model with $R_{ar} = 9$ at 600 mμ must be taken into account. Going stepwise in this way to shorter wavelengths, one model after the other is added. At the end the experimentally determined spectrum of the mixture is compared to the sample spectrum in order to apply some minor corrections, if necessary.

Table 4 summarizes results on extracts (mainly pyridine extracts) of

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Table 4.   Structural Parameters of Extracts as Determined from Light Absorption

Sample No. (see Table 1)	Extraction Yield Per Cent	Weight per cent of models used with R_{ar}:						$\bar{R}_{ar}$	$\bar{M}$
		2	3	4	5	7	9		
1	98(P)	13	27	30	26	2	3	3.9	210
3	97(P)	9	22	29	34	3	4	4.2	220
4	95(P)	3	22	28	35	3	6	4.4	230
	68(B)	5	28	33	26	1	1	3.9	210
5	82(P)	5	19	32	36	3	3	4.3	230
6	84(P)	6	17	33	37	3	5	4.4	230
7	75(P)	13	25	30	26	2	2	3.9	210
8	77(P)	3	17	33	39	3	4	4.4	230
9	83(P)	3	15	33	41	4	5	4.5	235
10	67(P)	5	14	29	43	5	5	4.5	235
	52(B)	6	17	33	38	2	1	4.2	220
11	33(P)	5	17	30	42	3	3	4.3	230
	26(B)	7	22	31	39	1	-	4.1	215
12	29(P)	4	20	32	39	3	2	4.3	225

(P) Pyridine
(B) Benzene

various pitches. It is surprising that although many properties of these pitches vary considerably, the light absorption of all the extracts is very similar. In all cases the major part of the extracts seems to consist of 3-, 4-, and 5-ring systems (average aromatic ring size $\bar{R}_{ar} \simeq 4$). It should be mentioned in this respect that the reconstruction method cannot distinguish between molecules which contain only one aromatic cluster and molecules which contain more than one (for example: the UV-absorption is the same for anthracene and 9,9-di-anthryl). Furthermore, since measurements are difficult below 280 mμ (no suitable solvents available) the weight per cent of aromatics with R_{ar} values of 2 and 3 may be somewhat overestimated. On the other hand, structures such as perylene ($R_{ar} = 5$), as used in the reconstruction, have a stronger long wave-length absorption than structures of similar size but derived from pyrene and fluoranthene. If these structures dominate, then the weight per cent of systems with $R_{ar} > 5$ could be somewhat higher than calculated in Table 4.

An interesting comparison can be made between the $\bar{R}_{ar}$ values derived from the graphical densimetric method (Table 3, column 7) applied to the whole pitches and from light absorption measurements on their pyridine extracts (Table 4, column 4). As long as the extraction yield is very high, pitch and pyridine extract shows approximately the same $\bar{R}_{ar}$ values.

However, with decreasing extraction yield of the pitch, $\bar{R}_{ar}$ determined on the latter by the graphical densimetric method starts increasing, whereas $\bar{R}_{ar}$ measured by light absorption on the corresponding extract remains roughly

constant. This shows that the whole pitch must contain a fair amount of molecules having a bigger number of aromatic rings than the determined average. Whether these are condensed to one large cluster or to several smaller clusters linked together per molecule remains to be seen.

From the $\bar{R}_{ar}$-values, a weight average molecular weight $\bar{M} \simeq 220$ can be calculated, a result which only has physical sense as a molecular weight if all molecules present in the extracts contain only one aromatic cluster.

Finally, the calculated aromaticity, which results from the sum of the weight per cents of compounds with $R_{ar} = 2-9$ is of the order $f_a \sim 1$ indicating that the nonaromatic part must be small.

3.4. Molecular Weight Determination

Molecular weights of various pitch extracts have been determined by the Hill-Baldes method [8], which is based on the vapor-pressure depression of the solvent by the dissolved material. The use of pyridine as a solvent eliminates errors due to association and moisture. If the material is easily soluble, and present as a true chemical solution the error should not be higher than ± 5 per cent. However, it should be kept in mind that this method yields number-average and not weight average molecular weights. The difference may be important and can be best illustrated on the following example. The mean molecular weight of a mixture of 200 grams of a substance having M = 100 and of 300 grams of a substance having M = 500 would be, if calculated on a weight per cent basis: 100 x 0.4 + 500 x 0.6 = 340. The number average molecular weight would be:

$$\frac{200 + 300}{2 + 0.6} = 192 \quad .$$

Quite generally it can be said that the number-average molecular weight is either equal to or smaller than the weight-average. The wider the molecular weight distribution in a mixture of compounds, the bigger is the difference between these two molecular weights.

The number average molecular weights have been determined for all pyridine extracts and can be considered as minimum values for reasons stated above. It can be seen (Table 5) that they increase with increasing softening point of the pitch and decreasing extraction yield. In Table 5 are also included average molecular weights calculated from light absorption for the extracts and molecular weights obtained from density measurements for the pitches themselves. Comparison of the sets of molecular weights for the extracts shows that the number-average (Hill-Baldes) is actually bigger than the weight-average (light absorption). This can only be understood if a fair amount of molecules contain more than one aromatic cluster. Indeed, it will be recalled that the reconstruction method of absorption spectra cannot distinguish between molecules containing one or more than one aromatic cluster (see Section 3.3.). The determination of $\bar{M}$ values from density is limited by the same uncertainty and it is therefore not unexpected that weight average molecular weights determined from density on the whole pitch and from light absorption on the extract should be comparable for samples where the extraction yield is high.

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Table 5. Experimental and Calculated Molecular Weights for Pitches and Pitch Extracts

	Pitch		Pyridine Extract		
Sample No. (see Table 1)	Softening Temperature (°C)	$\overline{M}$ (density)	Extraction Yield	$\overline{M}$ (Hill-Baldes)	$\overline{M}$ (Light Absorption)
1	20	180	98	325	210
3	92	220	97	365	220
4	99	290	95	375	230
5	99	280	82	330	230
6	100	250	84	375	230
7	104	250	75	330	210
8	106	270	77	440	230
9	124	260	83	470	235
10	167	360	67	520	235
11	320	390	33	450	230
12	350	380	29	410	225

3.5. Vapor Phase Chromatography

Pitch itself can be analyzed by high temperature vapor phase chromatography (VPC) but since it always contains some very heavy material, the VPC column deteriorates very quickly. On the other hand, it was observed that all the pitch material which can be eluted by VPC is present in its pyridine extract; therefore the pyridine extracts of various pitches were substituted for the pitches themselves in VPC investigations. Two important results can be reported: (a) all samples show the same peaks and it is only their relative intensities which vary from case to case, and (b) the amount of material which can be eluted under reasonable experimental conditions (up to systems with 5 condensed aromatic rings) represents at most ~ 50 per cent and normally 20 per cent or less of the pitch (Table 6).

It has been checked by varying the elution temperature that no condensation reactions take place in the VPC apparatus, and therefore that the rest of the material, which cannot be eluted from the column, must have a very high boiling point and thus also a high molecular weight.

Altogether 20 peaks could be distinguished on an Apiezon L column at temperatures from 220° to 400°C. Cuts were made and further analyzed by UV spectroscopy. Some of the VPC peaks were found to be complex and therefore each one was divided into different zones to be examined separately by UV[69].

In this way the following components have been qualitatively identified with a fair measure of certainty: naphthalene, substituted naphthalenes, acenaphthene, fluorene, phenanthrene, substituted phenanthrenes, fluoranthene, pyrene,

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Table 6. VPC Analysis on Pyridine Extracts

Sample No. (see Table 1)	Extraction Yield (per cent)	Pyridine Extract VPC Analysis, Wt Per Cent of Fractions 1 - 8**								Wt Per Cent of Material with R ar $\leq$ 5	
		1	2	3	4	5	6	7	8	VPC	UV and visible
1	98	1,5	2,1	2,2	12,8	4,4	5,3	6,6	4,7	40	96
3	97	0,2	0,4	0,5	2,6	2,3	11,8	16,1	16,3	50	94
4	95	0,2	0,5	0,9	2,9	2,7	3,3	5,6	5,1	21	88
5	82	-	0,5	0,3	2,9	3,0	3,0	5,9	9,0	25	92
6	84	-	0,4	0,7	4,1	2,9	3,5	4,3	3,3	19	93
7	75	-	0,4	2,3	4,8	3,2	3,8	5,1	3,9	24	94
8	77	0,1	0,4	0,4	2,3	3,0	2,4	5,5	6,8	21	92
9	83	-	0,4	0,5	1,5	1,9	1,9	5,4	7,2	19	92
10	67	-	0,1	0,1	0,2	0,5	0,5	1,2	5,7	8	91
11	33	0,2	0,2	0,6*	0,3	0,05	0,05	1,2	11,9	15	94
12	29	-	-	-	-	0,6	0,6	3,7	7,2	12	95

* Not identified, not present in other samples

** Fractions in the table:

1 Naphthalene, substituted naphthalenes
2 Acenaphthene
3 Fluorene, substituted fluorene
4 Phenanthrene, anthracene, substituted phenanthrenes

5 Fluoranthene
6 Pyrene, substituted pyrene
7 Chrysene, benzanthracene, substituted chrysene and benzanthracenes (chrysene is the most important)

8 Benzfluoranthenes, benzpyrenes (roughly 50/50 in most cases)

substituted pyrene, chrysene, substituted chrysene, 1,2-benzanthracene, benzfluoranthenes (3 isomers), benzpyrenes (2 isomers), substituted benzpyrene, dibenzanthracene, picene, substituted picene, dibenzpyrene, 1,12-benzperylene, dibenzfluoranthene. The UV spectra of peaks with still longer retention times seem to contain the naphthalene, phenanthrene, benzanthracene, pyrene and chrysene skeletons, but in view of the complexity of the spectra, these assignments are only tentative at this time. It should be further stated that the pure aromatic hydrocarbons dominate strongly the corresponding substituted structures (CH_3 or CH_2CH_3 groups) being present only in small amounts.

The quantitative analysis is not simple. It happens that several useful internal standards separate out from the sample. Another difficulty is that from chrysene onwards the measured quantities must be corrected in the light of results on synthetic mixtures. Otherwise measured values are found to be too low. The reason for this behavior is not understood completely, but may be in relation to tailing and to the assumed background.

Table 6 summarizes the results on pyridine extracts of various pitches. Systems with higher retention times than benzpyrene ($R_{ar} = 5$) have not been included, since the analysis gets uncertain, but the amount of systems with $R_{ar} = 6$ and $R_{ar} = 7$ is certainly small. Furthermore, the presence of alkyl substituted aromatics has been neglected, and, finally, in such cases where VPC peaks overlap (as for example benzfluoranthene and benzpyrene) no further separation has been attempted as yet.

If the amount of material with $R_{ar} \leq 5$ is compared to the same parameter derived from UV and visible absorption, it is seen that the latter is roughly constant and always much higher. A possible explanation for the discrepancy between these results would be the following: If some of the aromatic clusters with $R_{ar} \leq 5$ are linked together to form larger molecules, they would still be detected by UV and visible absorption as systems with $R_{ar} \leq 5$. However, in VPC such molecules containing more than one aromatic system may not be eluted from the column and thus the amount of material with $R_{ar} \leq 5$ as found by VPC could be much smaller than the corresponding value calculated from UV and visible absorption.

Furthermore, an interesting but expected trend for pitches can be seen from a comparison of softening point, volatile matter, extraction yield and amount of material with $R_{ar} \leq 5$ (see Table 7): An increase of the softening point accompanied by a decrease of the volatile matter as well as extraction yield runs parallel with the decrease of the amount of material with $R_{ar} \leq 5$.

4. INVESTIGATION OF PYRIDINE INSOLUBLE RESIDUES OF PITCHES

The pyridine insoluble residue of pitch is generally considered to be a mixture of highly condensed aromatics and carbon black [10]. As a result of the complete insolubility any nondestructive chemical investigation is impossible. All optical methods (UV-, visible- and IR-absorption) fail to yield useful information since only very unspecific spectra with very high background absorption are obtained. However, the presence of very large condensed aromatic systems is strongly suggested by electrical conductivity measurements and electron spin resonance studies.

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Table 7. Correlation of VPC-Eluted Material with Pitch
         Properties

Sample No.(see Table 1)	Softening Point (°C)	Volatile Matter (Wt Per Cent)	Extraction Yield in Pyridine (Wt Per Cent)	Weight Per Cent with $R_{ar} \leq 5$
1	20	76.9	98	39
3	92	67.6	97	48
4	99	61.3	95	20
5	99	60.2	82	20
6	100	57.9	84	16
7	104	61.6	75	18
8	106	54.0	77	17
9	124	53.4	83	16
10	167	39.3	67	5.5
11	320	23.9	33	4.5
12	350	20.3	29	3.5

4.1.   Electrical Conductivity

It has been shown that aromatic hydrocarbons behave as organic intrinsic semiconductors[11]. Their resistivity decreases with increasing temperature, a fact which is due to thermal activation of electrons which pass from a non-conducting to a conducting state. The corresponding electron activation energy ($\Delta\varepsilon$ in eV) can be calculated from the temperature dependence of the resistivity (ρ), using the equation:

$$\Delta\varepsilon = 0.397 \text{ x } \frac{\log\rho_2 - \log\rho_1}{1/T_2 - 1/T_1}$$

In general, $\Delta\varepsilon$ decreases with increasing size of the condensed aromatic system. As one example, for phenanthrene and anthracene $\Delta\varepsilon$ is ~ 3 eV, for chrysene ~ 2 eV and for ovalene ~1 eV, [12]. Therefore, the $\Delta\varepsilon$ value of an unknown but mainly aromatic sample provides a useful estimation of the size of the condensed aromatic system present.

The results on several pyridine-insoluble residues are summarized in Table 8. No model studied so far has a $\Delta\varepsilon$ value as low as these samples, but the $\Delta\varepsilon$ values of the pyridine insoluble residues are of the same order of magnitude as those of anthracites[13], where the aromatic systems are known to be very large[14].

In this respect, however, it should be mentioned that aromatic clusters linked together by direct bonds have significantly smaller $\Delta\varepsilon$ values than the individual clusters and therefore the low $\Delta\varepsilon$ values of the pitch residues may be due at least in part to crosslinked aromatic systems[15].

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Table 8. Electron Activation Energies and Free Radical
Concentrations of Pyridine Insoluble Residues

Sample No.(see Table 1)	Pyridine Insoluble Residue		
	Yield Wt Per Cent	$\Delta\varepsilon$ (eV)	10^{18} radicals/g
1	2	0.25	-
2	15	0.25	-
3	3	0.2	-
4	5	0.3	-
5	18	0.4	60
7	25	0.5	25
10	33	0.3	25
11	67	0.6	40

Furthermore, a definite trend can be observed from the results: $\Delta\varepsilon$ increases with increasing yield of the residue; a possible explanation for this behavior is that the relative amount of carbon black (very low $\Delta\varepsilon$),decreases with increasing yield of residue.
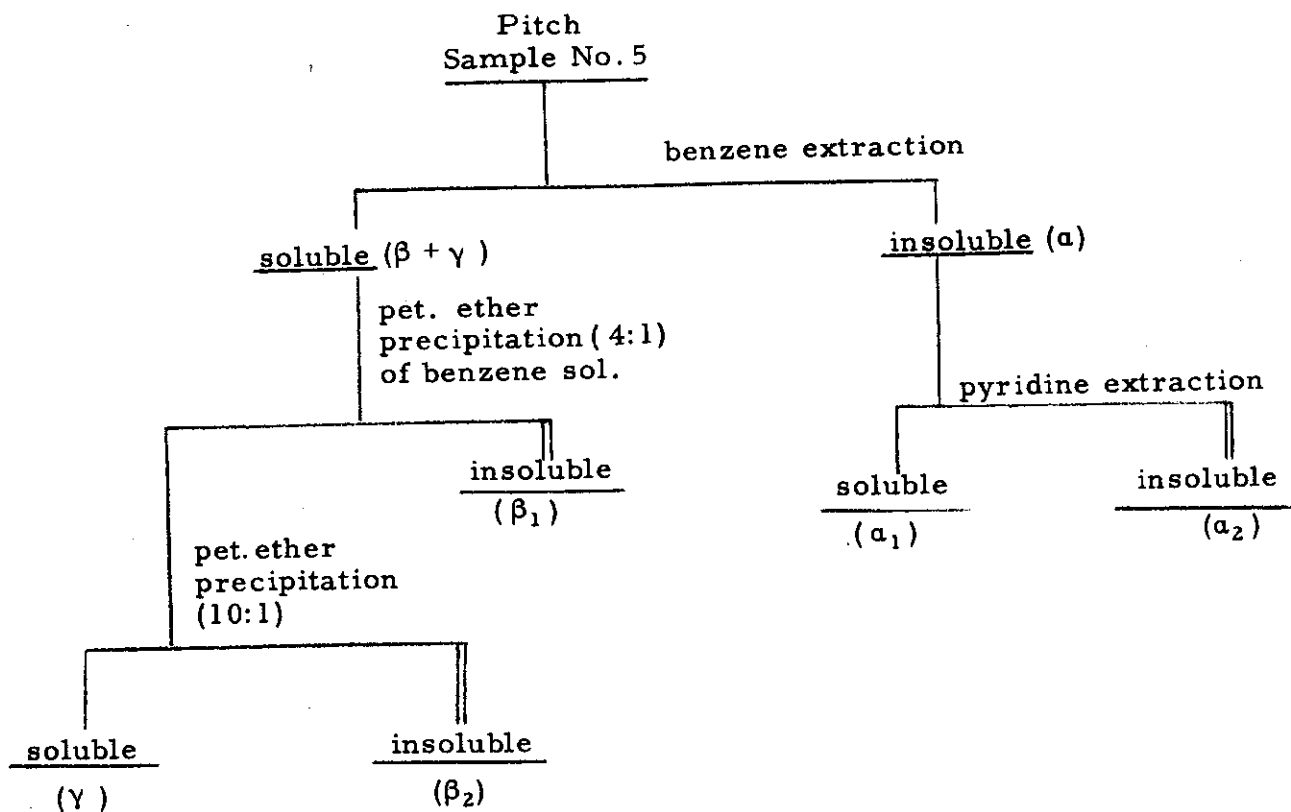
4.2.   Electron Spin Resonance

The presence of stable free radicals in coal and related products is now well established[16]. Although there is no direct proof, it is reasonable to conclude that these free radicals are stabilized by resonance with the aromatic systems[16]. Since the size of the aromatic system then largely determines the extent and probability of stabilization, the measured free radical concentrations may be considered as a qualitative measure for the size of the aromatic systems present.

The fact that the radical concentration of the pyridine insoluble residues (Table 8) is 20 to 30 times higher than in the corresponding pyridine extracts suggests strongly the presence of much larger condensed aromatic systems in the former than in the latter. Furthermore, the free radical concentrations of the pyridine residues are of the same order of magnitude as those of anthracites[16], where the aromatic clusters, as already mentioned, are very large.

5. INVESTIGATIONS ON PITCH NO. 5 AS A STANDARD SAMPLE

Pitch Sample No. 5 shows properties which may be considered as average of 30 Medium Pitch which is widely used as a binder and was available in ample quantity. It was therefore chosen for further study.

It was fractionated according to the overall scheme given in the following flow sheet:

Pitch
Sample No. 5

benzene extraction

soluble ($\beta + \gamma$) — insoluble (α)

pet. ether
precipitation (4:1)
of benzene sol.

insoluble
(β_1)

pyridine extraction

soluble
(α_1)

insoluble
(α_2)

pet. ether
precipitation
(10:1)

soluble
(γ)

insoluble
(β_2)

Benzene was chosen as the first solvent in the overall procedure because the higher solubility in pyridine causes technical difficulties in the sharp separation of soluble from insoluble material, in particular in the course of filtration. In practice, a 500 g sample of pitch was extracted. Analytical data for the various fractions are collected in Table 9.

Table 9. Analytical Data and Structural Parameters of
Pitch Sample No. 5 and its Fractions

	Pitch No.5	α	α_1	α_2	$\beta + \gamma$	β_1	β_2	γ
C	92.9	93.1	91.8	92.7	92.7	90.5	93.3	93.6
H	4.2	3.0	4.0	2.7	4.8	4.5	4.9	5.3
O	1.2	1.7	1.7	2.1	1.1	1.9	0.9	1.0
v.m.	60.2	13.6	36.4	9.9	84.6	66.0	93.0	99.2
ash	0.2	0.8	0.4	0.6	-	0.7	-	-
Extr. yield	-	33	8	25	67	32	12	23
$\overline{M}$ (Hill-Baldes)	-	-	-	-	325	450	380	305
d_{He}	1.317			1.596		1.330		
d_{H_2O}	1.321		1.32					

Table 9.   Analytical Data and Structural Parameters of
Pitch Sample No. 5 and its Fractions Cont'd.

	Pitch No. 5	α	α_1	α_2	$\beta + \gamma$	β_1	β_2	γ
$(H/C)_{exp}$	0.538		0.519	0.347		0.592		
$(H/C)_{calc}$	0.545		0.522	0.345		0.578		
$\overline{R}_{ar}$	6		6-7	20		5		
C_{ar}	22		~ 25	58		19		
H_{ar}	12		~ 13	20		11		
O_{tot}	0.3		~0.3	1		0.3		
A:K	2:1		2:1	1:4		1:3		
$\overline{d}$	4.02		4.00	3.80		3.83		
$\overline{M}_d$	280		330	720		250		
$\overline{R}_{ar}$ (UV)					3.9			
$\overline{M}$ (UV)					210			
$\Delta\varepsilon$ (eV)				0.4				

Extraction yields reported in Table 9 are calculated relative to the starting pitch.

The combined yields of benzene- and pyridine-soluble extracts correspond to 75 per cent of the starting pitch instead of 82 per cent reported in Table 2 for a one-step extraction with pyridine. This small discrepancy is probably due to the benzene-soluble material present as a part of the pyridine extract in the one-step extraction, and which peptizes part of the otherwise pyridine-insoluble residue.

5.1.   Structural Parameters from Density and Elemental Analysis

The background of the graphical densimetric method and the method of calculation of the various structural parameters has been discussed in Section 2.2. Examination of the results so far available for Pitch No. 5 and its fractions (Table 9) shows that:

(a)   The $\overline{R}_{ar}$ and $\overline{M}$ values of α_1 and β_1 are of the same order of magnitude, whereas for α_2 they are much bigger. These

results are in accordance with what should be expected from the extraction procedure. The high $\overline{R}_{ar}$ for a_2 is confirmed by the very low electron activation energy $\Delta\epsilon$ from electrical conductivity measurements.

(b) The mean order (A:K) and $\overline{d}$ are the same for pitch and a_1, but completely different in a_2 and β_1. The results found for a_2 are in accordance with the high $\overline{R}_{ar}$ value. The high degree of order (A:K,$\overline{d}$) accompanied by the rather small $\overline{R}_{ar}$ in β_1 can be understood if the aromatic size distribution is very narrow.

5.2. Light Absorption

The reconstruction of the UV and visible absorption spectrum of the benzene extract ($\beta + \gamma$ fraction) has already been reported in Section 3.3., Table 4.

The absorption spectra of β_1, β_2, and γ fractions have also been measured and some important conclusions may be drawn (cf. Figure 2):

(a) As will be shown later, roughly 2/3 of the γ fraction can be analyzed by VPC, whereby aromatic systems with R_{ar} up to 6 have been eluted. It is still a question whether the remaining 1/3 consists of still bigger aromatic clusters. From the long wavelength absorption edge of the γ fraction in Figure 2 it can be seen that aromatic systems with $R_{ar} > 6$ can only be present in rather small amounts. Furthermore, the absorption spectrum of a mixture of the compounds found by VPC in their true concentrations is fairly similar to that of the γ fraction itself, an indication that the part undetected by VPC should consist of aromatic systems of essentially the same aromatic cluster size as that found for the detected 2/3, but linked together to form bigger molecules.

(b) The spectra found in Figure 2 show the same general trend, especially in the region of strongest absorption ($K > 10, \lambda < 400\,m\mu$). This indicates that the aromatic cluster sizes and even their relative amounts cannot be very different in the four fractions. In polymers the absorption spectra are often unspecific and therefore the gradual disappearance of detail in the spectra ($\gamma \rightarrow \beta_2 \rightarrow \beta_1$) could be explained by an increase in the degree of polymerization. This is in agreement with the experimental number-average molecular weights (Hill-Baldes; cf. Table 9).

The same loss of detail in going from fraction γ to β_1 is found in the infrared spectra. That the same strong bands in the 11 to $15\,\mu$ region occur in all three spectra is an indication of similar positions of substitution on the aromatics [17, 18].

5.3.   Vapor Phase Chromatography

Fraction γ was analyzed quantitatively by VPC with linear temperature programming from 75° to 375°C on a column consisting of 25 per cent silicone gum rubber on Chromosorb; this allowed recording of twelve well-resolved peaks. The material eluted up to 375°C corresponded to ~ 15 per cent of the
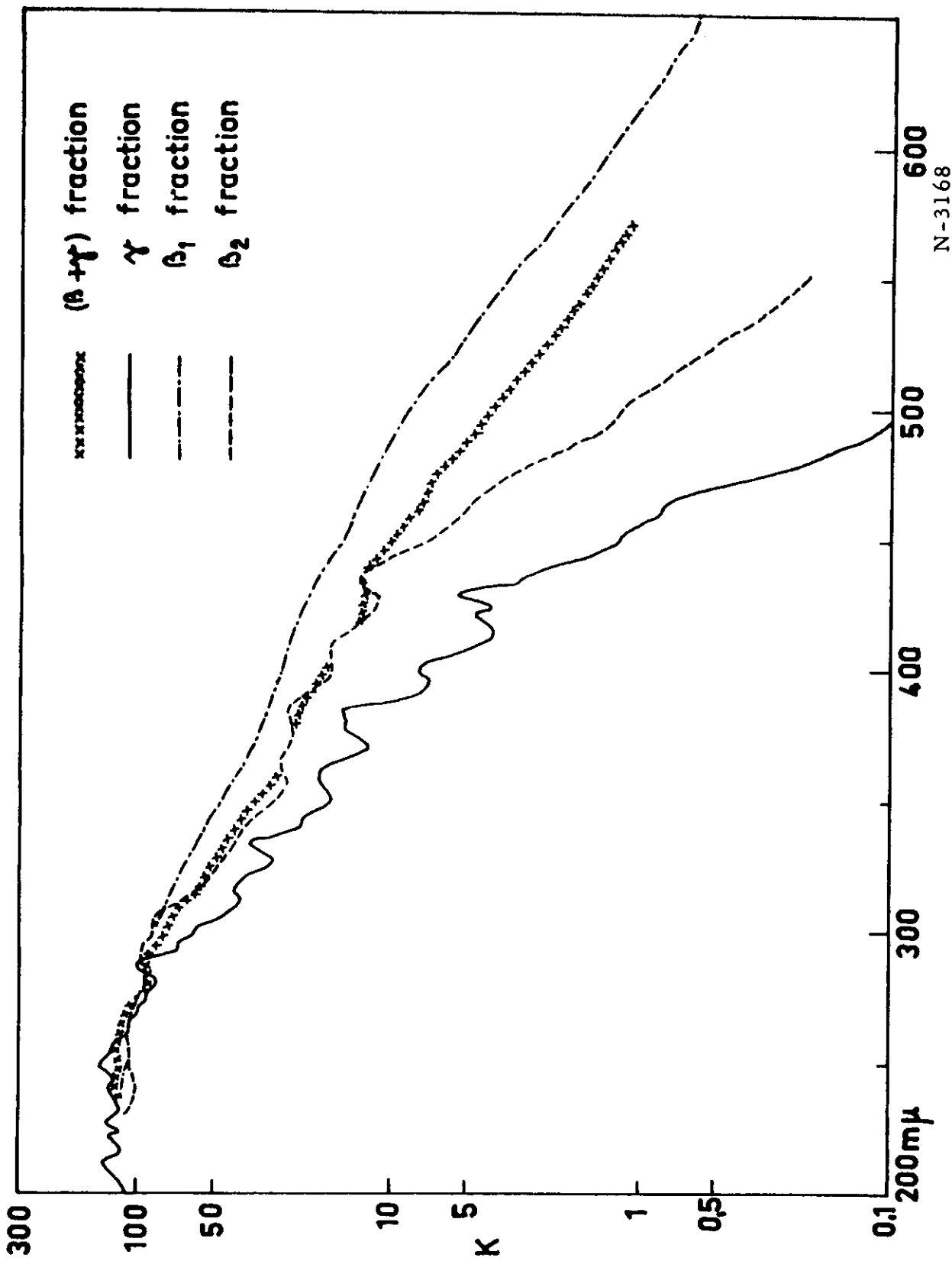
Figure 2. Absorption Spectra of Fractions from Pitch No. 5

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starting pitch (2/3 of the total γ fraction). The compounds corresponding to each peak were isolated and their UV spectra were taken for identification purposes [6]. Assignment of the peaks was confirmed by isolation of larger quantities of each substance, purification and melting point determination. Results are reported below:

Peak No.	Assignment	Per Cent in Pitch No. 5
1	Acenaphthene	0.3
2	Fluorene	0.1
3	Phenanthrene + Anthracene	1.2
4	Mixed methyl-phenanthrenes	0.3
5	Fluoranthene	1.5
6	Pyrene	1.3
7	1,2-Benzanthracene	0.7
8	Chrysene	2.7
9	Benzopyrenes	3.6
10	3,4-9,10-Dibenzopyrene	1.5
11	?	1.0
12	?	0.3

Two more polycyclics have been isolated from the γ fractions by adsorption chromatography; they are picene and coronene. It was not possible, however, to determine them quantitatively.

As can be seen from the above results, the amount of alkylated structures present in the eluted part of the γ fraction is very low. On the other hand, the identified substances show an increasing number of condensed aromatic rings.

5.4.   Stepwise Pyrolysis of the Pyridine Extract $(a_1 + \beta + \gamma)$ of Pitch No. 5

The pyridine-soluble extract of Pitch No. 5 was pyrolyzed in steps of 50°C at temperatures between 250° and 500°C : (a) under vacuum of 0.01 mg Hg, (b) under nitrogen, and (c) under a mixture of 88 per cent N_2 and 12 per cent O_2. For each step, the gases were analyzed and the amount of material collected in a cold trap next to the oven was determined ("tar"). Table 10 summarizes

Table 10.   Pyrolysis Products from the Pyridine Extract of Pitch No. 5 Under Various Conditions

Pyrolysis Condition:	H_2 (cm³/g pitch)	CH_4, C_2H_6 and C_2H_4 (cm³/g pitch)	$CO + CO_2$ (cm³/g pitch)	"Tar" (mg/g pitch)
Vacuum	0.64	2.05	0.33	627
Nitrogen	1.25	2.85	0.22	460
88 Per Cent N_2-12 Per Cent O_2	0.2	0.33	40.1	246

the main results. As can be seen, the amount of tar decreases if vacuum is replaced by nitrogen. Probably the more volatile parts can then escape less easily from the hot zone and condense partly to nonvolatile material. At the same time, a very small increase is found in H_2, CH_4, C_2H_6, and C_2H_4. If oxygen is present, the "tar" yield decreases further; oxygen probably produces some condensation reactions between the pitch molecules. When oxygen is present, H_2, CH_4, C_2H_6 and C_2H_4 are practically absent while large quantities of CO and CO_2 are found.

6. LIST OF SYMBOLS

v.m.	:	Volatile Matter
C.V.	:	Coking Value
f_a	:	Aromaticity (ratio of aromatic to total carbon)
M_c	:	Molecular Weight Reduced to One Carbon Atom
C_{ar}	:	Aromatic Carbon
I	:	Molar Increment
v_c	:	Atomic Volume of Carbon
v_H	:	Atomic Volume of Hydrogen
$\bar{d}$	:	Mean Interlayer Distance
d_{He}	:	Helium Density
d_{H_2O}	:	Water Density
$\bar{R}_{ar}$	:	Mean Number of Aromatic Condensed Rings
A:K	:	Amorphous to Crystalline Ratio
$\bar{M}$	:	Mean Molecular Weight
D	:	Optical Density
VPC	:	Vapor Phase Chromatography
$\Delta\varepsilon$	:	Electron Activation Energy
ρ	:	Resistivity
T	:	Absolute Temperature
H_{ar}	:	Aromatic Hydrogen

7. REFERENCES

1. D. W. Van Krevelen, H. A. G. Chermin and I. Schuyer, Fuel 36, 313 (1957).

2. V. Rona, Brennstoff-Chem. 40, 346 (1959).

3. V. Sandor, Unpublished work.

4. W. Ruland, Private communication.

5. H. A. Stuart, "Die Struktur des freien Moleküls", Springen-Verlag (Berlin, 1952), Vol. I, p. 98.

6. R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds", John Wiley & Sons, Inc., New York, (1951).

7. E. de Ruiter and H. Tschamler, Brennstoff-Chem. 39, 362 (1958).

8. E. J. Baldes, J. Sci. Inst. 11, 223 (1934).

9. E. Clar, "Aromatische Kohlenwasserstoffe (Polycyclische Systeme)", Springen-Verlag, Berlin, (1952).

10. H. G. Franck, Brennstoff-Chem. 36, 12 (1955).

11. H. Akamatu and H. Inokuchi, Proc. of the "Third Conference on Carbon", Buffalo, 1957; Pergamon Press, London, 1959; p. 51.

12. E. de Ruiter, R. Leutner and H. Tschamler, Rec. trav. Chim, 81, 5 (1962).

13. J. Schuyer and D. W. Van Krevelen, Fuel 34, 213 (1955).

14. L. Cartz and P. B. Hirsch, Phil, Trans. Roy. Soc. London, Ser. A, 252, 557 (1960).

15. E. de Ruiter, R. Leutner and H. Tschamler, Fuel 41, 118 (1962).

16. D. J. E. Ingram, Proc. of the "Third Conference on Carbon", Buffalo, 1957; Pergamon Press, London, 1959; p. 93.

17. L. J. Bellamy (W. Brügel), "Ultrarot-Spektrum und chemische Konstitution" Steinkopff-Verlag, Darmstadt, (1955).

18. J. G. Hawkins, E. R. Ward and D. H. Whiffen, Spectrochim. Acta, 10, 105 (1957).