BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1417—1424 (1969)

Characteristic Chemical Constitution of Pitch Materials Suitable for the MP Carbon Fiber

Sugio ŌTANI and Akira YOKOYAMA*[1]

Faculty of Technology, Gunma University, Kiryu, Gunma

(Received September 16, 1968)

Pitch materials suitable for the MP carbon fiber were prepared from petroleum asphalt, coal tar pitch, and polyvinylchloride. The present investigation was undertaken to clarify the characteristic chemical constitution of each suitable pitch material and to define the significance of the special treatment required to prepare the pitch materials. The suitable pitch materials are generally composed of several structural units with aromatic fused rings and more or less alkyl side chains. The suitable pitch material finally obtained from the petroleum asphalt is characterized by a relatively high molecular weight and many quite long alkyl side chains. Special treatment is required to increase the aromaticity and the removal of the low-molecular-weight component. The suitable pitch material from the coal tar pitch is characterized by aromatic fused rings of the condensed type and only a few alkyl side chains, such as, the methyl group. The most desirable effect of the treatment is to accelerate the condensation between molecules without increasing the insoluble matter and to remove the low-molecular-weight component. The results concerning the polyvinylchloride pitch lend some support to the scheme suggested before.

In previous papers,[1-3] it has been reported that carbon fibers were prepared from polyvinylchloride (PVC), petroleum asphalt, coal tar pitch, and other pitch-like materials. We refer to the fiber so produced as the MP carbon fiber.

Pitch materials suitable for MP carbon fibers must have at least two characteristics - excellent spinnability and the ability to be easily converted into an infusible form by oxidation in the low-temperature range. The above raw materials than PVC pitch leave much to be desired. Some special treatment, therefore, is required to achieve the desirable characteristics. Up to now, only an experimental approach seems useful in discovering suitable pitch materials, because the relation between the desirable characteristics and the structures of the pitch materials is still obscure. From this point of view, it appeared of interest to investigate further the fundamental features of the pitch materials in order to improve the preparation method and the properties of the MP carbon fiber.

The present investigation was undertaken in order to clarify the following two questions the characteristic chemical constitution of the suitable materials prepared from a petroleum asphalt and coal tar pitch, and the significance of the special treatment required.

For these purposes, the pitch materials at each stage of the treatment were fractionated by extraction in turn with several solvents, and then use was made of the NMR, IR and UV spectra as well as of elemental analysis and the measurement of the mean molecular weight by the vapor-pressure osmometer method.

Experimental and Results

Raw Materials and Special Treatment. The starting raw materials and the special treatments used in this experiment are shown in Fig. 1. The PVC powder was supplied by the Kureha Chemical Ind. Co., while the PVC pitch was the pyrolyzed residue itself and was used without any further treatment. The petroleum asphalt was treated according to a procedure described previously.[2,3] In the case of the coal tar pitch, the treatment procedure was modified as is shown in Fig. 1, since the present method, in comparison with the previous method,[3] gave a better spinnability of the pitch and better mechanical properties of the carbon fiber finally obtained. The modification is characterized by the removal of the insoluble matter from the raw coal tar pitch and by heat

*[1] Present address: Yokohama Plant, Nihon Carbon Co., Ltd., 1-1, Shinurashima, Kanagawa-ku, Yokohama.

1) S. Ōtani, *Carbon*, **3**, 31 (1965).
2) S. Ōtani and K. Yamada, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **69**, 626 (1966).
3) S. Ōtani, K. Yamada, T. Koitabashi and A. Yokoyama, *Carbon*, **4**, 425 (1966).

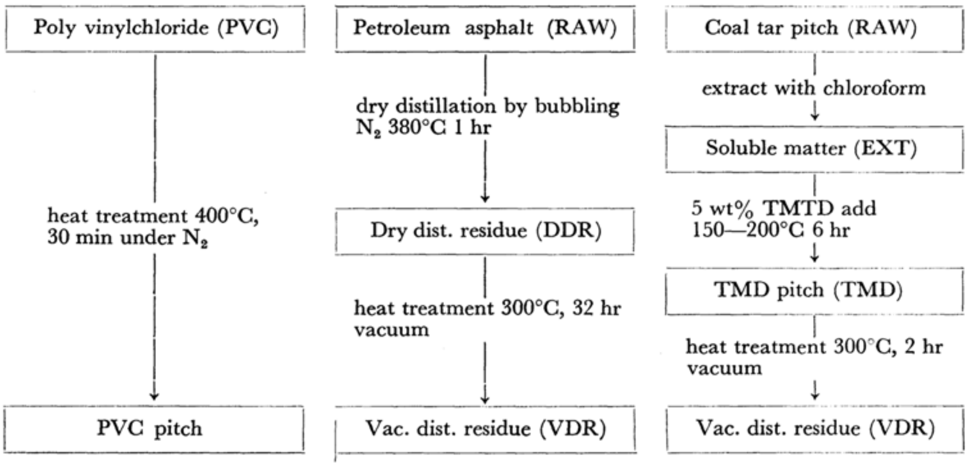

Fig. 1. Starting raw materials and the procedure of treatment.

Table 1. Chemical composition of pitch material

Material	Stage	C%	H%	S%	N%	O% diff.	Atomic ratio H/C	Molecular weight
Petroleum asphalt	RAW	85.5	9.7	4.39	0.61	0	1.36	840
	DDR	85.3	8.3	5.27	0.73	0.4	1.16	880
	VDR	86.5	7.9	4.92	0.68	0	1.09	1530
Coal tar pitch	RAW	91.2	4.7	0.40	1.46	2.2	0.62	340
	EXT	90.9	4.7	0.24	1.46	2.7	0.62	320
	TMD	91.7	4.9	0.58	1.12	1.7	0.64	370
	VDR	92.4	4.2	0.70	0.93	1.8	0.54	990
PVC pitch		92.7	6.3	0	0	0.9	0.84	800

treatment with five percent of tetramethylthiuram disulfide (TMTD) in a low-temperature range.

The chemical composition and the mean molecular weights of the pitch materials at each stage of the above special treatments are presented in Table 1.

In Table 1, DDR is an abbreviation of the dry distilled residue, while VDR is that of the vacuum-distilled residue finally obtained. EXT is the soluble matter obtained by chloroform extraction, and TMD indicates the pitch materials heated together with TMTD. The value of the H/C atomic ratio for PVC pitch lies between those of the asphalt group and of the coal tar group. In the course of the treatment, especially during the final treatment under a vacuum. the H/C atomic ratio decreases and the mean molecular weight increases. In spite of the addition of the sulfur compound (TMTD) during the treatment, the sulfur content in the coal taı pitch material finally obtained is less than one percent. Therefore, the presence of sulfur and the other heteroatoms in the coal tar pitch material was disregarded and will not be discussed any further.

Solvent Analysis. A flow chart of the fractionation is shown in Fig. 2. The extraction was carried out at room temperature in order to prevent any possible change in quality. The bar graphs in Fig. 3 depict the results.

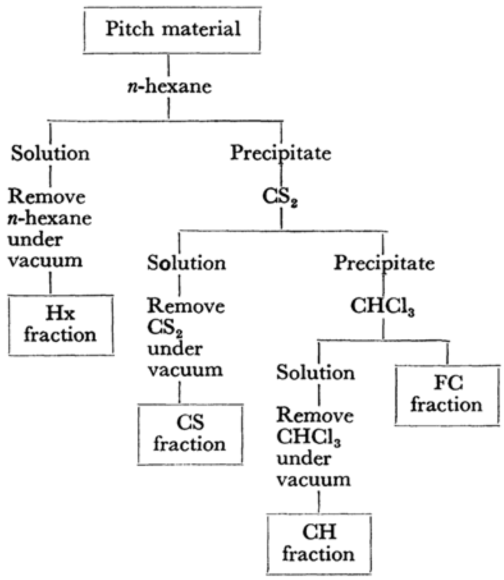

Fig. 2. Flow chart of extraction method.

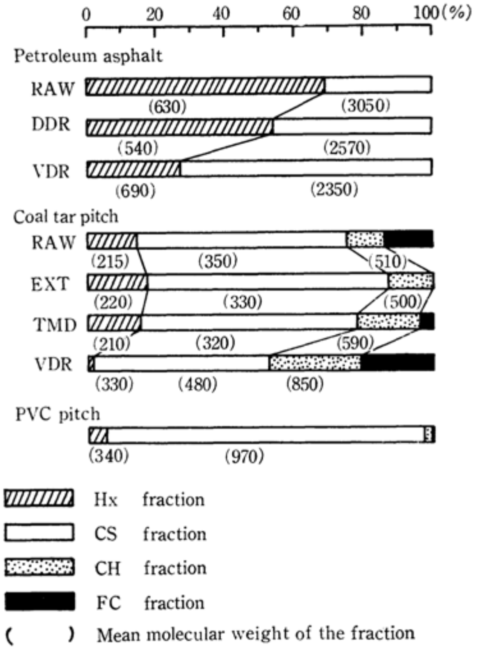

Fig. 3. Result of the solvent analysis.

The PVC pitch is characterized by a large CS fraction, and the CS fraction of the petroleum asphalt was increased to 73% by the treatment. In the case of the coal tar pitch, the mean molecular weight of each fraction increased, especially during the final treatment, and the low-molecular-weight component, the Hx fraction, vanished finally.

Chemical Composition of Each Fraction. The diagrams of the H/C atomic ratio *vs.* the stages of the treatment are shown in Figs. 4 and 5.

Figure 4 indicates that the final treatment under a vacuum for the coal tar pitch prompts a slight decrease in the atomic ratio of CH and FC. In the cases of both the fractions of the petroleum asphalt (Fig. 5), the decrease in the ratio is limited to the first step. However, the value of the entire

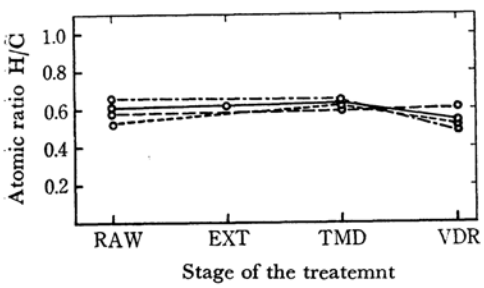

Fig. 4. The variation of atomic ratio H/C with the treatment (coal tar pitch).
—— before fractionation
—— CS
-·-·- CH
------ FC

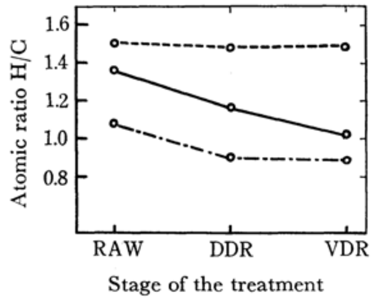

Fig. 5. The variation of atomic ratio H/C with the treatment (petroleum asphalt).
—— before fractionation
------ Hx
-·-·- CS

sample continues to decrease during the final stage as a result of the increase in the CS content.

Spectroscopic Observations. *Infrared Spectra* Figure 6 indicates the infrared spectra of the samples before fractionation at each step of the treatments. These spectra consist of the absorption bands due to a saturated alkyl and an aromatic structure; no other band showing the presence of a hetero-atom or of unsaturated double bond is observed. Moreover, it seems that the asphalt is rich in an alkyl hydrogen, while, on the other hand, the coal tar pitch is rich in an aromatic hydrogen.

PVC pitch lies midway between the asphalt and the coal tar pitch in this case, too. Each VDR

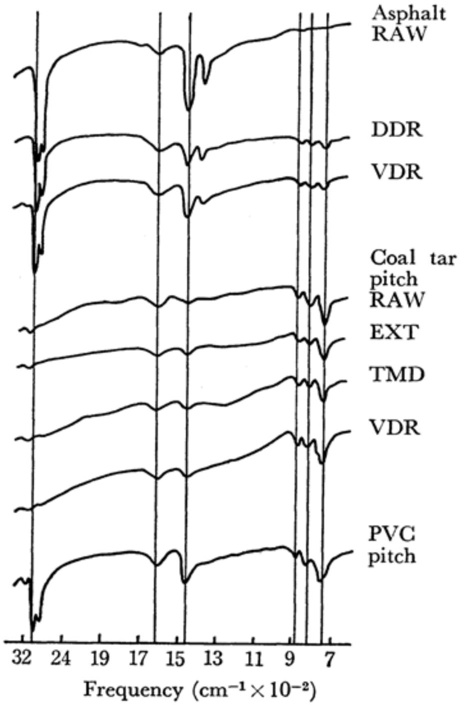

Fig. 6. Infrared spectra of the pitch materials before fractionation.

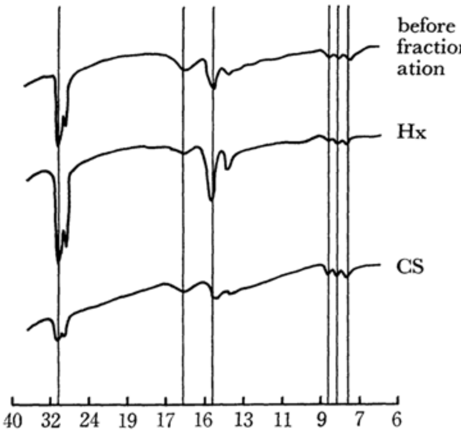

Fig. 7. Infrared spectra of petroleum asphalt (VDR).

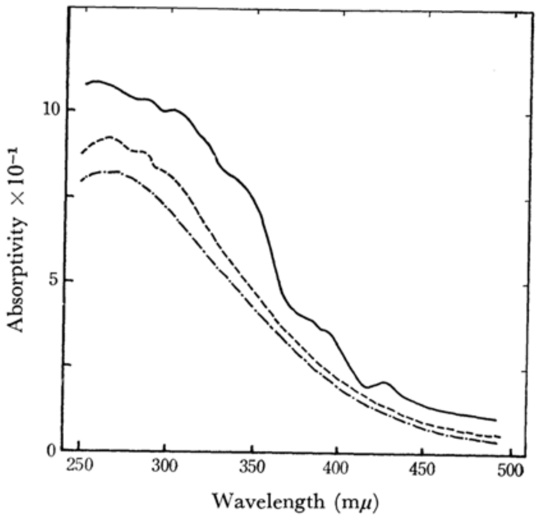

Fig. 8. UV and Vis. spectra of the pitch materials finally obtained.

-·-·- Asphalt (VDR)
—— Coal tar piteh (VDR)
------ PVC pitch

fraction of the coal tar pitch was almost identical in infrared spectra with the sample before fractionation. In the case of the petroleum asphalt (Fig. 7), Hx exhibited a larger absorption band due to an alkyl structure than that of CS.

The Hx fraction of PVC pitch, although their content is only less than 6%, had the same tendency.

Ultraviolet Spectra. In order to get some useful information about the structure of the aromatic part, we have observed the ultraviolet and visible spectra. The spectrum of PVC pitch has been reported in our previous work,[1,4,5] in one paper,[1] we attempted to isolate the unit aromatic component by decomposition with nitric acid. On the basis of the data thus obtained and the other general information available, we concluded[1] that the spectrum of PVC pitch gives evidence of the presence of condensed aromatic nuclei composed of three or four rings, such as anthracene, chrysene, and phenanthrene. When the spectra of the two other pitch materials shown in Fig. 8 are compared with that of PVC pitch, the spectrum of coal tar pitch, VDR, is seen to be characterized by the presence of some obvious absorption bands in the range over 300 mμ.

It may be assumed that these bands are due to a sort of pyrene (250 and 340 mμ), benzpyrene (370, 380, and 390 mμ), coronene (300, 340, and 400 mμ), perylene (400 and 430 mμ), and other similar aromatic compounds. On the other hand, the spectrum of the petroleum asphalt has only one broad absorption band, that centering around 270 mμ. The two fractions (CS and Hx) of the petroleum asphalt treated at each stage were identical in ultraviolet spectra, although some general difference in intensity was found throughout the wavelengths of the spectrum. When cyclohexane was used as a solvent, it was found that Hx exhibits another broad band in the range of 210—240 mμ in addition to the band at 270 mμ. The two fractions (CS and Hx) of the coal tar pitch treated at each stage were also identical in ultraviolet spectra except in intensity to that of the each entire sample before fractionation. However, the profile of the spectra changed considerably during the final treatment under a vacuum, as is shown in Fig. 9.

When the spectrum of the Hx of PVC pitch is compared with that of CS, the displacement of the wavelength of the maximum absorption is not

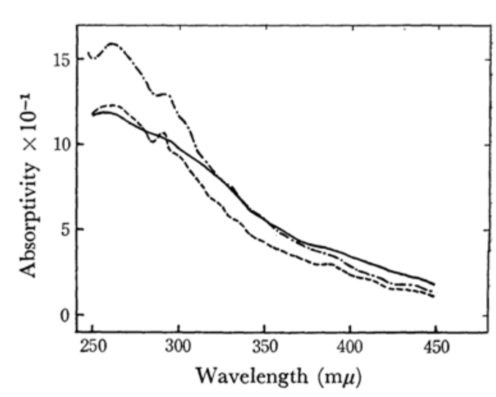

Fig. 9-a. Variation of UV and Vis. spectra of coal tar pitch with the treatment (CS fraction).

CS fraction
-·-·- RAW
------ TMD
—— VDR

4) S. Ōtani, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **61,** 1324 (1958).
5) S. Ōtani, *ibid.*, **65,** 1617 (1962).

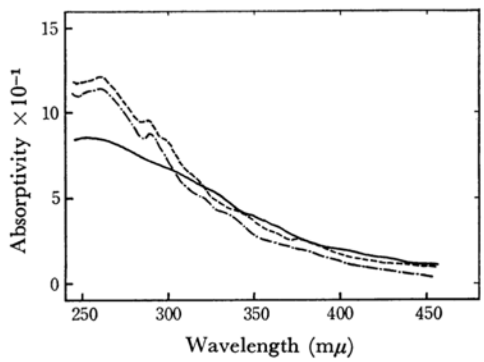

Fig. 9-b. Variation of UV and Vis. spectra of coal tar pitch with the treatment (CH fraction).
CH fraction
----- RAW
------ TMD
—— VDR

observed. However, the absorption in the range over 300 mμ apparently decreases in intensity.

Proton Magnetic Resonance Spectra. Some typical spectra are shown in Fig. 10.

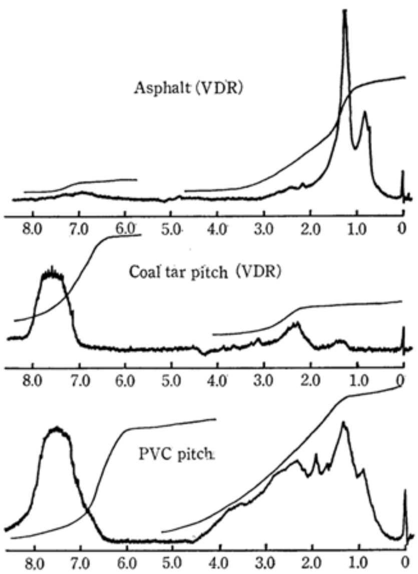

Fig. 10. Typical spectra of proton magnetic resonance.

The left-side peaks are due to an aromatic hydrogen, while the right-side peaks indicate the presence of some kinds of aliphatic hydrogen. The contents of aromatic and aliphatic hydrogen, as calculated from the peak area, are listed in Table 2.

The values in Table 2 clearly show the characteristics of each material. The treatment of the asphalt causes a slight increase in the aromatic hydrogen content. In the case of the coal tar pitch,

Table 2. Content of aromatic and aliphatic hydrogen of the samples before fractionation

Material	Stage	Aromatic H (%)	Aliphatic H (%)
Coal tar pitch	RAW	82	18
	EXT	81	19
	TMD	80	20
	VDR	81	19
Petroleum asphalt	RAW	5	95
	DDR	7	93
	VDR	10	90
PVC pitch		41	59

the content remains almost constant throughout the whole process. No difference in the content is observed between the fractions of the coal tar pitch; however, in the cases of the other two materials, some difference is observed, as is shown in Table 3.

Table 3. Content of aromatic and aliphatic hydrogen of the fraction of asphalt and PVC pitch

Fraction		Aromatic H (%)	Aliphatic H (%)
Petroleum asphalt VDR	Hx	5	95
	CS	13	87
PVC pitch	Hx	35	65
	CS	40	60

A further classification of the alkyl hydrogen atoms has been attempted on the basis of the chemical shifts, and the content of each class has been calculated from the peak area. The results obtained are listed in Table 4. Some errors are, of course, unavoidable in this classification, but they are not serious, we think. In the case of the asphalt, Hx exhibits a larger content of II-type hydrogen and a smaller content of V-type hydrogen than does CS. This fact probably indicates that Hx has a longer side chain. The coal tar pitch is only 20% aliphatic hydrogen, and all the fractions are almost identical in their spectra.

Effect of the Improvement on the Procedure Used for Coal Tar Pitch. We pointed out previously[3] that the pitch material prepared from a coal tar pitch material leaves something to be desired. The procedure of the treatment has since been improved to some extent by the addition of the two steps of the extraction and TMTD treatment shown in Table 1. Table 5 shows the effect of these changes. By the removal of the insoluble residue from the raw material, the FC of the final is reduced to about half and the spinnability is doubled. The addition of TMTD results in a remarkable increase in the mean molecular weight.

TABLE 4. CLASSIFICATION OF THE ALKYL HYDROGEN

Materials	Fraction	H content *vs.* total H content (%)				
		~1.0 (ppm) CH_3-C- (I)	1.0—1.5 CH_3-C-Ar, -C-CH_2-C- (II)	1.5—2.0 Ar-C-CH_2-, Ar<(C-CH_2)(C-CH_2) (III)	2.0—2.5 Ar-CH_3 (IV)	2.5~ Ar-CH_2-, Ar-CH_2-Ar (V)
Petroleum asphalt VDR	entire*	18	42	12	8	10
	Hx	18	54	10	7	7
	CS	14	33	13	10	15
PVC pitch	entire*	7	11	9	9	22
	Hx	8	20	12	11	17
	CS	7	12	12	10	25
Coal tar pitch VDR	entire*	0	2	1	6	12

* Sample before fractionation.

TABLE 5. EFFECT OF THE EXTRACTION AND THE ADDITION OF TMTD

Procedure No.	1	2	3
Starting material	RAW	EXT	EXT
TMTD (wt%)	5	no	5
Heat treatment under N_2	180°C 1 hr	150—200°C 6 hr	150—200°C 6 hr
Heat treatment under vacuum	250°C 1 hr	300°C 2 hr	300°C 2 hr
Content of FC fraction	46.9%	22.0%	21.2%
Chemical composition C%	92.0	92.2	92.4
Chemical composition H%	4.0	4.4	4.2
Mean molecular wt.	—	670	990
Spinning speed m/min	240	470	490
Spinning temperature	250°C	270°C	300°C

Discussion

Characteristic Chemical Constitution of the Pitch Materials. Even when the pitch materials are treated by the method above described, the pitch materials are, of course, very complex mixtures composed of many kinds of molecules. The pitch materials are, indeed, too complex for their chemical structure to be determined in detail, and so the data obtained in our experiment are limited. However, the results obtained seem to lead to some significant conclusions concerning the characteristic chemical constitution of each suitable pitch material finally obtained. Moreover we feel that the presentation of the scheme of each pitch material, including most of the configurations mentioned above, will be helpful in clarifying the characteristic nature of the suitable pitch materials.

The major portion (94%) of the PVC pitch is CS, so it may be considered that this fraction represents the entire PVC pitch. On the basis of the proton magnetic resonance spectra, the atomic ratio of the aromatic hydrogen to the aliphatic hydrogen of CS is about 40/60. This value and the results presented in Table 4 are in good agreement with that calculated from the scheme (structural model) suggested previously.[1] The other results obtained in the present experiment are essentially identical with those previously reported. However, in the infrared spectra of the range from 700 cm^{-1} to 900 cm^{-1}, the absorption band at 740 cm^{-1} which is due to the four adjacent ring hydrogen atoms is the greatest in intensity. In order to ex-

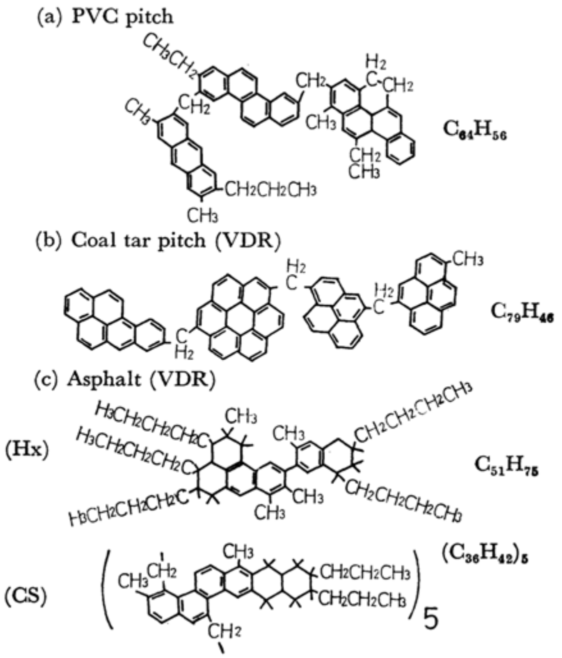

Fig. 11. Schemes including most of the characteristic configuration obtained.

plain this, it seems most reasonable to correct the model as shown in Fig. 11-a.

The pitch material finally obtained from the coal tar pitch is characterized by a small H/C atomic ratio, and its UV spectra indicates the existence of some condensed type of aromatic nuclei, such as pyrene, perylene, and coronene. The results of the proton magnetic resonance spectra (Table 4) suggest that only one methyl group is substituted in each molecule. From the results concerning the chemical composition of the entire VDR and its mean molecular weight, the experimental formula seems to correspond to $C_{79}H_{46}$. The proposed structural model is presented in Fig. 11-b. No remarkable difference has been found between fractions throughout the treatment with the exception of the mean molecular weight. Therefore, it seems reasonable to conclude that each fraction is distinguished by the number of the aromatic nuclei in a molecule. The most characteristic feature of the pitch materials prepared from the petroleum asphalt is the small value of the ratio of the aromatic hydrogen to the aliphatic hydrogen. From the UV spectra, it seems reasonable to assume that the aromatic nuclei of these materials are composed of similar aromatic fused rings to that of PVC pitch and/or some smaller aromatic fused rings such as naphthalene. When Hx is compared with CS in Table 4, it may be found that the content of II-type hydrogen of Hx is larger and the content of V-type hydrogen is smaller. These facts probably indicate that Hx has longer side chains than CS. The results of the IR spectra lend some support to this assumption. The existence of sulfur atoms in the petroleum asphalt causes some knotty problems in making up the structural model of the material. Previous investigations of sulfur in a heavy component of petroleum have given no information on its definite position in a molecule. It is said, in general, that sulfur atoms often form a C–SH (thiol) group in a side chain and/or a heterocyclic structure such as thiophene. Although the sulfur content of VDR is 3.9% corresponding to three or four atoms in a molecule, in the present spectroscopic examination, no clear characteristic information as to the presence of a sulfur atom is obtained. If the experimental formulae of CS and Hx are determined on the basis of the H/C atomic ratio and the mean molecular weight, that is, ignoring the possible presence of sulfur and other hetero-atoms, they correspond to $C_{51}H_{75}$ and $C_{180}H_{210}$ respectively. The structural models shown in Fig. 11-c are designed to satisfy the experimental formulae and the results of our spectroscopic observation. If the possible presence of sulfur atoms in taken into consideration, it seems most reasonable to correct by introducing three of four sulfur atoms into a molecule of CS in the form of thiophene and/or thiol; the atoms may then be converted to a C–S–C bond by heat treatment. In the case of Hx, one sulfur atom is introduced in the same form.

In Table 6, the values calculated from the structural models shown in Fig. 11 are listed together with those observed. As has been described above, the pitch materials are very complex mixtures and it is, of course, impossible to represent the molecules in all the pitch materials by the use of one molecular formula. However, on the basis of the results shown in Table 6 and described above, it may be concluded that these structural models express consistently the characteristic features of the pitch materials.

The Significance of the Special Treatment. *Petroleum Asphalt:* The most noticeable changes observed with the treatment are the increase in the CS content, the decrease in the H/C atomic ratio, and the variation in the mean molecular weight. The increase in CS content, of course, is mainly due to the removal of the Hx. However, the results for the fractions make it apparent that Hx and

TABLE 6. COMPARISON OF THE OBSERVED VALUE WITH THAT OF CALCULATED FROM THE STRUCTURAL MODE SHOWN IN FIG. 11

			H/C Atomic ratio	Mean molecular weight	Arom. H / Total H (%)	Alkyl H/Total H (%)				
						CH_3–C–	CH_3–C–Ar, –C–CH_2–C–	Ar–C–CH_2–, Ar<(C–CH_2)(C–CH_2)	Ar–CH_3	Ar–CH_2–, Ar–CH_2–Ar
PVC pitch		Obsd	0.84	800	41	7	11	9	9	22
		Calcd	0.87	824	39	5	11	4	16	25
Coal tar pitch VDR		Obsd	0.54	900	79	0	2	1	6	12
		Calcd	0.58	994	80	0	0	0	7	13
Petroleum asphalt VDR	Hx	Obsd	1.50	690	4	18	54	10	7	7
		Calcd	1.46	687	5	20	42	9	12	11
	CS	Obsd	0.96	2350	15	14	33	13	10	15
		Calcd	1.17	2370	14	14	33	5	14	19

CS change in quality. The nature of CS changes to a much larger extent through the first distillation process at 380°C than through the vacuum-distillation process at 300°C. In the first step, for example, it has been found that the mean molecular weight, 3050 in the original, decreases to 2570; the H/C ratio, 1.57 in the original, decreases to 1.46, and the three absorption bands in the range from 700 to 900 cm^{-1} of the IR spectrum become apparent with the decrease in intensity of the bands due to an alkyl group. In view of these facts, it seems that the treatment causes, to some extent, the abscission and the aromatization of the alkyl side chains of the molecules in CS. No remarkable change in any fraction has been observed in the final step; the most important role of the step seems to be the removal of the lower-molecular-weight components which are present in the original and which are formed by the treatment.

Coal Tar Pitch: Even in the original pitch material itself, the aromaticity is satisfactory for our purposes. However, it is a great defect that the major portion of the material has a very low molecular weight and a low softening point below 80°C. It is possible to elevate the softening point and to increase the mean molecular weight by various heat treatments. However, heat treatment at higher temperatures often causes a remakable increase in FC. In general, the use of pitch materials with a large FC content results in less spinnability and in the formation of rough carbon fiber. It is desirable, therefore, to elevate the mean molecular weight without increasing the FC. In view of the results described above, the present procedure seems to fulfil the purpose quite well. Although the mechanism of the reaction with TMTD is not obvious even after the present experiments, it is certain that the addition of TMTD accelerates the condensation between the molecules. The condensation occurs more remarkably in the final treatment under a vacuum at 300°C. (Figs. 3, 4, and 9 and Table 5) The unavoidable formation of FC in this step may indicate that the treatment temperature is still too high.

Conclusion

Suitable pitch materials for MP carbon fiber are generally composed of several structural units with an aromatic fused ring and more or less alkyl side chains, as is shown in Fig. 11.

The suitable pitch finally obtained from the petroleum asphalt is characterized by a relatively high molecular weight and by many relatively long alkyl side chains.

The special treatment required promotes the increase in the aromaticity and the removal of the low-molecular-weight component.

The suitable pitch material from the coal tar pitch is characterized by aromatic fused rings of the condensed type and only a few alkyl side chains, such as, the methyl group.

The most desirable effect of the treatment is to accelerate the condensation between molecules without increasing the insoluble matter and to remove the low-molecular-weight component.