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THE INFLUENCE OF SOLID PARTICLES IN PITCH ON THE PREPARATION AND BAKING OF THE CARBON BLOCKS

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The solid particles in pitch are determined by filtration from pitch dissolved in very good solvents (quinoline, pyridine, anthracene oil). They comprise particles of different origin: carbonaceous particles formed by cracking of tar vapors, entrained coal and coke and insoluble particles formed from the liquid phase by heat soaking during the production of pitch. All these different species can be identified by microscopy and usually semiquantitatively determined by chemical methods. The concentration of the pyrolytic solid particles is a sensitive indicator of the degree of dehydrogenation of tar vapors during carbonization. C/H ratio of isolated solid particles might be an indicator of heat soaking during the pitch fabrication but only microscopy gives the definite answer. Solid pyrolytic particles influence the determination of the softening point and viscosity to a different degree. Nevertheless, within a narrow range of concentration of pyrolytic solid particles, there is a definite correlation between the viscosity and softening point. During heat soaking or carbonization of pitch the pyrolytic particles are pushed together by spherical bodies of mesophase and reinforce the plastic liquid which does not penetrate readily into the porous structure of the filler. This phenomenon has a significant influence on the properties (baked density, strength, resistivity) of the baked body. The pyrolytic solid particles influence also to a significant degree the viscosity of the green paste and therefore, the shaping operation (mixing with the petroleum coke and flowability of the green paste).

Introduction

Tar produced by high temperature carbonization of coal contains an insoluble phase, called "Quinoline Insolubles" (QI) on the basis of the common method of determination. The quantity of QI in tar ranges from less than 1% to more than 12% and depends upon coal origin, charge density, and especially coking conditions (temperature, length of carbonization cycle, and hot charging). Other variables affecting the QI content are: size of the free space above the charge, temperature in the collecting main, and condition of the ovens. Usually air present in the carbonization space due to leaking doors or through heating walls causes local over-heating and incomplete conbustion of gaseous products; thus, additional insolubles are produced in the tar.

Pitch is the distillation residue of coal tar and amounts to approximately 50% of the original tar. The QI in the tar, being non-volatile, remains in the pitch in a concentration depending on the amount contained in the original tar and on the amount of distillate removed. The QI plays an important role in most of the major applications of pitch, and the level of QI is therefore contained, directly or indirectly, in most pitch specifications.

It should be remembered that coal tar is only a by-product of the manufacture of coke, and operating conditions in the coke ovens are always adjusted to reach optimum coke yield and quality regardless of the characteristics of the tar. For this reason, most tar processors will receive crude tars of varying composition, particularly with regard to QI concentration. The successful production of pitch with optimum properties and with minimum variation depends on the ability to blend and treat tars so that a uniform quality of the product can be maintained.

Nature and Properties of QI

A. True or primary QI is formed by thermal cracking of tar vapors and components of the carbonization gas as they pass through the layer of the hot coke, along the heating walls and through the oven space above the charge. Such QI is finely distributed in pitch and is small in size - average diameter corresponds to about one micron.

B. Secondary QI or mesophase is formed when pitch is subjected for extended periods of time to temperatures in excess of about 350°C. Contrary to the primary QI, the mesophase particles are formed in the liquid and not in the gas phase. These particles are about one to two orders of magnitude larger than primary QI and, during the progress of heat exposure, get larger and larger and start to coalesce to form the typical structure of coke.

C. Since QI is determined by dilution with solvent followed by filtration, the insolubles will also contain impurities through the entrainment of coal and coke particles by gas leaving the coke oven and entering the collecting main. As coal always contains sizable concentrations of ash, an increased concentration of QI due to the entrainment becomes apparent by an increase of the ash content in the pitch. These particles can be readily detected by microscopy. They have sharp contours and vary greatly in size. Under normal conditions the amount of these impurities in the pitch is quite small and the considerations following below will neglect their presence.

QI and Coking Value

The amount of QI in pitches distilled directly from tar without any additional treatment is an indicator of the degree of cracking to which the tar vapors were exposed during carbonization. As the coking value of QI is in excess of 95%, it is to be expected that pitches containing high concentrations of QI will have high coking values. Also, under conditions resulting in a high degree of cracking, the soluble part of the pitch has been aromatized to a high degree. This is apparent from the high coking value of pitches made from high-QI tars from which the QI was removed by filtration as shown graphically in Fig. 1.

The coking value is a good practical indicator of pitch aromaticity. Other indicators like density, C/H ratio, infrared aromaticity index, and concentration of aromatic hydrogen determined by NMR are usually consistent with the coking value and may be used for additional characterization of pitch aromaticity.

QI and C/H Ratio

C/H ratio of primary QI isolated from pitch reflects the C/H ratio of the pitch itself. The atomic C/H ratio of QI ranges from 3.5-4 in medium QI pitches to about 5-5.5 in high QI pitches. The C/H ratio of such pitches would be about 1.75 and 1.85, respectively.

The particles of secondary QI (mesophase) are products of the partial dehydrogenation of pitch when exposed to temperatures close to 400°C for an extended period of time. They are quite different from "natural" or "primary QI," not only by shape and size but also by chemical composition. The atomic C/H ratio of mesophase is about 2.5. Therefore, it was believed that the characteristic feature of heat treated pitches is a low C/H ratio of the QI.

Also a high concentration of beta-resins might be considered as an additional crude indicator of heat treatment. Usually, as the severity of heat treatment goes up the content of beta-resins (benzene insolubles minus quinoline insolubles) goes up until it reaches a maximum level and then starts to drop as soon as the generation of the secondary QI (mesophase) sets in (Fig. 2).

Nevertheless, the low C/H ratio of QI is not the final proof whether or not the heat treatment has taken place during the production of pitch. If it were possible to measure the concentration of carbon and hydrogen of individual QI particles present in a pitch, one would probably find a whole range of C/H ratio for individual particles. QI in tars obtained under milder cracking

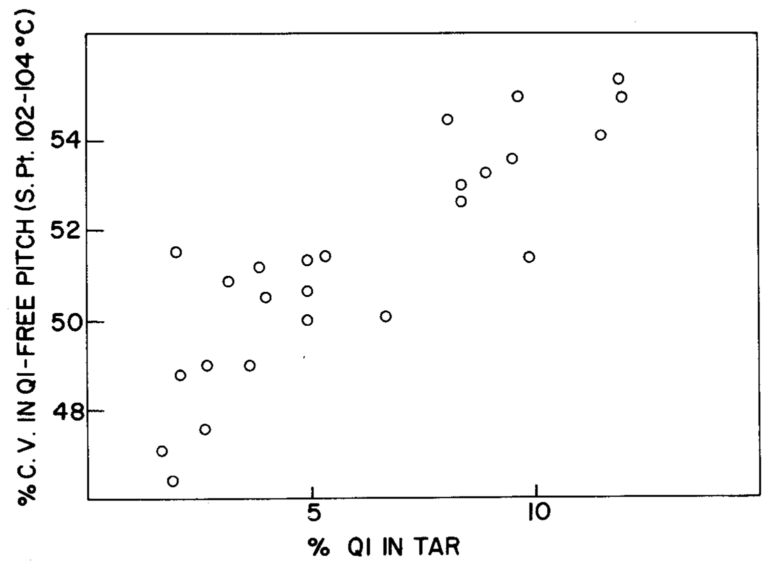

Fig. 1 The Coking Value of QI-free Pitches as Function of QI Concentration in the Parent Tar.

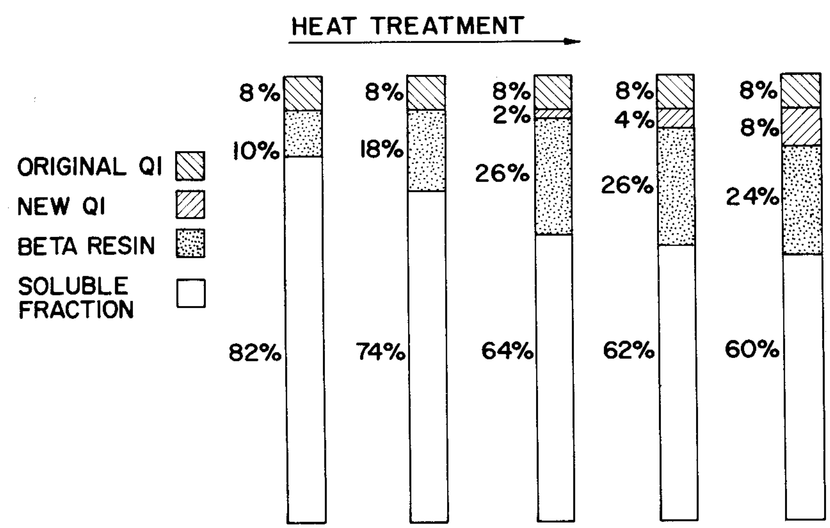

Fig. 2 Change of Beta-Resin Concentration During the Heat Treatment of Pitch.

conditions contain a smaller concentration of highly dehydrogenated particles with high C/H ratios. Therefore, the average C/H ratio of the total amount of QI in such pitches is lower, and heat treatment of pitch might be suspected.

However, the final proof of whether or not the pitch has been treated during its preparation should be the microscopic evaluation of the pitch sample. This technique allows to detect the presence of the secondary QI (mesophase) formed during the heat treatment.

QI and Viscosity

Pitch customers have asked frequently whether differences in QI concentration affect the viscosity of pitches. The answer is not straightforward and needs some explanation of the rheological behavior of pitches.

For several years we have been measuring the viscosities of pitches using the Haake Viscobalance, which is a modification of the falling ball viscometer. Based on these data, we have found a fairly good correlation between the viscosity of straight distilled coal tar binder pitches and the softening point determined by the Mettler instrument.

The viscosity of coal tar pitch changes with temperature as illustrated in Fig. 3. As can be seen, the higher the softening point of the pitch, the more the viscosity-temperature curve shifts to the right along the X axis. In the range of QI content common for electrode binder pitches (8-20% QI) these curves are essentially parallel. Only very low QI or QI-free pitches give curves with slightly higher slopes; i.e., their viscosity changes faster with temperature (Fig. 4).

The softening point is essentially a temperature of equal viscosity (equiviscous temperature) determined by the softening point apparatus. Equiviscous temperatures can be read easily from the viscosity-temperature curves for the chosen levels of viscosity. We selected two viscosities (1000 cP and 4000 cP) and determined from the viscosity-temperature curves the corresponding equiviscous temperatures, i.e., temperatures at which the pitch sample attains the viscosity of 1000 cP or 4000 cP, respectively (see Fig. 3). These equiviscous temperatures for 150 pitches were correlated with the corresponding softening points.

The following equation can be used to calculate the equiviscous temperatures from the known softening point:

for 1000 cP: $EVT_{1000} = 32.3 + 1.231 \times S.\ Pt.$
Standard deviation for 95% confidence limit = ± 4°C

for 4000 cP: $EVT_{4000} + 26.2 + 1.117 \times S.\ Pt.$
Standard deviation for 95% confidence limit = ± 5°C

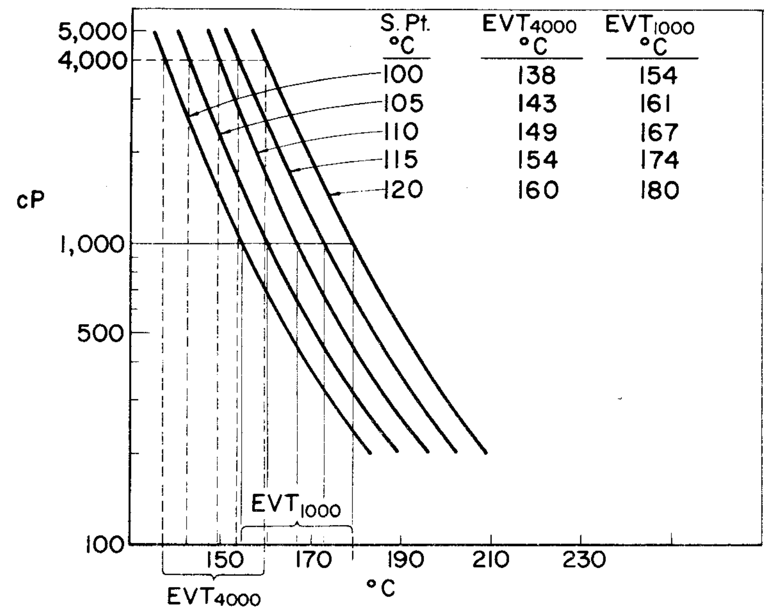

Fig. 3 Viscosity-Temperature Correlation of Pitches with Increasing Softening Point and Equiviscous Temperatures for 4000 and 1000 CP.

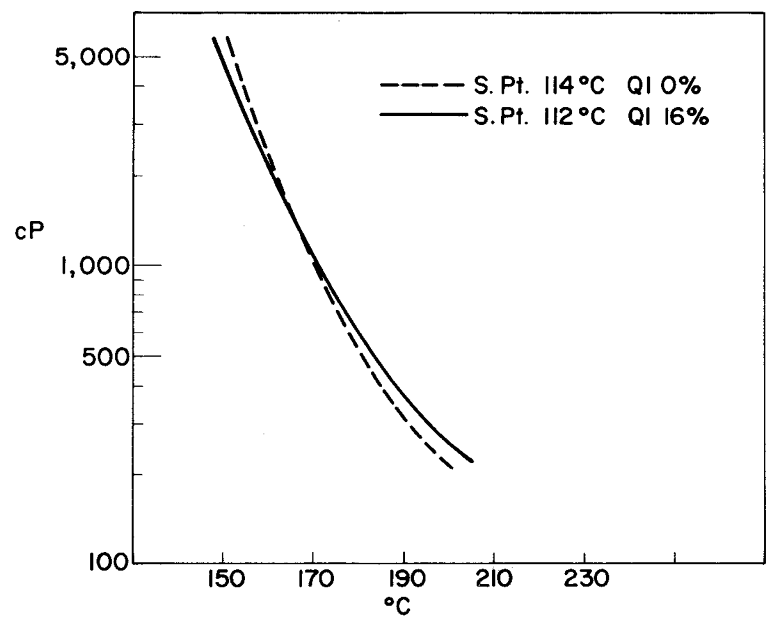

Fig. 4 The influence of QI on the Slope of the Viscosity-Temperatur Correlation.

These correlations are valid for straight distilled coal tar binder pitches (S. Pt. 100-120°C) with QI content from about 8 to 20%.

Adding QI to pitch causes an increase in both the viscosity and the softening point. This was illustrated by adding a known amount of lamp carbon black (as a model for QI) to two QI free pitches, prepared from two different tars from which the QI had been removed by filtration. In the case of the pitch from tar #1, the equiviscous temperatures and the softening points changed by the same increment (Fig. 5); for the pitch prepared from tar #2 (Fig. 6), the equiviscous temperatures changed faster than did the softening points. This difference probably causes the scatter of values around those calculated from the two equations given above. We have no good explanation for this phenomenon.

We repeated the above experiments, but used QI instead of carbon black. The results (Fig. 7) are qualitatively similar to those with carbon black; the softening point and the viscosity both increased as the concentration of QI increased. Quantitatively we can see a larger influence of the carbon black addition on the softening point and viscosity (steeper slope of the EVP_{4000} and softening point curve).

Our finding that carbon black affects both viscosity and softening point helps explain why adding carbon black to the tar before it is distilled to pitch or to the pitch itself does not change the coking value of the pitch.

This latter phenomenon has been reported at this conference by Dr. McNeil of the British Carbonization Research Association. He believes that carbon black absorbs some of the lower molecular weight components so that they are retained in the pitch and, having a lower coking value, off-set the increase due to the carbon black addition.

We have another explanation of this phenomenon: If we distill two pitches, one without carbon black and one with carbon black added, to the same softening point, then the one prepared with carbon black addition contains a carbon black free portion lower in softening point and consequently lower in coking value. Therefore, the increase of the coking value due to the carbon black addition is off-set by the lower coking value of the carbon black free portion.

The QI level originally in pitch influences significantly the magnitude of the viscosity change when pitch and fillers are blended. To demonstrate this trend we added 5 and 10% carbon black to two pitches with identical softening points but different QI levels, and followed the increase of the softening point and EVT_{4000} after the addition. The results of this experiment are given in Table I. The increase of the softening point due to the addition of 5% and 10% carbon black is considerably larger in the case of pitch with higher level of QI.

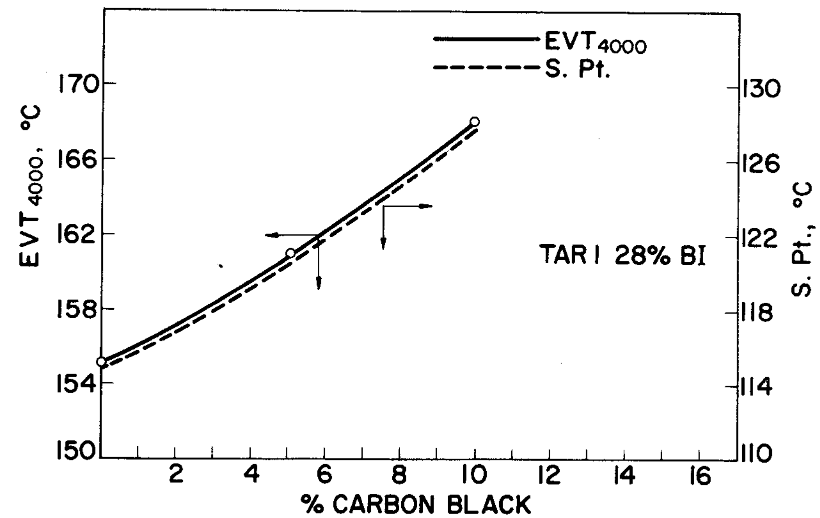

Fig. 5 Change of the Pitch Viscosity and Softening Point Due to the Addition of Carbon Black.

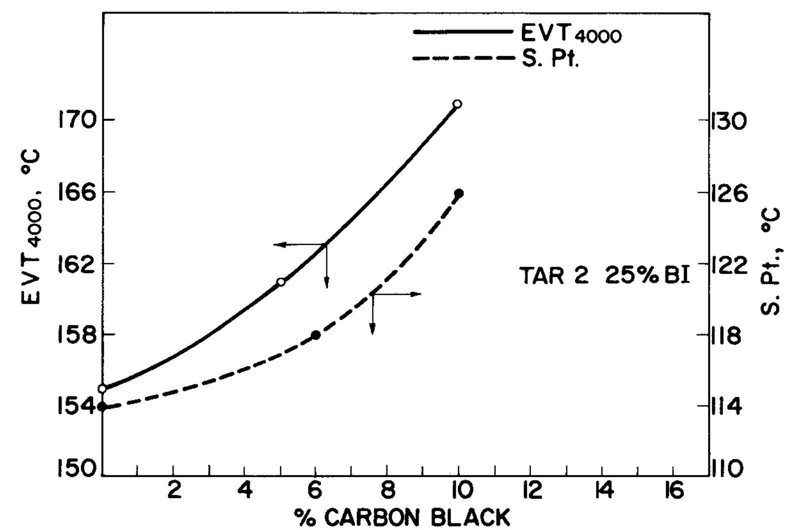

Fig. 6 Change of the Pitch Viscosity and Softening Point Due to the Addition of Carbon Black.

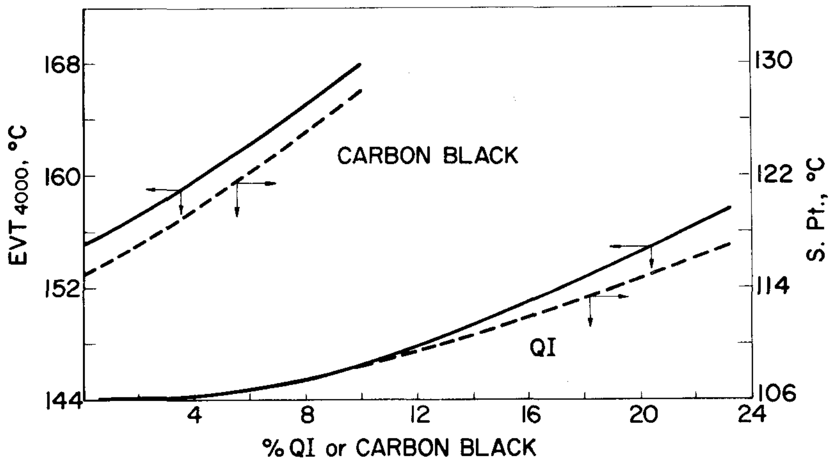

Fig. 7 Change of the Pitch Viscosity and Softening Point Due to the Addition of Carbon Black and QI.

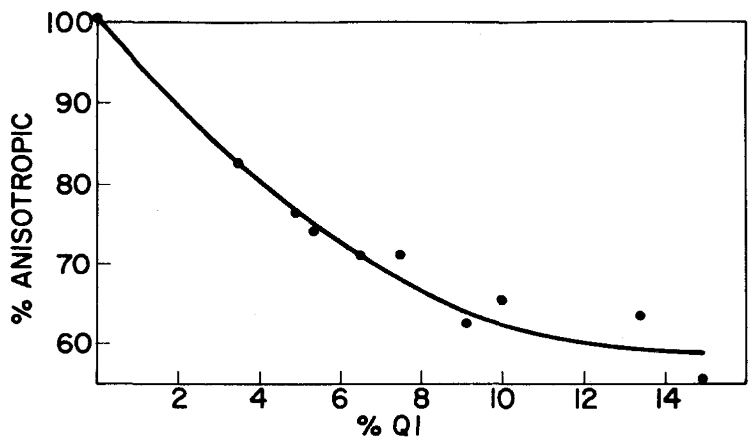

Fig.8 Correlation Between QI and the Anisotropic Portion of the Polished Pitch Coke.

Table I

The Change of S. Pt. and Viscosity (EVT) Due to the Addition of Carbon Black to Pitches with Different Level of QI

	Original Pitch							
	QI	S. Pt.	EVT_{4000}	C. Black in Pitch	S. Pt.	ΔS. Pt.	EVT 000	ΔEVT_{4000}
Pitch No.	%	°C	°C	%	°C	°C	°C	°C
3915	3.9	111	150	5	117	6	158	8
				10	126	15	166	16
3827-44	18	110	150	5	119	9	160	10
				10	140	30	179	29

The influence of the QI level in pitch on the extent of the viscosity change due to the addition of an equal amount of fines is reflected by the Elektrokemisk flowability test.[1] In this test the liquid binder is mixed with petroleum coke fines in the ratio 1:1 and test cylinders are molded. These are placed on a sloping board provided with grooves for the test cylinders. After inserting the sloping board in a thermostat-regulated oven held at approximate temperature for 60 minutes, the flowability of the test cylinder is measured as the percent increase in elongation over the original length of the cylinder. The effect of the QI originally in the pitch on elongation is shown in Table II.

Table II

Elongation of Test Cylinders (Elektrokemisk Method) Using Pitches with Different Level of QI

			Elongation		
	S. Pt.	QI	@ 140°C	@ 180°C	LTC*
Pitch No.	°C	%	%	%	
1069-121	108	12	32	59	2.4
1069-75	107	10	27	48	2.3
1068-171	109	18	27	37	1.2

*Logarithmic temperature coefficient $LTC = \dfrac{\log F_2 - \log F_1}{\log t_2 - \log t_1}$

F_1 - Elongation (%) at temperature t_1(°C)
F_2 - Elongation (%) at temperature t_2(°C)

It can be seen that the test cylinder with pitch containing 18% QI elongates at 180°C significantly less than test cylinders with pitches containing 10-12% QI. Also the susceptibility of the paste flowability to temperature changes characterized by the logarithmic temperature coefficient (LTC), is significantly lower in case of pitch with higher QI level.

In summary it can be concluded that although the QI level in pitch of the same softening point does not influence significantly its viscosity, it has a marked effect on the viscosity of the green paste.

QI and Binder Coke Formation

If we carbonize pitch produced from tar from which QI has been artificially removed, we see a characteristic pattern in the micrograph of the coke obtained. We call it coarse mosaic and it is either striated or irregular. This coke is highly anisotropic; i.e., if we observe the polished sample in polarized light and rotate the microscopic state, dark parts become bright and bright parts turn dark again. Such coke is very easily graphitizable when heated to temperatures over 2600°C. Even if heated to about 1000°C it fractures mostly parallel with the carbon atom planes which start to develop already at this stage of heat treatment. Therefore, QI free pitch is a good source of so-called needle coke used as a filler by the carbon industry.

If QI is present in pitch we see typical fine grain isotropic clusters in the micrograph of the coke. The concentration of these clusters depends on the concentration of QI. Fig. 8 illustrates the correlation of the microscopically determined (by counting procedure) anistropic fraction (i.e., QI-free) of the polished pitch coke against the concentration of QI in pitch.

In the best binder pitches the granular (QI derived) structure is evenly distributed in anisotropic substrate. Inferior pitches do not show this even distribution but granular (isotropic) and anisotropic structures are separated and concentrated into large areas. Addition of carbon black is also characterized by separation of large anisotropic areas from fine grain clusters of added carbon black.

Very important for the satisfactory performance of the carbon electrodes is the formation of binder coke (from the pitch) between the grains of the filler coke. It seems that the role of QI is significant in this mechanism and explains the higher strength of electrodes and lower electrical resistivity of carbon products made with pitches having the optimum concentration of QI.

We followed the formation of the binder coke on the basis of a model prepared from graphite rods in the shape of a cup and a plug (Fig. 9). The binder under investigation was introduced into the cup, the plug inserted and a weight put on it during carbonization in nitrogen atmosphere. After carbonization the assembled components were mounted into epoxy resin and when the resin was set the sample was cut in the center along its axis and the layer of binder coke between two graphite planes was investigated by microscopic techniques.

A typical coal tar binder pitch yields at temperatures of about 600°C a solid micrograin layer of binder coke on top of the filler. Cracks start to be apparent at higher temperatures (700°C). If there is no QI present, the pitch penetrates into the pore system of the filler. These phenomena are better seen if the scanning electron microscope (SEM) is used for the observation of the fractured sample. A good binder pitch forms a compact layer of coke with small pores only. Poor binder pitch forms coke which is full of large pores.

During our microscopic study of mesophase formation by heat treatment of coal tar pitches, we confirmed the finding made by others that QI particles are not accepted by the mesophase spherical particles and stay on the surface of the spheres.

This phenomenon has two significant consequences. First, the coalescence of mesophase spheres is prevented or at least significantly retarded. Therefore, the development of parallel carbon layers is obstructed. For this reason pitches containing high concentration QI cannot yield needle coke. This special coke (needle coke) is produced generally from QI free highly aromatic petroleum materials. There is no reason why it could not be also produced from coal tar pitches if there were economical means available for removing QI from coal tar.

Second, we believe that mesophase formed in the presence of QI concentrates the QI particles into some kind of space structure reinforcing the liquid binder which cannot readily infiltrate into the porous structure of coke and therefore stays at its surface. A very strong bond is thus provided between the coke particles. In the absence of QI the pitch penetrates rapidly into the coke, reducing the effective thickness of the binder coke. In addition, the layer of the binder without reinforcing QI particles shrinks more due to its excessive plasticity during carbonization and consequently forms cracks and often disbonds from the filler.

The insoluble particles probably influence also the wetting by the binder pitch. They decrease the surface tension of the liquid fraction due to the partial saturation of unbalanced forces at the surface of the liquid. Also a deposition of some of the particles on the surface of the solid filler coke influences the wetting, by changing the character of the solid surface. We cannot be more specific on this subject, because the procedures for following wetting of the filler by the binder are not yet developed and understood to our satisfaction. The interpretation of the results is very difficult due to many variables involved and it will still take some time before we learn more about this aspect.

As shown above the process of binder coke formation and its ultimate properties are strongly influenced by the concentration of QI in the pitch. Higher QI content is clearly associated with higher strength of the baked carbon blocks. However, judging from results obtained on laboratory test cylinders with a large number of pitches, we observed that strength levels off at a QI content of about 7% (Fig. 10).

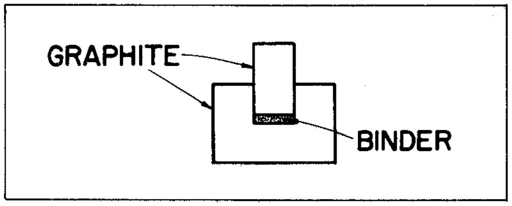

Fig. 9 Graphite Holder for Microscopic Observation of the Mechanisms of the Bond Formation Between the Binder and the Filler.

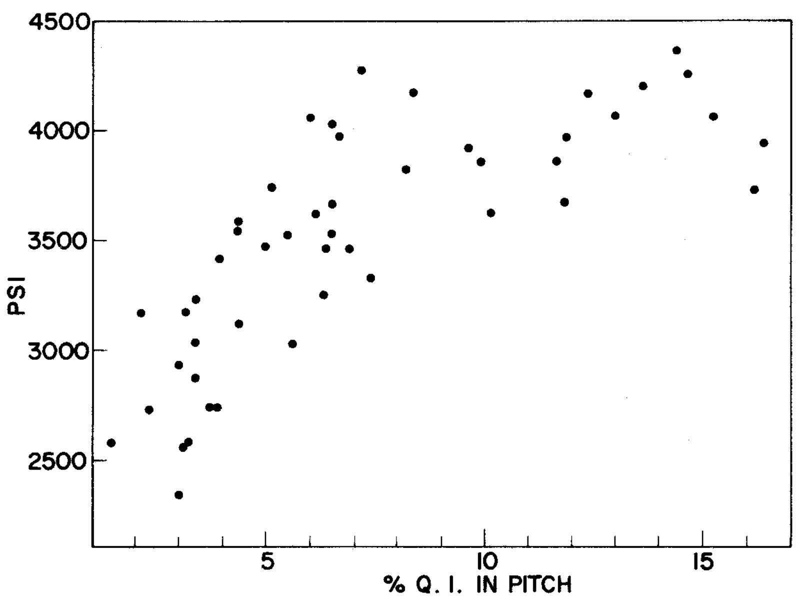

Fig. 10 Compressive Strength of Test Carbon Cylinders as Function of QI Concentration.

Conclusion

Although there is enough evidence that the QI content of a pitch has an important role in the formation of the binder coke, one should not forget that the soluble (i.e., plastic) portion of the pitch also has a significant effect. The latter represents the major part of the pitch (80-95%). At present, this portion is very poorly characterized by a single value (insolubles in benzene called BI). The pyrolysis of tar vapors during carbonization changes the chemical nature of the soluble part according to the severity of cracking which is characterized by the level of QI (i.e., true QI and not entrained coal, coke or mesophase). Unfortunately, the BI value is too crude and inaccurate to reveal such changes. Therefore, solely increasing the concentration of QI, for instance by addition of solids such as carbon black, without simultaneously increasing the aromaticity of the accompanying major part of the soluble portion does not yield the desired high quality binder pitch.

Finally, in the aluminum and carbon industry pitch is always used in combination with petroleum coke. The properties of petroleum coke (its grain size distribution; degree of calcination, porosity and purity) are other very significant variables in the process of carbon block production.

In order to shape the properties of the binder so that optimum properties of the carbon product are obtained requires a joint effort and exchange of technical information between the producer and the user of pitch.

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