CONSTITUTION OF COAL TAR PITCH AND ITS EFFECT ON PROPERTIES

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Introduction

Pitches used as binders and impregnants in graphite manufacturing are obtained from the distillation of coal- or petroleum-derived tars. Softening point and carbon yield are key specification parameters for commercial pitches. However, another property that is important from a safety standpoint, particularly for impregnation pitches, is the pitch flash point.

Commercial pitches are produced by distilling the precursor tar to remove sufficient quantities of low boiling components for achieving a product with the desired softening point. The efficiency in which these components are removed controls final pitch properties and specifically the balance between softening point, flash point, and carbon yield. If excess amounts of the most volatile low molecular weight components are retained after distillation, then the flash point can be unacceptably low, even if the required softening point is achieved.

In this study, we have tried to demonstrate how pitch composition can affect the flash point and softening point during distillation. A commercial coal tar was distilled in the laboratory to produce pitches with different softening points. The constitution of the lowest boiling components was determined using gas chromatography (GC). The results were then used to correlate pitch composition with the changes in flash point and softening point during distillation.

Experimental

Pitch Preparation--A commercial coal tar containing 1.5% quinoline insolubles (QI) was employed as the precursor. This tar is the type that would be used in the production of coal tar impregnation pitches. The distillation was initially performed using a 4-liter reaction flask fitted with a condenser for distillate collection. Distillation was performed at atmospheric pressure using a sparge of inert argon gas to assist in removing the low boiling volatiles. The liquid temperature was kept below 360 °C to minimize any chemical reaction. After a solid pitch with a softening point of 82 °C had been achieved, the distillation was continued in a smaller reaction flask and portions of pitch were then removed at different stages for measurement of softening point (SP) [1], Cleveland Open Cup flash point (FP) [2], and modified Conradson Carbon (MCC) values [3]. Five

pitches with SP values ranging from 82-103 °C were produced through this procedure and the volatiles were also collected for additional analysis.

GC Analysis--A portion of each pitch was analyzed by GC for the 16 polynuclear aromatic hydrocarbons (PAHs) listed in Table II that are used for wastewater [4] and air monitoring [5]. A GC analysis was also performed on the distillate during pitch preparation. An HP5890 GC equipped a flame ionization detector and a DB-5 capillary column (30 m long, 0.32 mm ID, 0.1 μm film thickness) was used for all analyses. 2,7-Dimethylnaphthalene was used as the internal standard.

Results

The properties of the prepared pitches, including yield, SP, FP and MCC, are listed in Table I. A gas chromatogram for pitch A (82 °C SP) is shown in Figure 1. The 16 identified PAHs are appropriately labeled.

Summarized in Table II are the quantitative contents of the 16 PAHs for the five pitches. From the results, it can be seen that only four PAHs, phenanthrene, anthracene, fluoranthene and pyrene, continually decrease with increasing extent of distillation.

Figure 2 presents a gas chromatogram for the total distillate fraction collected during transformation of the 82.4 °C SP pitch (Pitch A) to the 98.0 °C SP pitch (Pitch B). It is apparent that the four aforementioned PAHs are by far the main components of the distillate, although peaks corresponding to smaller amounts of other constituents are also evident.

The properties of the four cited PAHs including melting point (MP), boiling point (BP), and FP are summarized in Table III.

TABLE I: Pitches Obtained From Distillation of Coal Tar (1.5% QI)

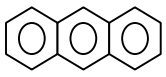
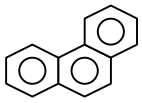
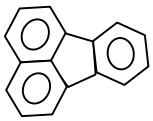
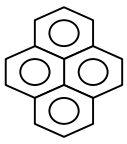
Pitch	Pitch Yield %	SP °C	FP °C	MCC %
A	61.9	82.4	241	41
B	58.6	87.9	261	44
C	57.4	91.4	263	44
D	53.9	98.0	277	47
E	51.9	103.2	291	48

TABLE II: GC Analysis of Laboratory Pitches from Distillation of Coal Tar

Pitch	**A**	**B**	**C**	**D**	**E**
S.P. °C	82.4	87.9	91.4	98.0	103.2
F.P. °C	241	261	263	277	291

PAH in Order of Elution	**Average Percent PAH in Pitch**				
Naphthalene	<0.01	<0.01	<0.01	<0.01	<0.01
Acenaphthylene	<0.01	<0.01	<0.01	<0.01	<0.01
Acenanaphthene	<0.01	<0.01	<0.01	<0.01	<0.01
Fluorene	<0.01	<0.01	<0.01	<0.01	<0.01
Phenanthrene	0.82	0.38	0.20	0.10	0.03
Anthracene	0.18	0.09	0.04	0.02	0.00
Fluoranthene	2.21	1.85	1.46	1.19	0.79
Pyrene	1.81	1.61	1.27	1.12	0.81
Benzo(a)anthracene	1.23	1.29	1.05	1.14	1.01
Chrysene	1.53	1.52	1.30	1.46	1.23
Benzo(b) and Benzo(k)fluoranthene	2.16	1.97	1.71	1.83	1.82
Benzo(a)pyrene	0.94	0.97	0.76	0.91	0.89
Indeno(1,2,3-cd)pyrene	0.54	0.44	0.39	0.57	0.40
Dibenzo(a,h)anthracene	0.11	0.12	0.10	0.13	0.09
Benzo(g,h,i)perylene	0.48	0.39	0.34	0.49	0.39

TABLE III: Properties of Most Volatile Major Pitch Components

Compound	Structure	M.P. ºC	B.P. ºC	Flash Pt. ºC
Anthracene		215	340	121
Phenanthrene		99	340	165*, 171
Fluoranthene		108	384	196*
Pyrene		151	404	199*

Note: All values are from the literature [6] except those marked by an asterisk (*) which were measured for this study.

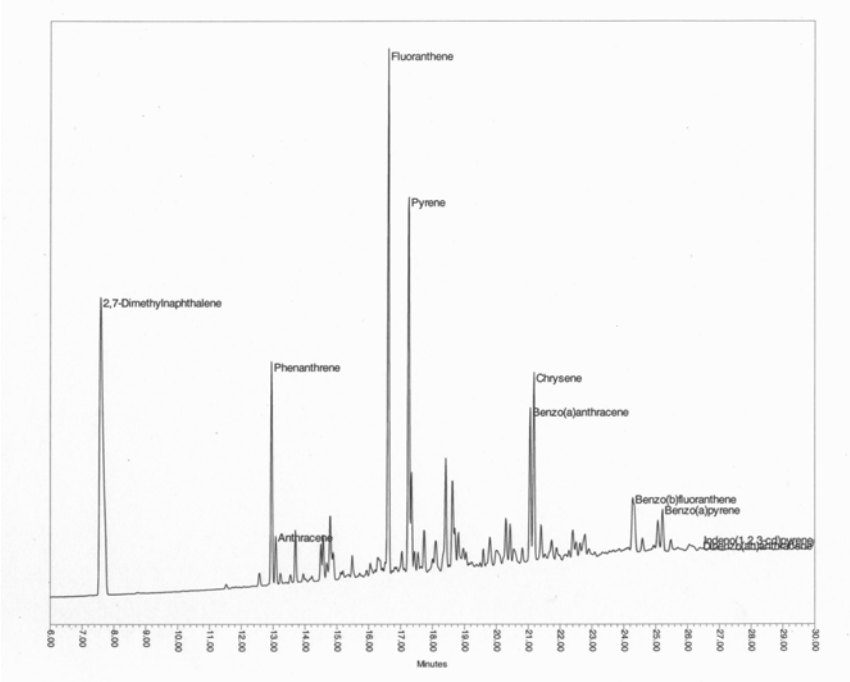


Figure 1: GC chromatogram for pitch A.

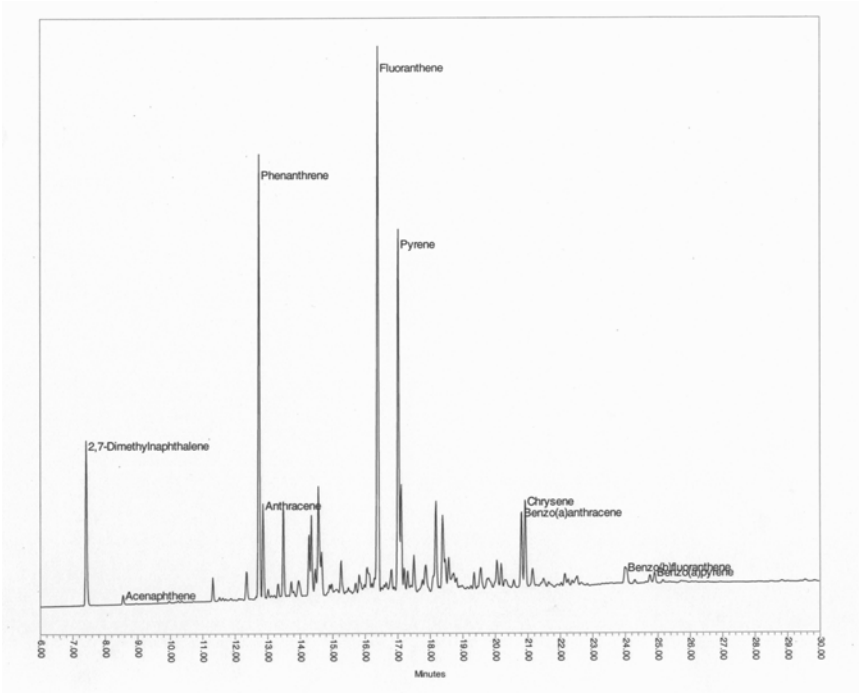


Figure 2: Gas Chromatogram of distillates collected during conversion of 82.4 °C SP Pitch (Pitch A) to 98.0 °C SP Pitch (Pitch D)

Discussion

Both the pitch softening point and flash point are directly related to the amount of low boiling components removed during the pitch distillation process. In the transformation from 82 to 103 °C softening point, which is the general range for commercial coal tar impregnation pitches, the 3-ring aromatics (phenanthrene, anthracene and fluoranthene) plus pyrene are the main components of the distillates. The removal of these compounds raises both flash point and softening point. However, the flash point is considerably more sensitive to their presence than is the softening point. This conclusion is apparent in Figure 3 where both SP and FP are plotted versus the content of these four PAHs. The slope of the FP relation is more than twice that of the one for SP. As can be seen, every percent removal of these compounds raises the flash point by about 14 °C. We have found this relation of FP to content of the four PAHs to hold for some commercially produced coal tar impregnation pitches as well. It is therefore evident that efficient distillation for removal of these compounds is required for achieving the optimum balance of flash point and softening point.

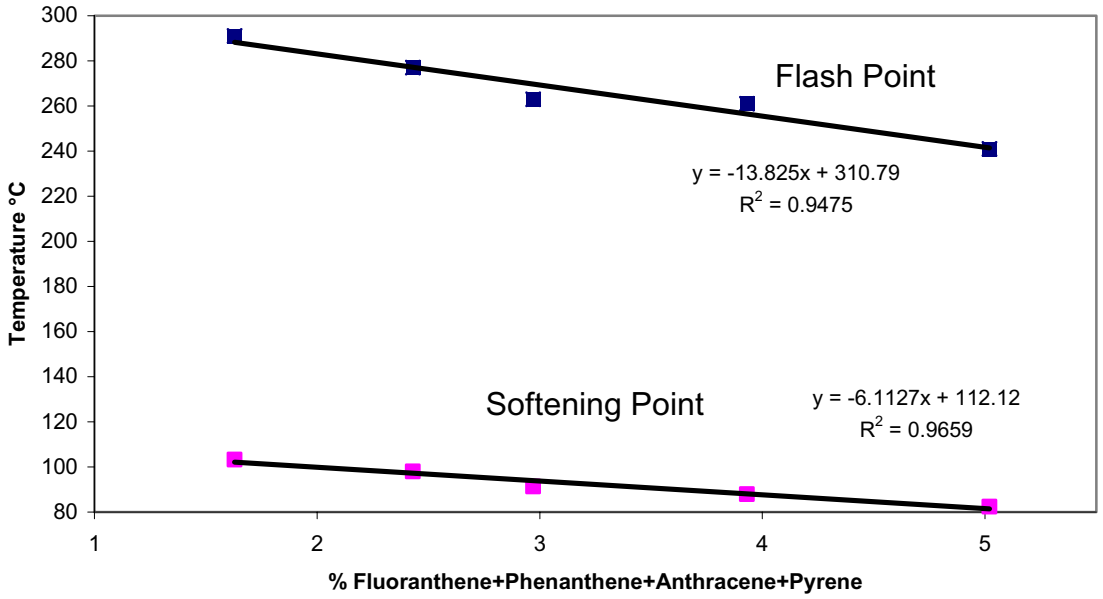


Figure 3: Correlation of the flash point and softening point with the amount of 3-ring aromatic PAHs (phenanthrene, anthracene, and fluoranthene) plus pyrene.

Conclusions

1. In the coal-tar pitch distillation process, the preparation of pitches in the softening point range of about 82-103 °C involves largely the removal of the 3-ring aromatics (phenanthrene, anthracene, and fluoranthene) plus pyrene.

2. The removal of those compounds raises both pitch flash point and softening point.

3. The flash point temperature is more sensitive than the softening point temperature to the presence of the four compounds with the flash point increasing by about 14 °C for every percent removal.

4. From a safety standpoint, it is desirable to have the flash point of the pitch as high as possible and definitely well above temperatures at which exposure with air is possible during the graphite production process.

References

[1] ASTM D3104, Standard Test Method for Softening Point of Pitches (Mettler Softening Point).
[2] ASTM D92, Standard Test Method for Flash and Fire Points by Cleveland Open Cup Tester.
[3] ASTM D2416, Standard Test Method for Coking Value of Tar and Pitch (Modified Conradson).
[4] EPA Method 610, Polynuclear Aromatic Hydrocarbons.
[5] NIOSH 5506, Analysis of PAHs in Indoor Air.
[6] Material Safety Data Sheets Compilation, Schenectady, New York: Genium Publishing Corp, 1984.