

# CHEMICAL CHANGES DURING THE MILD AIR OXIDATION OF PITCH

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## Introduction

Oxidation and air blowing is an important step in processing of certain carbonaceous materials. Air oxidation has been used in the manufacture of asphalts<sup>1</sup>, preparation of binder pitches<sup>2</sup>, and in thermosetting pitch fibers<sup>3</sup>. Extensive oxidation is known to introduce cross-linking and lead to disordered carbon structures.<sup>3,4</sup> Chemical mechanism<sup>5</sup> and mesophase formation<sup>6</sup> studies on the effects of oxidation on carbonaceous materials have also been reported.

This paper presents the results of an investigation of the effect of mild air oxidation on well-graphitizing pitches derived from coal tar and petroleum. Various techniques have been used to monitor the chemical changes which occur during the oxidation process and to relate the results to subsequent graphite development.

## Experimental

### A. Materials

The coal tar and petroleum pitches were commercially available materials. The Mettler softening point of the coal tar pitch was 110°C, whereas the petroleum pitch exhibited a Mettler softening point of 122°C.

### B. Air Blowing

The apparatus used in the air blowing experiments consisted of a heated resin flask fitted with a stirrer, condenser, and fritted glass inlet tube for the air. The temperature of the pitch was monitored by using a thermocouple immersed in the liquid pitch. The samples (650 grams) were heated rapidly to their softening points, and then at a rate of 38°C/hr. to 250°C. Air flow was maintained at 1 to 1.5 liters/minute. Air blowing was continued at 250°C for 6 to 8 hours to achieve softening points of 175° to 180°C.

### C. Distillation

The distillation was performed at a pressure of about one micron using standard laboratory glassware.

## Experimental Results

### A. Pitch Properties

Pitches with softening points of 175±5°C were prepared by air blowing and by vacuum distillation of the coal tar and petroleum pitches. The products were characterized by solubility in benzene and quinoline and by elementary analysis. These data, along with the product yields, are given in Table I. The results show that the air oxidation of both materials leads to a greater

increase in the benzene insolubles content than is found for the distilled pitches. This effect is greatest for the petroleum pitch. The solubility in quinoline was essentially unaffected by the air blowing.

Both distillation and air blowing lead to an increase in atomic carbon-hydrogen ratio. Furthermore, the carbon-hydrogen ratios were equal after distillation and air blowing of each pitch. Only the petroleum pitch showed a small increase in oxygen content as a result of air blowing.

### B. Infrared Analysis

The infrared spectra of the air-blown coal tar and petroleum pitch did not show absorptions which could be attributed to oxygen containing functional groups. The oxidized petroleum pitch showed a slight decrease in aliphatic hydrogen absorptions.

Table I

Summary of Properties of Distilled and Air Blown Pitches

Property	Coal Tar Pitch		
	As Rec'd	Distilled	Air Blown
Softening Point, °C	110	173	174
Yield of Distilled/Air Blown, %	---	80	93
Benzene Insoluble, %	32.7	42.7	49.0
Quinoline Insoluble, %	13.2	16.1	16.7
Carbon, %	93.2	94.3	94.0
Hydrogen, %	4.24	4.00	4.01
Oxygen, %	1.4	1.2	1.6
Atomic C/H Ratio	1.83	1.96	1.95

  

Property	Petroleum Pitch		
	As Rec'd	Distilled	Air Blown
Softening Point, °C	122	178	181
Yield of Distilled/Air Blown, %	---	75	93
Benzene Insoluble, %	8.6	13.1	29.4
Quinoline Insoluble, %	0.3	0.1	0.1
Carbon, %	93.6	94.1	93.4
Hydrogen, %	5.58	5.34	5.26
Oxygen, %	0.39	0.50	1.2
Atomic C/H Ratio	1.40	1.47	1.48

### C. NMR Analysis

High resolution proton NMR spectra were obtained for the pitches before and after oxidation. The petroleum pitch was much more aliphatic than the coal tar pitch and contained numerous alkyl side chains. The aromatic

hydrogen contents for the two starting materials were 57% and 91% respectively. After oxidation, the soluble portion of the petroleum pitch showed a slight increase in aromaticity while the NMR spectrum of the coal tar pitch was relatively unchanged.

#### D. Gel Permeation Chromatography (GPC)

Molecular weight data for toluene soluble portions of the pitches by GPC were obtained by procedures described previously<sup>7</sup>. The results are listed in Table II.

Table II

Molecular Weight Analysis (GPC) for Treated Pitches

Pitch	Toluene Sol. %	$\overline{M}_w$	$\overline{M}_n$	$\overline{D}$
Untreated Petroleum	85	606	564	1.075
Distilled Petroleum	78	654	595	1.099
Oxidized Petroleum	59	635	579	1.098
Untreated Coal Tar	58	521	507	1.029
Distilled Coal Tar	45	519	504	1.030
Oxidized Coal Tar	43	518	503	1.029

The data show a decrease in solubility and an increase in molecular weight with air oxidation of the petroleum pitch. There was essentially no difference in the GPC data for the distilled and air blown coal tar pitches.

#### E. Mesophase Development

Samples of the distilled and air oxidized pitches were heat treated further in an inert atmosphere to produce mesophase. There was little difference in the nature and amount of mesophase produced by the subsequent heat treatments, although the air oxidized pitch contained a large amount of nonmesophase pyridine insolubles.

#### F. Graphite Structure

The pitches were heat treated to 3000°C and x-ray analyses were obtained for the graphitized samples. The x-ray interlayer spacing data are given in Table III.

Table III

X-ray Interlayer Spacings for Graphitized Pitches (3000°C)

Pitch	$C_0/2, \text{\AA}^*$
Untreated Coal Tar	3.363
Distilled Coal Tar	3.363
Oxidized Coal Tar	3.362
Untreated Petroleum	3.360
Distilled Petroleum	3.355
Oxidized Petroleum	3.357

\*Average of (004), (006), and (008) spacings.

#### Discussion

Our results show that the effects of mild oxidation on well-graphitizing pitches lead mainly to an increase in molecular weight without necessarily introducing oxygen into the product. This reaction appears more facile with the less aromatic petroleum pitch. Both mesophase formation studies and x-ray analysis of the derived graphites show that the oxidative treatments have little effect on the ultimate graphitization process. These conclusions are consistent with an oxidative mechanism involving a dehydrogenative condensation of the relatively high molecular weight aromatic components in the pitches.

#### References

1. E. J. Barth, Asphalt Science and Technology - Gordon and Breach Science Publishers, New York (1962), p. 386.
2. H. Abraham, Asphalts and Allied Substances, Volume II, D. Van Nostrand & Co., New York (1961), p. 98.
3. S. Otani, Carbon, **3**, 31 (1965).
4. J. S. Kipling, J. N. Sherwood, P. V. Shooter, and N. R. Thompson, Carbon, **1**, 315 (1964).
5. I. C. Lewis and L. S. Singer, Summary of Papers presented at the American Carbon Society Ninth Biennial Conference on Carbon, Boston College, June 16-20 (1969).
6. F. Gootarzi, G. Hermon, M. Iley, and H. Marsh, Fuel, **54**, 105 (1975).
7. I. C. Lewis and B. A. Petro, J. Poly. Sci., **14**, 1975 (1976).