

## Manufacture and Use of Solid Petroleum Pitch

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### INTRODUCTION

For many years there has been a continuing effort in the petroleum industry to increase the amount of distillate products obtained from crude oil. This effort has been motivated by the higher value of distillate oils and the poor economics of adding these higher value distillate oils to viscous residues to make them marketable as fuels. During the past decade some progress has been made on this problem. The residues from certain crudes can be processed effectively by thermal visbreaking to increase substantially the yields of distillate oils. The residues from any crude can be processed either by coking to make largely distillate oils and coke or by hydrodesulfurization to remove sulfur as well as to convert any required amount of the asphalt. In addition, many refiners today gain distillate yield by burning viscous residual oils as refinery fuel to avoid the blending-off of lighter oils required in the marketing of No. 6 Fuel Oil. The production and burning of solid petroleum pitch goes one step further than the use of a viscous residue. By concentrating further the heavy residual oils that the refiner now burns, additional distillate oil is removed and the asphaltic portion is converted to a hard, brittle solid which can be handled and burned as a solid fuel. There are several potential advantages in going to this added degree of reduction of petroleum residues. (1) A solid fuel can be stored and transported more easily than viscous fuel which requires heating to keep it pumpable when the fuel use is beyond the immediate refinery area. (2) The reduced yield of residual fuel when making a solid pitch results in a higher yield of more valuable distillate oil. While this distillate oil is "dirty" by normal standards for distillate stocks, improved refining techniques in modifications to catalytic cracking and in hydrocracking will now readily accept such oils as charge stocks. (3) The processing required to produce a solid petroleum pitch is more simple and less costly than is required for either coking or hydrodesulfurization.

### DESCRIPTION OF SOLID PETROLEUM PITCH

Solid petroleum pitch is an asphalt concentrate from crude oil where enough oil has been removed from the asphalt to produce a high melting point, coal-like solid. This material is brittle and easily pulverized; it can be stored outside without fusing or agglomerating and makes an excellent solid fuel having considerable less ash and more BTU'S per pound than coal. Table I gives a brief summary of the physical properties of petroleum pitch compared to bituminous coal, a coal tar pitch and petroleum coke. Although not shown in this table, petroleum pitch is more similar to certain natural occurring bitumens, such as gilsonite than it is to coke, coal or coal tar pitch. Petroleum pitch differs from coal and petroleum coke in that it has a melting or softening point. This softening point is high enough, however, (about 350°F.) to allow pitch to be stored in 40-foot piles at 170°F. without the agglomeration of particles.

Needless to say, the advantage for producing a solid petroleum pitch from a crude oil will vary widely and will be most advantageous to those refiners having high asphalt-content crudes and in a depressed marketing area for residual fuel oils. In looking to the future, the need for such a process is expected to increase when our fuel economy must rely more heavily on low-gravity crudes, tar sands, and low grade hydrocarbon deposits.

Table I

PROPERTIES OF VARIOUS CARBONACEOUS SOLIDS

	<u>Petroleum Pitch</u>	<u>Typical Bituminous Coal</u>	<u>Coal Tar Pitch</u>	<u>Petroleum Coke (Delayed)</u>
Specific Gravity	1.05-1.15	-	1.20-1.30	1.28-1.42
Softening Point: °F.	300-400	-	110-320	none
Solubility in Benzene: %	75-99	-	45-75	-
Volatile Matter: %	50-70	34	40-50	8-17
Heating Matter: BTU/Lb.	16,500-17,600	14,400	-	14,600-16,000

MANUFACTURE OF SOLID PETROLEUM PITCH

It can be seen from the volatile content in Table I that petroleum pitch is a concentrate of the asphaltic material in crude. By removing or eliminating oil which is included with normal vacuum reduced crudes, a pitch can be produced whose asphaltene concentration is sufficiently high to impart hardness properties, which permit satisfactory handling, storing, grinding and burning as a solid fuel. For certain crudes which have very hard asphalts, it is possible to produce solid petroleum pitch by simply increasing the severity of normal refinery vacuum distillation<sup>1</sup> by 50° to 100°F. (corrected to 760 mm. Hg). Certain Mississippi and Venezuelan Crudes are of this type. Such crudes are generally low in API gravity and sufficiently high in viscosity to meet the No. 6 Fuel Oil specification upon removal of a few per cent of gasoline. Baxterville Crude, for instance, can be distilled to produce 5% gasoline with the remaining 95% being a heavy fuel oil. By a combination of atmospheric and vacuum distillations (the latter carried out at 1070°F. corrected to 760 mm. Hg), there is obtained from this crude 5% of gasoline, 24% of furnace oil, 46% of fair-quality catalytic cracking charge stock, and 26% of a 360°F. softening point pitch. A simplified flow diagram for one of several possible methods for carrying out this operation is given in Figure 1. By varying the severity of distillation, pitches of varying softening point can be obtained; however, higher softening point pitches are more difficult and costly to produce and the resulting gas oils are of higher carbon residues and metal contents. As will be discussed later, it is believed that pitches of 350°F. minimum softening point can be handled and burned in most burners designed for either coal or heavy fuel oil with but minor modifications, and it is entirely possible that lower softening point (275°-325°F.) pitches can be handled and burned in specially-designed equipment. Yields and inspection data for pitch and catalytic cracking charge stock produced at three severities of vacuum reduction from Baxterville Crude are given in Table II.

The use of vacuum distillation to produce pitch is limited to crudes containing asphalts of very low oil content (hard asphalts). For other crudes it is necessary to remove a portion of the oil from the asphalt by cracking. Thermal visbreaking of

Table II

YIELDS AND INSPECTIONS OF PITCHES AND CATALYTIC CRACKING STOCKS  
FROM SEVERAL SEVERITIES OF VACUUM REDUCING BAXTERVILLE CRUDE

	Mild Vacuum Reduction	Moderately Severe Vacuum Reduction <sup>a</sup>	Severe Vacuum Reduction
Pitch			
Yield: % by Vol. of Crude	33.5	25.7	17.9
Ring and Ball Softening Point: °F.	275	360	441
Catalytic Cracking Charge Stock			
Yield: % by Vol. of Crude	37.7	45.5	53.8
Carbon Residue, Conradson: %	0.64	1.58	3.32
Vanadium: PPM	0.13	0.70	3.40
Flash Temperature, <sup>b</sup> Corrected to 760 Mm. Hg: °F.	969	1068	1201

<sup>a</sup> Recommended reduction to produce a solid fuel.

<sup>b</sup> When charging a gasoline-free Baxterville Crude to vacuum tower.

the normal vacuum residue from many crudes concentrates the asphaltenes by "cracking out" the oil so it can readily be removed by atmospheric distillation.<sup>2</sup> Here again, when producing pitch by visbreaking, the asphalt charge to the visbreaker must be relatively hard, preferably above 160°F. softening point; otherwise a very severe visbreaking operation is necessary or the subsequent distillation must be carried out under vacuum. A typical operation to produce pitch from a 12.5% reduced Eastern Venezuela Crude (165°F. softening point) requires single-pass visbreaking at furnace conditions of 915°F. outlet temperature and 200 psig. pressure. Operating conditions in this range are practical for heavy vacuum reduced crudes<sup>3</sup> as evidenced by several visbreaking operations for conventional purposes now carried out in Gulf's refineries. By visbreaking a 5.2 °API vacuum reduced Eastern Venezuela Crude and distilling the visbreaker residue, the following yields of products are obtained: 13.3% gasoline and naphtha, 13.3% furnace oil, 15.6% catalytic cracking charge stock, 12.2% fuel oil, and 45.3% pitch. The inspections of the distillate products are similar to products obtained from delayed coking and are given in Table III. The process flow, which is shown diagrammatically in Figure 2, is typical of thermal visbreaking except for the handling of the visbreaking effluent. The visbreaker effluent is distilled at atmospheric pressure in the presence of 5 to 40 pounds of steam per barrel of charge to obtain an approximately 350°F. softening point pitch and a cracking stock, as well as lighter distillates. A more severe visbreaking operation would reduce the steam requirements.

Most Venezuelan Crudes and domestic crudes containing hard asphalts such as East Texas, California, etc., are very readily processed by visbreaking to produce solid pitch. Crudes with softer asphalts require more severe visbreaking and distillations conditions than those given above for the Eastern Venezuela residue, and high softening petroleum pitches have been prepared from Kuwait, West Texas, and Mid Continent Crudes. •.5

Table III

PRODUCTION OF PITCH BY THERMAL VISBREAKING  
FOLLOWED BY ATMOSPHERIC REDUCTION  
OF REDUCED EASTERN VENEZUELAN CRUDE

300° F. End Point Gasoline (10 RVP)	
Yields: % by Vol.	8.0
Sulfur: %	0.61
Research Octane No., +3 Cc. TEL	85.6
300°-400° F. Naphtha	
Yield: % by Vol.	5.3
Furnace Oil Fraction	
Yield: % by Vol.	13.3
Sulfur: %	1.83
Gravity: °API	31.2
Characterization Factor	11.34
Catalytic Charge Stock	
Yield: % by Vol.	15.6
Sulfur: %	2.02
Characterization Factor	11.62
Carbon Residue	0.8
Heavy Gas Oil	
Yield: % by Vol.	12.2
Carbon Residue, Conradson: %	13.9
Pitch	
Yield: % by Vol.	45.3
Softening Point: °F.	364

In the manufacture of pitch, it is necessary to provide a means of cooling and solidifying the pitch after removal from the atmospheric or vacuum distillation column. The most practical means for most locations is through the use of a continuous moving stainless steel belt. The hot pitch from the distillation column is poured continuously onto the belt, which is cooled from beneath by water and may be cooled with auxiliary water sprays on top. Pitch produced by this manner consists of flakes about one-quarter inch thick which break at random into pieces one to six inches across. The pitch readily separates from the stainless steel belt upon cooling because of its different coefficient of expansion. A photograph of pitch produced in this manner is shown in Figure 3. Such material is quite brittle and breaks readily upon handling. With handling there is produced only a very small amount of fines which are not troublesome. There are other methods which may be more desirable in certain locations for cooling and solidifying the hot liquid pitch. These include the use of large cooling pits into which the pitch is pumped as a hot liquid and allowed to cool slowly in the atmosphere in a large mass. When solid, the pitch is then broken up and moved with power shovels. Hot liquid pitch also may be solidified by spraying into water or steam, or it may be solidified on a water-cooled rotary drum. From our experience, however, the simplest and most convenient method is that of the continuous moving belt.

## USES OF PETROLEUM PITCH

Because of the large quantities of crudes and residues processed in the petroleum industry, any scheme for producing solid petroleum pitch which would be effective in improving the ratio of distillate to residual oils would produce so much pitch that a fuel market must be considered as its primary use. Thus, it was on the basis of a fuel market that economics and process developments were carried out. Even a small unit charging 5000 barrels per day of Eastern Venezuela residue would produce 430 tons per day of pitch. In considering the use of petroleum pitch as a fuel it was necessary to determine the minimum softening point that would allow transportation, storage and grinding in hot weather without the pitch becoming tacky or plastic and possibly fusing. It was found that these properties of pitch depended on the crude source and method of production. For a typical pitch from Eastern Venezuela Crude, it was found that a 350°F. ring and ball softening point was sufficiently high to prevent fusion at temperatures and pressures which would be encountered under almost any circumstance. Figure 4 presents a plot of incipient fusion temperature of Eastern Venezuela pitch as a function of pitch softening point when under a pressure equivalent to 40 feet of pitch. This incipient fusion temperature is the temperature at which particles first adhere to one another but readily break apart with slight handling. From this plot it can be seen that a 350°F. softening point pitch only begins to fuse at 170°F. at these conditions. It is not until temperatures of about 15°F. higher that fusion becomes serious and permanent. Thus, an Eastern Venezuelan pitch of 350°F. softening point can be stored in piles 40 feet high at 170°F. before any evidence of particle adherence occurs. Obviously, lower softening point pitches would be satisfactory in locations with lower ambient temperatures. The burning characteristics of 350°F. softening point pitch have been evaluated in a two-foot diameter Babcock and Wilcox experimental cyclone furnace.<sup>6</sup>

Several modifications were made to the normal operation of the cyclone furnace.

1. Cold air was used in pulverizing and charging the pitch so it would not melt before entering the furnace.
2. An ash with a suitable fusion temperature was added to the pitch to form a fluid slag coating on the walls of the cyclone.

The ash which was added was from the burning of coal and the quantity, 5%, was chosen arbitrarily. This quantity could have undoubtedly been reduced or the slag could have been recycled if no such material were continuously available. The burning characteristics of the pitch were excellent in every respect. The flame was stable and clean, the appearance of the stack was excellent, and the oxygen content of the flue gas was 2% indicating about 10% excess air. There were no problems with ignition, dust carryover, or flame propagation. There was no build up of slag in the combustion chamber, and the burner itself was clean with no build up of pitch. The carbon loss to the stack was below that obtained with coal firing, which is in the range of one pound per 1000 pounds of flue gas. During the test, no particular effort was made to control the grinding of the pitch or the size of the slag particles. The pitch was ground in a hammermill and found to crush more readily than coal. About twice the percentage passing through a 200-mesh screen was obtained from pitch than from coal using the same crushing equipment. Based on the observations of these test runs, the furnace equipment manufacturer believes that petroleum pitch is a suitable fuel for a cyclone furnace and that it can be fired without difficulty, provided the minor modification to the furnace mentioned previously are made. In comparison with bituminous coal, petroleum pitch has a number of distinct advantages for use as a boiler fuel. It is much easier to pulverize, requiring lower power and maintenance costs; it requires a reduced capital cost by eliminating the requirements for fly-ash removal equipment; and it has excellent ignition and burning properties and a high BTU content.

There are many other interesting and potential uses for petroleum pitch other than that of fuel. A summary in Table IV gives properties of several pitches. Petroleum pitch as was mentioned earlier is somewhat similar to certain natural bitumens occurring in the western part of the United States. Petroleum pitch is potentially cheaper and undoubtedly could be used for many of the applications now requiring the naturally occurring bitumens. Petroleum pitch can be used satisfactorily as a binder for carbonaceous materials, although for this purpose it is not quite as good as coal tar pitch because of its higher volatile content. Another use for pitch is in beneficiation of non-coking coals when added in amounts of 10% to 20%. Various pitches have also been tested for many other lower volume uses.

#### PROPERTIES OF DISTILLATE PRODUCTS FROM PITCH MANUFACTURE

The economic advantage to the petroleum industry in making pitch is that of obtaining additional yields of gasoline, furnace oil, and catalytic cracking charge stock and decreased yields of No. 6 Fuel Oil.

When producing pitch by vacuum distillation, all distillate oils are straight run stocks and require further treatment only when the crude is high in nitrogen or sulfur content or when the heavy gas oil contains more metals or a higher carbon residue than is desired for catalytic cracking. Data from Baxterville Crude indicate that the entire gas oil fraction from producing a 360°F. softening point pitch is satisfactory as a catalytic cracking stock but that the furnace oil requires desulfurization to meet present day sulfur specifications.

When producing pitch by visbreaking followed by distillation, the resulting gasoline and furnace oil fractions require further treatment because of their poor stability, high sulfur content, and the low octane number of the gasoline. A large portion of the gas oil fraction can be catalytically cracked without a pretreatment, but treating the entire gas oil fraction with hydrogen greatly increases the amount of oil available for catalytic cracking. Inspections of distillate fractions from several crudes when making pitch by visbreaking followed by distillation are given in Table V. Many of these distillate fractions have been catalytically treated with hydrogen in the laboratory and all have shown considerable improvement. For example, a pretreated naphtha had a naphthene content slightly higher than that of straight run Kuwait naphtha and was shown to be a better reformer charge stock. The furnace oil fractions were easily treated with hydrogen to produce premium No. 2 Fuel Oils. The heavy gas oils, either treated or untreated, were found to be not quite as good as straight run oils for use as cracking stocks. A comparison of the the inspections and cracking characteristics of these stocks is given in Table VI.

#### ECONOMICS

The economics of producing solid petroleum pitch can vary widely depending upon the crude source, the refinery location and the availability of idle thermal cracking equipment. Illustrative economic studies showed a payout time after income tax of 5.6 years for making pitch from Baxterville Crude by vacuum distillation when assuming a value of \$8 per ton for pitch. This value for pitch is conservative since on a BTU basis one ton of petroleum pitch (17,000 BTU per pound) is equivalent to about one and one-third tons of bituminous coal (14,000 BTU per pound). A payout time of 3.4 years was obtained for making pitch by visbreaking a vacuum reduced Eastern Venezuela Crude and then distilling the visbreaker residue. If idle thermal cracking equipment were available, this payout time would be even lower. This latter payout is quite attractive, but in each case both economics and an adequate and permanent market must be developed.

Table IV

PHYSICAL PROPERTIES OF PITCHES

Crude Source	----- Baxterville -----	Eastern Venezuela	Kuwait
<u>Yield: % by Vol. of Crude</u>	<u>33.5</u>	<u>3.9</u>	<u>4.3</u>
Inspection:			
Gravity, Solid State			
Sp. Gr., 77°/77°F.	1.103	1.124	1.196
Ring and Ball	275	441	415
Softening Point: °F.			
Penetration, ASTM D 5-49	23	4	1
210°F., 100 G., 5 Sec.			
Sediment: %	---		---
ASTM D 473-48			
Carbon Residue, Conradson: %	36.5	53.7	1.46
Proximate Analysis, Dry Basis: %			63.2
Volatile Matter	65.5	51.8	41.0
Fixed Carbon	34.5	47.7	58.9
Ash	0.0	0.1	0.1
Analysis, Ultimate: % by Wt.			
Nitrogen	0.3	0.4	0.7
Sulfur	4.8	5.5	7.6
Hydrogen	8.6	7.8	6.6
Carbon	84.8	86.0	84.1
Undetermined	1.5	0.3	1.0
Ash as Oxide: %	---	0.11	0.14
Insoluble in Trichloroethylene: % by Wt.	0.13	0.11	0.13
Heating Value, BTU/lb.	17,400	16,740	16,400
Metals: PPM			
Vanadium	114.6	186.0	348.0
Nickel	53.2	83.9	99.5
Copper	1.7	2.3	---
Iron	45.0	375.0	224.0

Table V

DISTILLATE OILS FROM VISBREAKING TO MAKE PITCH

<u>Reduced Crude Charge</u>	<u>Baxterville</u>	<u>Western Venezuela</u>	<u>Eastern Venezuela</u>	<u>Kuwait</u>
<u>Charge Stock</u>				
% of Crude	33.3	46.4	11.5	14.4
Softening Point: °F.	280	162	180	165
Carbon Residue: %	34.9	25.1	26.5	27.7
<u>300°F. E.P. Gasoline</u>				
Yield, % by Vol.	1.9	10.1	8.8	11.2
Gravity: °API	58.4	63.2	63.5	64.3
Sulfur, L: %	0.88	0.84	0.72	0.93
Research Method: Octane No.				
Clear	68.0	79.0	77.9	73.0
+3 Cc. TEL	76.2	87.2	85.6	80.3
<u>Naphtha</u>				
Yield, % by Vol.	2.4	6.7	5.3	6.5
Gravity: °API	44.8	44.1	44.8	44.7
Sulfur, L: %	1.17	1.34	—	1.30
Research Method: Octane No.				
Clear	49.2	60.8	55.7	51.8
+3 Cc. TEL	57.2	70.2	65.8	60.6
Characterization Factor	11.70	11.60	11.67	11.66
<u>Furnace Oil</u>				
Yield, % by Vol.	5.5	14.7	13.3	14.5
Gravity: °API	30.5	29.6	31.2	27.9
Sulfur, Braun-Shell: %	2.57	2.34	1.83	3.47
Aniline Point: °F.	129	118	129	114
Characterization Factor	11.50	11.39	11.52	11.25
<u>Cracking Stock</u>				
Yield, % by Vol.				
670°F. IBP Gas Oil	7.1	19.3	18.1	14.9
Gravity: °API	19.1	15.5	19.0	13.0
Sulfur, Braun-Shell: %	3.36	2.94	2.11	5.20
Sediment: %				
ASTM D 473-48	0.02	<0.01	<0.01	0.01
Carbon Residue, Conradson: %	0.7	1.03	1.12	1.04
Ash, Humber: %	0.0004	0.0002	0.0057	0.0004
Metals: PPM				
Vanadium	0.02	0.08	0.03	0.03
Nickel	0.08	0.05	0.07	0.05
Characterization Factor	11.53	11.33	11.55	11.05
<u>Heavy Gas Oil</u>				
Yield, % by Vol.	2.9	9.3	9.7	12.7
Gravity: °API	10.0	7.1	8.5	1.0
Sulfur, Braun-Shell: %	3.61	2.96	2.34	6.12
Carbon Residue, Conradson: %	14.1	13.4	16.5	16.6
Characterization Factor	11.30	11.18	11.30	10.66

Table VI

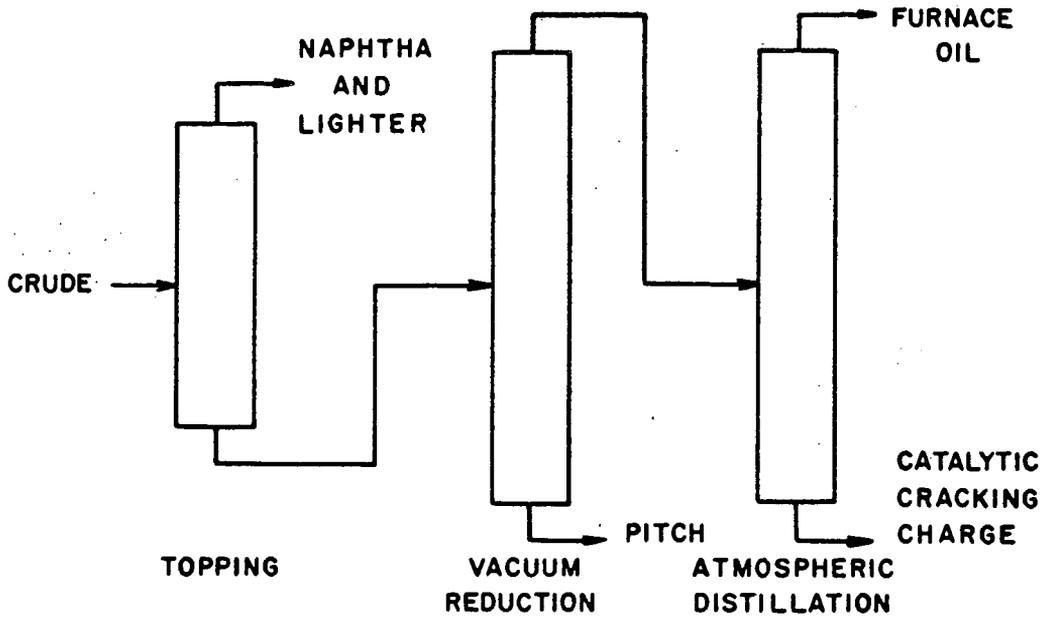
CATALYTIC CRACKING CHARACTERISTICS OF  
VIRGIN, CATALYTIC AND VISBREAKER GAS OILS

	<u>Virgin Kuwait Gas Oil</u>	<u>Kuwait Heavy Catalytic Gas Oil</u>	<u>Gas Oil From Visbreaking to Make Pitch</u>
Charge Stock Properties			
Gravity: °API	22.2	17.7	18.1
Sulfur: %	3.06	3.36	4.14
Carbon Residue: %	0.73	0.11	1.45
Vanadium, PPM	0.56	—	0.34
Characterization Factor	11.76	11.10	11.46
Conversion: % by Volume	53.8	34.2	43.3
Yields: % by Volume			
Depropanized Gasoline	49.1	25.6	35.0
Light Catalytic Gas Oil	20.7	18.7	20.4
Heavy Catalytic Gas Oil	25.5	47.1	36.3
Goke	5.2	6.6	6.6
Gasoline: Coke Ratio	9.5	3.9	5.2

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5. R. G. Goldthwait and W. R. Lehrian, U. S. Patent 2,944,958.
6. Watts, G. A. and Sage, W. L. Mechanical Engineering, Vol. 78, pp. 823-827, September, 1956.

**FIGURE 1**  
**PRODUCTION OF PITCH BY VACUUM REDUCTION**



**FIGURE 2**  
**PRODUCTION OF PITCH BY VISBREAKING**

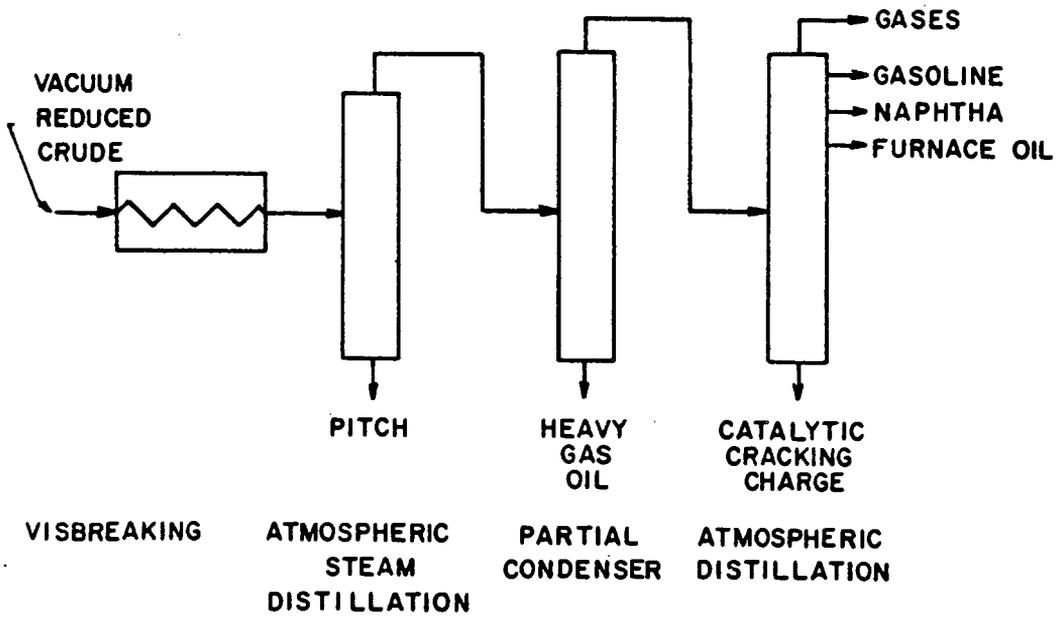
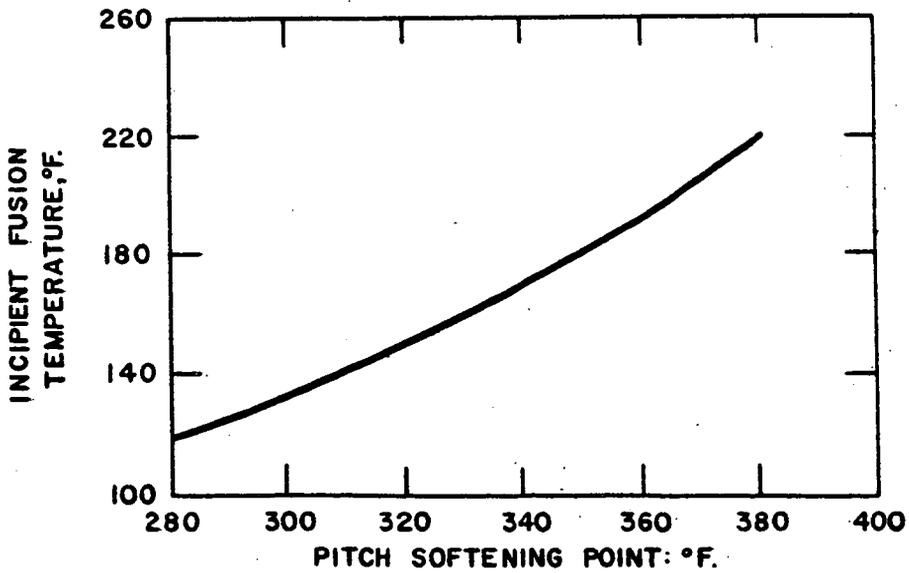




Figure 3  
PETROLEUM PITCH PRODUCED BY COOLING ON A STAINLESS STEEL BELT

FIGURE 4  
INCIPIENT FUSION POINT OF EASTERN VENEZUELA PITCH



STRUCTURE DETERMINATION OF RESINS FROM PITCH OF  
LOW-TEMPERATURE TAR BY COMBINED PYROLYSIS  
AND GAS-LIQUID CHROMATOGRAPHY

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This report is the second by this laboratory on investigations of the composition of the resins from pitch in connection with the Federal Bureau of Mines' research on the nature of coal and its products. The first report concerned the structure determination of resins by ring analysis and spectral characterization<sup>1</sup>. The present work involves structure determination of resins from pitch of low-temperature tar by combined pyrolysis and gas-liquid chromatography.

Pyrolysis or thermal degradation of complex substances is one of the oldest methods of structure determination. Gas-liquid chromatography makes it possible to isolate the pyrolysis products immediately upon formation so that they can be identified before they are lost or altered in secondary reactions. There are apparently no previous reports in the literature on structure determination of resins from pitch by pyrolysis. The characterization of low-temperature tar resins is important, however, because they are major components of the pitch, and, in the case of some bituminous tars, make up as much as half the weight of the total tar.

The conditions of pyrolysis were chosen to yield, insofar as possible, primary products that would give the maximum information about the structure of the resin. The products of greatest interest were those large enough ( $C_5$  and greater) to yield meaningful clues to structure. The pyrolysis temperature was generally in the range  $520^\circ$ - $530^\circ C.$ , or above the temperature at which no volatile pyrolysis products are observed, and the heating time was only a few seconds. In addition, because the sample was heated in the absence of air in a glass container, catalytic effects should have been quite low if not non-existent. Under these conditions the pyrolysis products could be considered to represent primary fragments from the resin molecule.

#### EXPERIMENTAL

Many pyrolysis experiments were made under a wide variety of conditions to gain some insight into the behavior of the various resins from several pitches. This report has been limited to the experimental procedures and results that are of greater interest.

### Apparatus

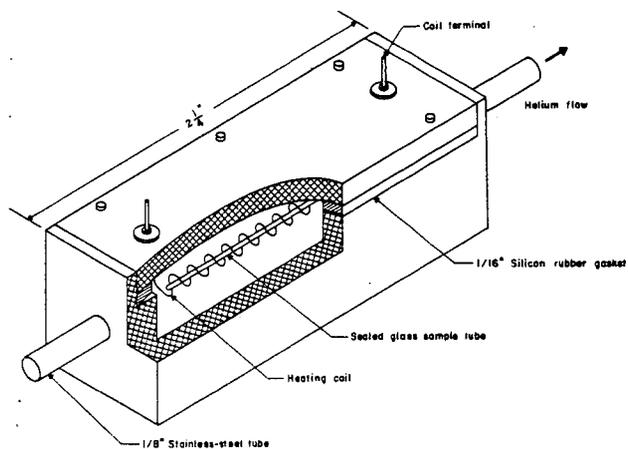
The pyrolysis apparatus consisted of a small coil (diameter, 1/8-inch) made from a 25.5-inch length of 28-gauge nichrome wire suspended in a stainless-steel chamber connected directly to a gas-liquid chromatographic unit by a short length of 1/8-inch stainless-steel tubing, as shown in Figure 1. The chamber, the connecting tubing, and a longer preheating section of tubing were all electrically heated to approximately the same temperature, which was a few degrees below the GLC column temperature. Helium carrier gas was passed through the preheat section and the pyrolysis chamber into the column. A 30-second maximum electrical timing switch and powerstat were used to control the firing period and voltage for the pyrolysis coil. The maximum temperature obtained during firing was determined in calibration runs with a thermocouple; the helium flow and other conditions were the same as during the pyrolysis runs. This thermocouple was placed inside a glass tube, which in turn was inside the coil. The thermocouple leads passed through gas-tight fittings in the lid of the pyrolysis chamber. In addition, the maximum temperature of the coil surface itself was estimated by means of thin films of materials selected to melt at specified temperatures.

Two different columns were used in order to determine the pyrolysis products under different conditions. One column was constructed of 15 feet of 1/4-inch diameter aluminum tubing and packed with 25 weight-percent polyphenyl ether on 30 to 60 mesh firebrick. The other column consisted of a 20-foot length of 1/4-inch copper tubing filled with 75 g. packing made from 25 percent Apiezon L grease on 30 to 60 mesh firebrick. A column temperature of 220 °C. was used so that relatively high-boiling products, such as phenols and naphthalenes, would be readily detected, if present.

Gas-liquid chromatographic fractions were collected for infrared spectra. The higher boiling fractions were collected in 6-inch 18-gauge needles cooled in powdered dry ice. A U-trap of 1/4-inch aluminum tubing was required for the lower boiling fractions (below benzene) in order to have enough cooling surface to condense this material from its dilute mixture in the helium carrier gas. This U-trap could then be warmed, and the evolved gas readily condensed in a 6-inch needle. The needles were stoppered at both ends with Teflon plugs and kept in Dewar flasks filled with powdered dry ice until the infrared spectra could be obtained. To determine the spectra, each needle was given a single rinse with 15  $\mu$ l. carbon disulfide introduced into the hub end with a micro syringe. The solution was allowed to flow from the point of the needle into a 0.5 mm. ultramicrocavity cell, which was then stoppered and placed in a liquid cell holder. The cell holder in turn was placed in the 6X beam condenser in the spectrophotometer. The details of this cell holder have been described elsewhere<sup>2</sup>.

### Pyrolysis results

The results of the pyrolysis of the semi-solid, benzene-soluble, petroleum ether-insoluble resin from Nugget, Wyoming, subbituminous coal tar pitch may be cited as an example. The resin was pyrolyzed at about 528 °C. in a chamber preheated to 175 °C., using a sealed glass tube technique. This procedure consisted of placing about 25 mg. of the finely divided resin in a glass capillary tube that was then evacuated,



sealed, and inserted in the coil. With this size sample and a setting of about 22.5 volts, the tube shattered at 8.4 seconds. The maximum temperature inside the glass tube after this length of time was determined from the calibration runs with a thermocouple. The volatile pyrolysis products were swept immediately and directly into the gas-liquid chromatographic column by the stream of helium. The pyrolysis residue appeared to consist of a mixture of char and an unknown amount of essentially unaltered resin.

Although the resin is subjected to a high pressure in the last few seconds before the tube shatters, this increased pressure has little apparent effect on the nature of the pyrolysis products as compared to heating a film of resin on the coil. This was shown by depositing a thin layer of the resin from solution on a coil and firing at various known maximum temperatures. At coil temperatures around 500°C., the low molecular weight resins (M, 400 to 500) simply evaporated from the coil and were deposited on the cooler walls of the pyrolysis chamber. A small peak was obtained on the chromatogram at the retention time for air, which had apparently been trapped in the semi-solid resin film. There were no other peaks, indicating that the resin had been distilled at about 500°C. without decomposition to lower boiling materials. [This suggests the possibility that at least some of the resins found in tars produced by low-temperature carbonization (500°C.) are essentially unaltered "coal molecules."] The medium molecular weight resins (M, 500 to 650) however, did not completely evaporate from the coil under these conditions, and at higher temperatures (around 530°C.), decomposition occurred. The chromatograms of these pyrolysis products were basically the same as those obtained with the sealed tube technique. The main difference between the two methods was the sharper, better resolved peaks with the sealed tube method. Pyrolysis of resins in evacuated sealed glass tubes thus had five distinct advantages: (1) no sample was lost from the pyrolysis zone by evaporation; (2) the resin was not heated on a metal surface so possible catalytic effects were avoided; (3) the pyrolysis products were swept into the gas chromatographic column during an exceedingly brief interval when the tube shattered; the resulting chromatogram had sharper and better resolved peaks; (4) the tube shattered so violently and into such small pieces that no sample remained in the pyrolysis zone; and (5) the little "spike" produced on the recording by this pressure surge was an accurate indication of zero time.

A typical chromatogram obtained with the subbituminous resin using the sealed tube technique and the Apiezon L column is shown in Figure 2. A recording with the methane peak 1 off-scale was chosen so that the minor component peak 12 would be evident. (All peaks were recorded at the same attenuation.) On other chromatograms, it was clear that peaks 4 and 5 were separate. The relative retentions of the pyrolysis products producing these peaks are compared with the relative retentions of pure compounds in Table 1. The wavelengths of some of the observed infrared absorption bands of the trapped fractions corresponding to peaks 7 through 14 are also shown in Table 1, as well as the quantities of pyrolysis products determined from corrected peak areas and spectra of trapped fractions. The identities of the pyrolysis products with relative retentions less than that for n-pentane were not considered pertinent to the present work. Nevertheless, evidence was obtained showing that peaks 1 through 4 are undoubtedly produced by the C<sub>1</sub> through C<sub>4</sub> hydrocarbons, all of which are gases. Several attempts were made to obtain evidence for pyrolysis

Table 1. Relative retentions and infrared-absorption bands of pyrolysis products

Compound	Relative retention <sup>a</sup>		GLC peak no.	Some observed I. R. bands, wavelength, $\mu$	Weight percent <sup>b</sup>
	Pure	Pyrolysis product			
Methane	0.37	0.37	1		
		0.43	2		
		0.49	3		
		0.57	4		
1-Pentene <sup>c</sup>	0.60	0.59	5		9.7
2-Methyl-1-pentene <sup>c</sup>	0.70	0.71	6		2.7
2,2,4-Trimethylpentane	0.93	0.93	7	7.33, 7.81, 8.03, 8.32, 8.57, 10.21	24.7
Benzene	1.00	1.00	8	2.44, 3.20, 3.25, 5.12, 5.52, 9.65, 14.85	19.3
2,3,4-Trimethylpentane	1.15	1.15	9	7.25, 7.32, 8.93, 9.30, 10.07, 10.32, 10.92	26.9
2,2,4,4-Tetramethylpentane	1.23	1.23	10	8.03, 8.54, 10.28	7.0
Toluene	1.37	1.37	11	9.28, 9.71, 13.74, 14.43	3.5
2,6-Dimethyl-1,4-heptadiene <sup>c</sup>	1.53 <sup>e</sup>	1.55	12		0.5
p-Xylene )	1.92	1.93	13	8.95, 12.60 (para)	0.9
m-Xylene )				8.57, 9.13, 13.02, 14.53 (meta)	2.1
o-Xylene	2.14	2.15	14	7.22, 8.96, 9.53, 9.81, 13.46	2.7
					100.0

a Relative to benzene on Apiezon L grease at 220°C.

b On the basis of the total liquid pyrolysis products.

c This compound is typical of several equally likely possibilities.

d See text for discussion of olefin bands.

e Retention obtained from log retention-boiling point correlations.

products with retention times greater than that for o-xylene. However, even with the largest sample size of resin, the highest sensitivity setting of the GLC apparatus, and a more sensitive flame detector instead of a thermal conductivity detector, the recording beyond the o-xylene peak remained a straight line, including the region for higher boiling compounds such as phenol and naphthalene. Under the same conditions it was known that very small quantities of these compounds could be detected.

In addition to the infrared absorption bands listed in Table 1, there were several bands, characteristic of different types of olefins, which were readily observed. These were bands at  $10.14\mu$  and  $11.06\mu$  due to  $\alpha$ -olefins, a band at  $11.30\mu$  due to branched (2-position)  $\alpha$ -olefins, a band at  $14.44\mu$  due to cis-olefins, a band at  $10.38\mu$  due to trans-olefins, and a band at  $12.32\mu$  possibly due to branched internal olefins. The band at  $6.1\mu$  due to the C=C stretching vibration in olefins was detected, this being a weak band as is observed for non-conjugated compounds. No individual olefin compound could be identified with certainty. It appeared likely, however, that most of these olefins had the same highly branched carbon skeleton as the saturated hydrocarbons. This condition was verified by the complete absence of the band at  $13.80\mu$  due to the  $-(CH_2)_4-$  group or larger. Conversely, the  $8.57\mu$  band for the "isopropyl" grouping of carbon atoms was frequently observed to be a major band. Bands at  $7.23\mu$  and  $7.30\mu$  also indicated the presence of the  $(CH_3)_2CH-$  group.

#### DISCUSSION

From the large number of pyrolysis experiments that were made, it appeared from the repeated evidence of characterizing infrared absorption bands and the excellent agreement with relative retentions, that the 3 major liquid pyrolysis products of the subbituminous resin were 2,3,4-trimethylpentane, 2,2,4-trimethylpentane, and benzene, in that order of decreasing quantity. The large quantity of highly branched, relatively high carbon number ( $C_8$ ) saturated hydrocarbons was of unusual interest.

As previously mentioned, it appeared reasonable to assume that, under the conditions adhered to in this work, these pyrolysis products represented primary fragments from the resin molecule. It was recognized that the actual fragments were very likely free radicals at the instant of formation, that is, that a free radical mechanism was involved in the thermal degradation around  $500^\circ C$ . It appears almost certain that the benzene rings found in the pyrolysis products existed as such in the resin molecule. These monocyclic aromatics (benzene, toluene, the 3 xylenes) are present in the same quantities at the threshold temperature for pyrolysis (slightly over  $500^\circ C$ .) as at much higher temperatures (up to about  $650^\circ C$ .). Non-catalytic aromatization is generally considered to become significant only for temperatures at or above about  $650^\circ C$ . In the absence of specific catalysts, the rate of formation of aromatics from non-aromatics at about  $500^\circ C$ . is presumably too slow to account for their production during the 2 or 3 seconds that the resin is heated above 300 or  $400^\circ C$ . DHONT has pyrolyzed a wide variety of pure compounds over "Chromosorb" at  $550^\circ C$ ., the products being immediately analyzed by gas-liquid chromatography<sup>3</sup>. Compounds containing a benzene ring (such as benzyl alcohol) yielded benzene as a pyrolysis product. Aliphatic compounds yielded no benzene under these conditions.

From the pyrolysis results, it would appear that the resin molecule contains isolated benzene rings joined together by saturated, fused multi-ring systems with saturated bridge carbons, including quaternary carbons. From previous work on the resins as well as the non-resinous portions of the tar, it is known that the great majority of alkyl groups on aromatic rings are methyl groups, with very small amounts of ethyl and propyl groups, and negligible amounts of butyl groups. Thus alkyl groups could contribute products only to the permanent gases, in particular methane. The aliphatic compounds above  $C_4$  in the pyrolysis products must therefore come from internal structures, that is, ring structures, rather than side chains.

A resin molecule containing as part of its structure a unit like 5,6,6a,7,8,12b-hexahydro-6,7-dimethylbenzo[c]phenanthrene could conceivably split up (with, of course, transfer of hydrogen from other structural units) to form 2,3,4-trimethylpentane, as shown in Figure 3. Only those methyl groups required for the formation of 2,3,4-trimethylpentane are shown; additional methyl groups would be present, as determined in previous work<sup>1</sup>. One of the benzene rings in this unit could be released as such, or both benzene rings could be incorporated in the formation of the pyrolysis residue or char. The fact that the resins are rich in oxygen (10 to 15 weight-percent) whereas no oxygen-containing organic compounds could be identified in the volatile pyrolysis products would indicate that the oxygen-containing units in the resin (primarily benzene rings with phenolic hydroxyl groups) are involved in char formation. Under these circumstances, there would be a greater proportion of aliphatic compounds than aromatic compounds in the volatile products, such as was actually observed.

Although the pyrolysis results might appear unusual or unexpected, nevertheless the general structure of the resins indicated by these results is the same as that indicated by ring analysis (including ring arrangement), infrared spectra, and ultraviolet spectra<sup>1</sup>.

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(Grateful acknowledgment is made to W. C. Warner for obtaining many of the infrared spectra in this work.)

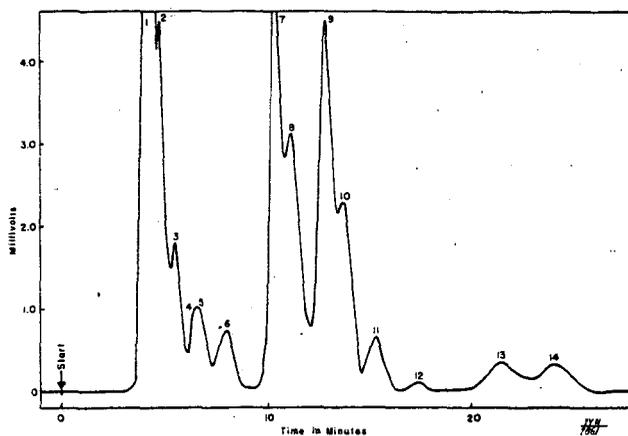


Figure 2. Chromatogram of pyrolysis products from a subbituminous resin.

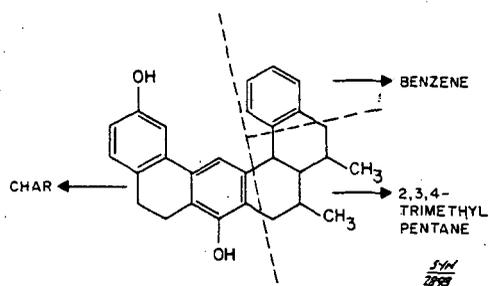


Figure 3. A representation of the pyrolysis of a hypothetical resin molecule.

THE STRUCTURE OF PETROLEUM ASPHALTENES  
AS INDICATED BY PROTON MAGNETIC RESONANCE

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### Introduction

Proton magnetic resonance has been used in the past to provide information on the structure of asphalt fractions. In a paper by R. B. Williams,<sup>1</sup> the proton magnetic resonance data are combined with infrared data to yield information suggesting the size of the clusters of aromatic rings in a number of asphalt fractions, including asphaltenes. Gardner, Hardman, Jones, and Williams<sup>2</sup> used proton magnetic resonance to provide information on the structure of thermal diffusion fractions of petroleues from an asphalt.

In the present study, the proton magnetic resonance data have been combined with other analytical data and contributions from the literature to yield information about the structures of four asphaltenes. The four asphaltenes include two asphaltenes from asphalt crude oils, an asphaltene produced by air blowing, and another produced through a cracking process.

### Proton Magnetic Resonance Data

Proton magnetic resonance spectra were obtained on a Varian Model A-60 NMR spectrometer at 14,090 gauss. The solvent used was carbon disulfide. Spectra used as a basis for quantitative analysis were taken with a sweep width of 1000 cycles per second, a sweep time of 250 seconds, an RF field of 0.08 milligauss, and a filter band width of one cycle per second.

Characteristic spectra for the four asphaltenes are given in Figures 1, 2, 3, and 4. The horizontal scale of the spectra, labeled PPM, shows the "chemical shift" downfield from a reference material, tetramethylsilane, at which the various proton types appear. The magnitude of the shift is expressed in parts per million of the reference field, 14,090 gauss.

The Varian A-60 spectrometer resolves the hydrogens into four classes. These classes are methylene, methyl, benzylic, and aromatic. Aromatic protons are seen at 6.5 to 8 ppm. Benzylic protons appear at 2 to 3 ppm. The methylenic hydrogens give the tall peak at 1.2 ppm, while the methyl protons produce the peak at 0.8 ppm on the shoulder of the methylene peak.

The amplitude of the peaks is governed by the concentration of the particular hydrogen type and also by the instrument settings. Thus, it has no absolute value and the spectra have a purely arbitrary vertical scale. For the purposes of this study, only the intensity of the various peaks relative to that of the methylene peak is required.

Encl.-Tables I and II  
Figures 1 through 8  
(RD 622541, RD 622542,  
RE 622497, RE 622498,  
RD 622499, and RE 622500)

The peaks obtained were compared by planimetry. The repeatability in the area measurement obtained this way was better than 1% in the case of the large peaks. For the smallest peaks, such as that due to the aromatic proton of the asphaltene from the air-blown California residuum, the repeatability was + 6% to 8%. The peak from the aromatic proton of the Venezuelan asphaltene was too small to measure. The error in repeatability of the spectra themselves was negligible.

Figure 1 shows the spectrum of an asphaltene from a Venezuelan crude oil which is widely used for asphalt manufacture. Figure 2 is the spectrum of an asphaltene from a crude oil of the San Joaquin Valley Area in California. This oil is also widely used for asphalt manufacture. The spectrum of Figure 3 is that of an asphaltene produced by laboratory air blowing at 475° F of the residuum from the California crude oil of Figure 2. In this process, about 85% of the total asphaltenes contained in the air-blown asphalt are formed in the air-blowing process. Figure 4 shows the spectrum of the benzene soluble, heptane insoluble asphaltenes produced in cracking the California residuum of Figure 2. This cracking was done by a refinery thermal cracking unit operating at a temperature of 900° F.

Analytical data on these asphaltenes are given in Table I. It is recognized that asphaltenes are heterogeneous substances and that these data, therefore, refer to the average composition. However, it is not possible to deviate very widely from these analytical results and still have asphalt fractions which retain the solubility characteristics of the asphaltene class.<sup>3</sup>

The areas under the peaks of Figures 1, 2, 3, and 4 were measured for each of the classes of protons to give a quantitative measure of the relative amounts of each type of proton present. The base line for these areas is that of the minimum shown in the spectra between the peaks for the aromatic and benzylic protons.

The areas so obtained were all divided by the area for the methylenic protons in that particular spectrum to provide ratios between the amounts of the different proton classes present. These ratios are given in Table II.

#### Average Molecular Structures

Using the ratios between the four classes of hydrogens and other chemical and physical data, one can construct formulas which are consistent with these data. This has been done to provide the average molecular structures of Figures 5, 6, 7, and 8. The ratios between the hydrogen types shown on the figures are those of the molecular structures drawn. They fit as closely as was possible the data of Table II on the asphaltenes.

A brief justification for the drawing of average asphaltene molecules may be desired at this point. It is recognized that asphaltenes are a heterogeneous classification and that the possibilities for variation from molecule to molecule are almost infinite. Also, the average structure of various fractions from asphaltenes will differ. Nevertheless, there is an over-all average ring size, an average content of polar atoms, and some arrangements which are preferred over others. For the very reason that the individual molecules are different, we are forced to consider average structures. We believe that these are sufficiently helpful in giving a general idea of the nature of the species to overcome the criticism that they are only average structures.

Among the pertinent literature which is drawn upon to arrive at the structures portrayed may be cited the high mass spectrograph data of Clerc and O'Neal<sup>4</sup> on

asphalt, wherein polynuclear aromatic ring systems were identified and also the work of Carlson and O'Neal<sup>5</sup> on heavy petroleum compounds wherein it was deduced that the rings in these compounds were condensed together and that the aliphatic portion of the molecule was primarily one long chain. Sergienko and Pustil'nikova<sup>6</sup> and Fischer and Schramm<sup>7</sup> have conducted hydrogenation experiments on asphalts leading to the conclusion that sulfur and oxygen compounds form the majority of the connecting links between segments of the asphaltene molecules. Goppel and Knotnerus<sup>8</sup> deduced from chemical analyses that three fifths of the bonds formed in the air-blowing process were ester bonds. Evidence that the nitrogen in asphaltenes is primarily included in the condensed ring portion of the molecule was provided by the studies of Ball, et al.<sup>9</sup> Additional evidence regarding the types of oxygen containing functional groups was provided by Knotnerus.<sup>10</sup> X-ray diffraction studies by Erdman and coworkers<sup>11</sup> indicated that the asphaltenes consisted of systems of polynuclear aromatic plates carrying side chains and connecting links of paraffinic nature. The size of the condensed ring systems in the molecules of Figures 5 through 8 is consistent with Erdman's X-ray diffraction data.<sup>11</sup>

The molecular weights of the asphaltenes of this study were not determined. They are assumed to fall in the range between 2000 and 3000 molecular weight which is indicated by recent research<sup>12,6,7,13</sup> on asphaltene molecular weights. In systems where association of the asphaltenes can occur, extremely high molecular weights, up to 500,000, can be obtained.<sup>12</sup> However, where conditions of the determination are such as will minimize asphaltene association, the values appear to fall in the vicinity of 2000 to 3000.<sup>6,7,13</sup> A lower molecular weight is assumed for the cracked tar asphaltene, as it is derived by degradation of natural asphaltenes with breaking off of side chains and aliphatic connecting links between ring systems.

The air-blown asphaltene of Figure 7 is purposely shown less condensed than the natural asphaltenes (Figure 5) as the air-blown asphaltenes are made by condensation and aromatization of the smaller and less polar resin molecules. The natural asphaltenes may also polymerize; however, in the air-blown California residuum the bulk of the asphaltenes come from nonasphaltene precursors. Ester links between the segments are shown in accordance with the findings of Goppel and Knotnerus.<sup>8</sup> We suspect that these ester groups arise from the rearrangement of peroxide links which formed originally through the coupling of free radicals produced by the reaction with oxygen.

The cracked tar asphaltene of Figure 8 is related to the natural asphaltene of Figure 6 and can be made from it by aromatizing portions of the ring system of Figure 6 and by breaking off aliphatic fragments from the natural asphaltene. These processes are known to occur in cracking of petroleum hydrocarbons.

A few hypothetical structures for asphaltenes have been presented in the literature. None of these is entirely consistent with the proton magnetic resonance data reported in this paper. The asphaltene drawn in a previous paper by Winniford<sup>3</sup> contains too much benzylic hydrogen and not enough methyl hydrogen. That drawn by Carlson, et al,<sup>14</sup> is much too low in methylene hydrogen and also has too much benzylic and not enough methyl. The structure drawn by Gardner, Hardman, Jones, and Williams<sup>2</sup> for their petroleum Fraction No. 10 is a near asphaltene in chemical composition; but its loose structure contains far too much aromatic hydrogen for an asphaltene and probably, therefore, it should be drawn as a more compactly condensed molecule. The structure drawn by Given<sup>15</sup> for bituminous coals cannot be correct for petroleum asphaltenes as it contains far too much oxygen and shows no methyl or methylene hydrogen at all.

The chemical nature of asphaltenes can by no means be considered settled by the brief results of this study. It is not believed that large deviations from

these results on the ratios of various classes of hydrogen will be found. However, more information is needed on the nature of links between the ring systems and on the size of the ring systems. Also, the disposition of the heterocyclic atoms, oxygen, sulfur, and nitrogen should be further clarified.

#### Acknowledgment

The authors wish to express their appreciation to the American Bitumuls and Asphalt Company for their support of this work.

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:caf

TABLE I  
ANALYTICAL DATA ON ASPHALTENES

<u>Per Cent</u>	Asphaltene			
	Venezuelan	Californian	Air-Blown Californian	Cracked Californian
Carbon	81.17	85.54	86.22	88.43
Hydrogen	7.86	8.08	8.22	6.63
Nitrogen	2.02	3.33	2.0	2.08
Sulfur	6.89	1.28	1.89	2.24
Oxygen	2.02	2.48	3.74	0.62
Carbon/Hydrogen Ratio	0.86	0.89	0.88	1.12

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TABLE II

RATIOS OF THE AMOUNTS OF METHYLENIC,  
METHYL, BENZYLIC, AND AROMATIC PROTONS  
SHOWN BY THE PMR SPECTRA

	Venezuelan	Californian	Air Blown Californian	Cracked Californian
Methylene	1.00	1.00	1.00	1.00
Methyl	0.39	0.60	0.90	0.49
Benzylic	0.29	0.45	0.44	0.72
Aromatic	Trace	0.19	0.16	0.66

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FIG. 1  
ASPHALTENE FROM VENEZUELAN  
CRUDE OIL

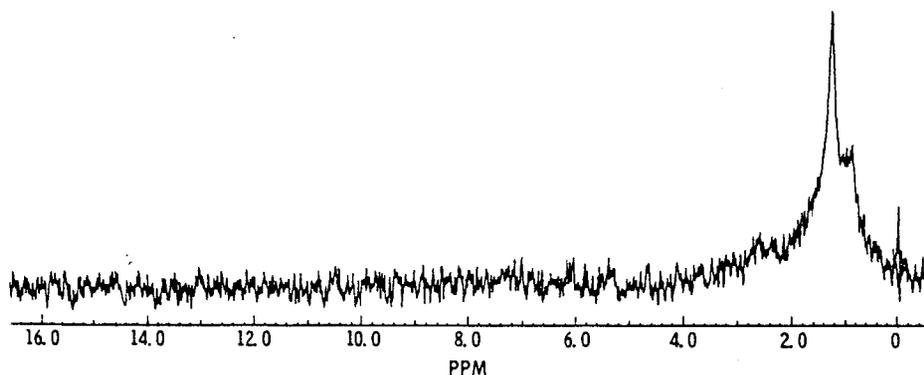
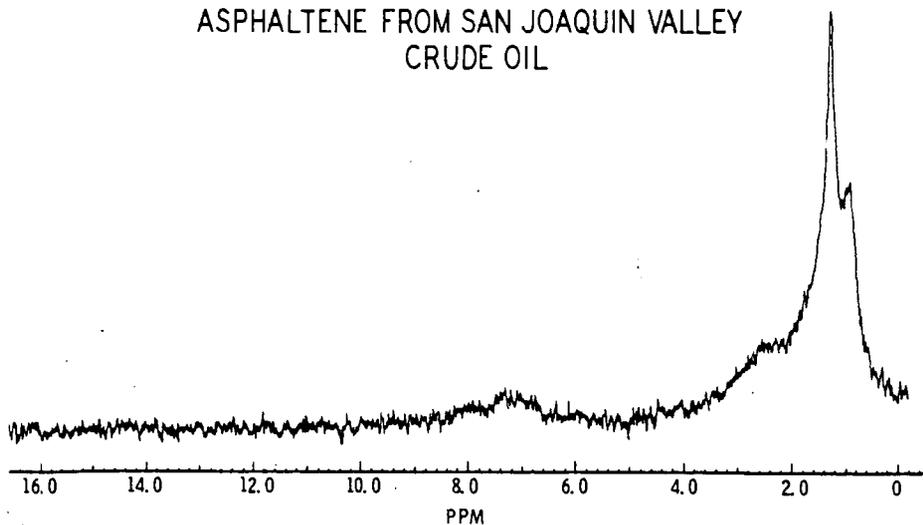


FIG. 2  
ASPHALTENE FROM SAN JOAQUIN VALLEY  
CRUDE OIL



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FIG. 3  
ASPHALTENE FROM AIRBLOWN  
SAN JOAQUIN VALLEY RESIDUUM

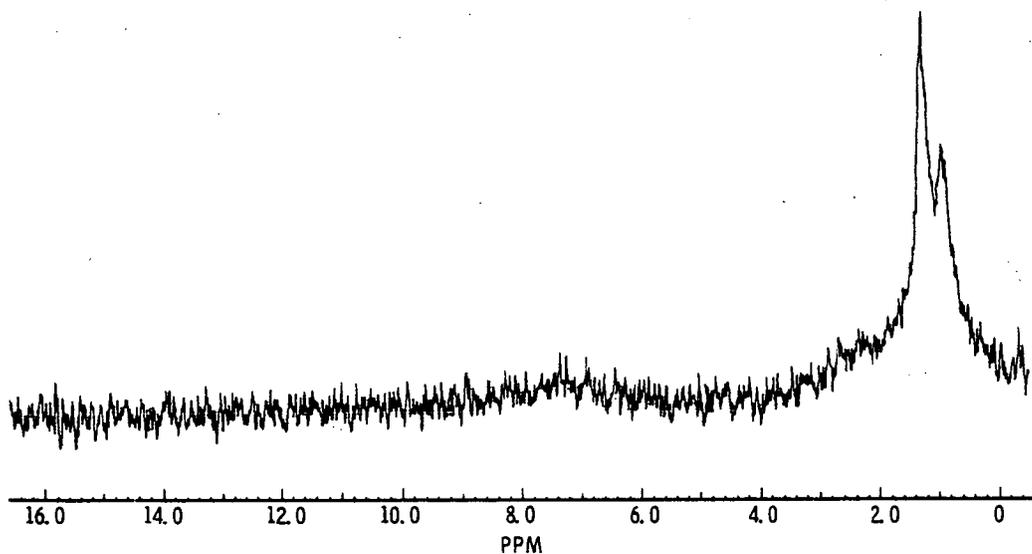
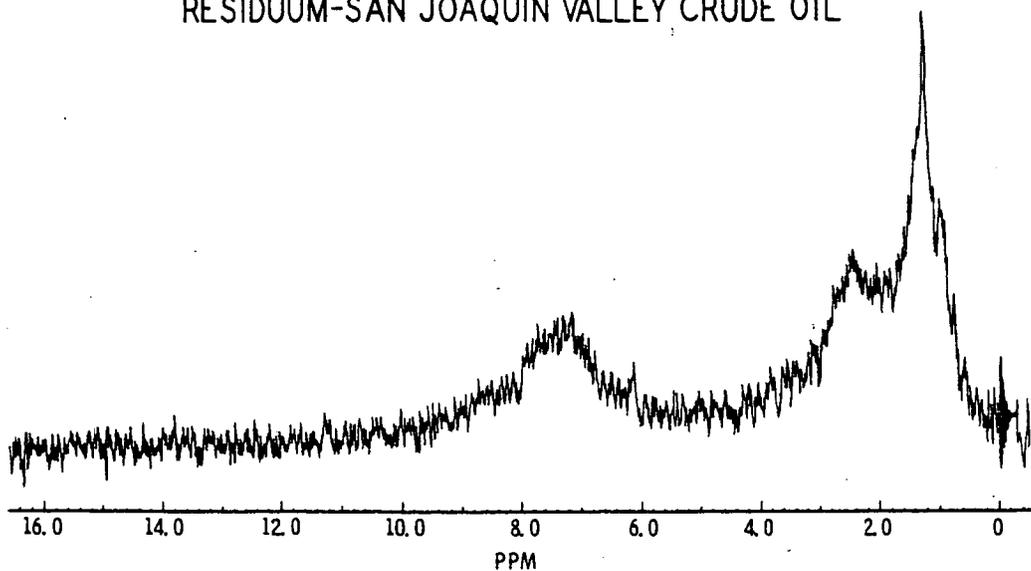


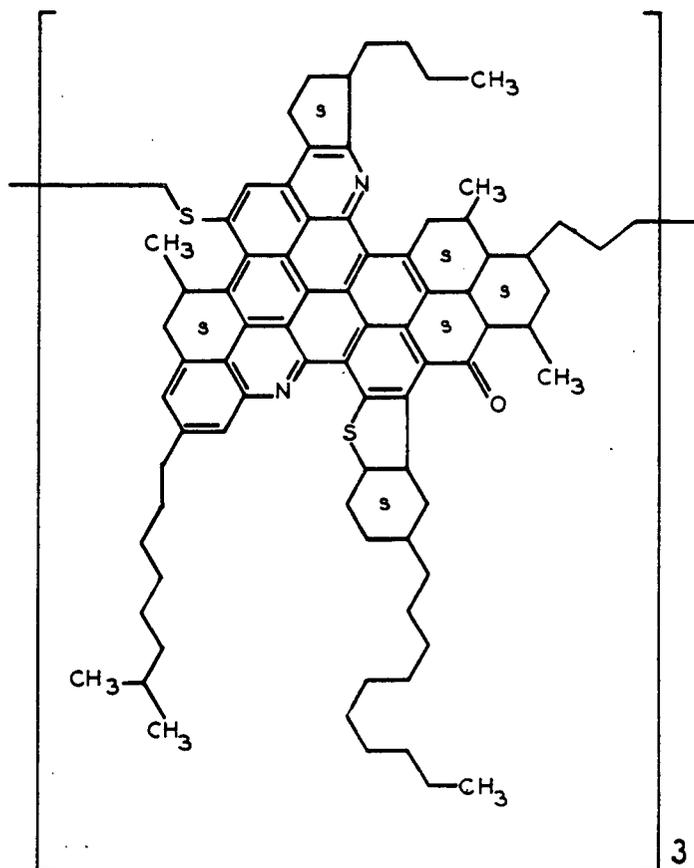
FIG. 4  
ASPHALTENE FROM THERMALLY CRACKED  
RESIDUUM-SAN JOAQUIN VALLEY CRUDE OIL



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FIG. 5  
 ASPHALTENE FROM VENEZUELAN  
 CRUDE OIL



$(C_{79}H_{92}N_2S_2O)_3$   
 Mol Wt 3449

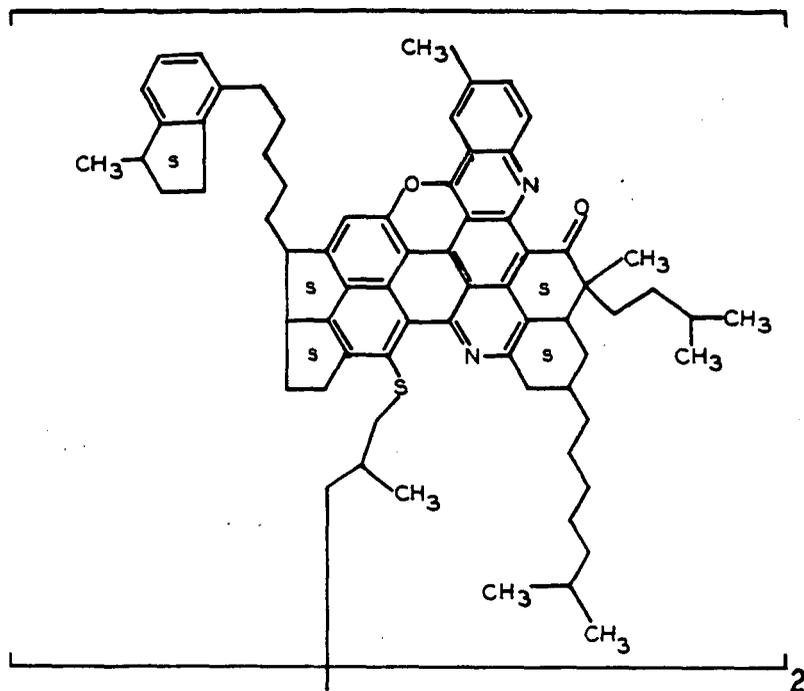
**Hydrogen Distribution**

Ratios	
Methylene	1.00
Methyl	0.40
Benzyllic	0.28
Aromatic	0.06

**Composition**

% C =	82.5
% H =	8.0
% N =	2.5
% O =	1.4
% S =	5.6
C/H Ratio =	0.86

FIG. 6  
 ASPHALTENE FROM SAN JOAQUIN  
 VALLEY CRUDE OIL



$(C_{70}H_{79}N_2O_2S)_2$   
 Mol Weight 2024

Hydrogen Distribution  
 Ratios

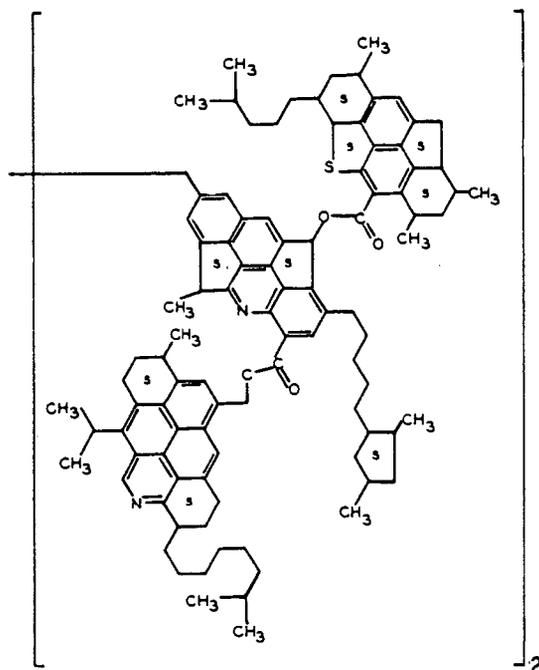
Methyl	0.58
Methylene	1.00
Benzylic	0.42
Aromatic	0.19

Composition

% C =	83.0
% H =	7.8
% N =	2.8
% O =	3.2
% S =	3.2
C/H Ratio =	0.89

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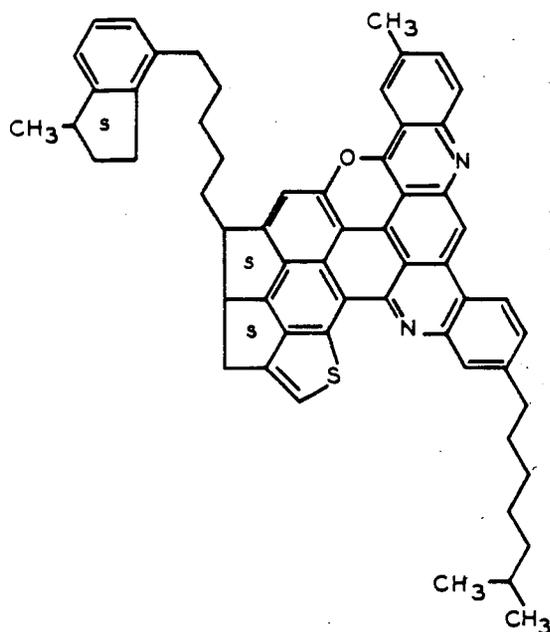
FIG. 7  
 ASPHALTENE FROM AIRBLOWN SAN JOAQUIN  
 VALLEY RESIDUUM



$(C_{98}H_{113}N_2O_4S)_2$   
 Mol Weight 2830

Hydrogen Distribution Ratios		Composition	
Methylene	1.00	% C =	83.1
Methyl	0.89	% H =	8.1
Benzylic	0.47	% N =	2.0
Aromatic	0.18	% O =	4.5
		% S =	2.3
		C/H Ratio =	0.87

FIG. 8  
 ASPHALTENE FROM THERMALLY  
 CRACKED RESIDUUM-SAN JOAQUIN VALLEY  
 CRUDE OIL



$C_{59}H_{54}N_2SO$   
 Mol Wt 838

Hydrogen Distribution  
 Ratios

Methylene	1.00
Methyl	0.47
Benzyllic	0.74
Aromatic	0.63

Composition

% C =	84.5
% H =	6.4
% N =	3.3
% S =	3.8
% O =	1.9
C/H Ratio =	1.09

PROTON MAGNETIC RESONANCE SPECTROMETRY  
IN THE CHARACTERIZATION OF COAL-TAR PITCHES

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Introduction

Coal-tar pitch is the residue, boiling at temperatures above 350° C, from the fractional distillation of coal tar. Although it constitutes about 50% of the tar yield from high-temperature carbonization in coke ovens, its chemical composition is not nearly as well known as that of many of the smaller, more-volatile fractions. Coal-tar pitch has numerous large-scale uses, some of which call for modification of the material by physical or chemical techniques. However, much of this modification is empirical to the extent that the results are measured in terms of efficacy for a specific end-use rather than in terms of change in chemical structure. Additional investigations of the chemistry of this rather intractable material are desirable toward developing new uses and placing pitch-treating procedures on a more scientific basis. With the development of proton magnetic resonance (PMR) techniques, a promising method of examining the types of hydrogen in pitches became available. Attention was therefore turned to the results which might be obtained by PMR examination of pitches.

Chemically speaking, pitch cannot be considered as a single type, but rather there are large differences between pitches, depending upon their source. Coke-oven pitches, which are of primary concern in this paper, are produced from high-rank (coking) coals at very high temperatures (1000° to 1300° C). The severe conditions control the product so that coke-oven pitches constitute a narrow class among coal-tar pitches, as indicated by Volkmann.<sup>1</sup> They are the most aromatic of the pitches, and a precise aromaticity determination is necessary to distinguish one from another.

The aromaticity of a pitch can be defined by two parameters. One is the ratio of the aromatic structures to the whole pitch. The other is the degree of condensation of the aromatic portion. This degree of condensation could range from the polyphenylene- to the graphite-type. Aromaticity factors can be calculated from various types of data, including density, atomic C/H ratio, and the ratio of aromatic hydrogen (Har) to total hydrogen (H). The latter is the most sensitive method for highly aromatic materials like coke-oven pitches, since the proportion of non-aromatic hydrogen atoms is greater than that of non-aromatic carbon atoms. For example, methylphenanthrene with 6.7% non-aromatic carbon atoms has 25% non-aromatic hydrogen atoms.

Considerable work has been reported toward establishing an infrared Har/H measurement,<sup>2,3,4,5,6</sup> but more detailed and reliable data are reported from PMR measurements.<sup>2,6,7,8,9</sup> Three types of hydrogen were estimated in pitch-like materials by PMR methods: aromatic hydrogen (Har); hydrogen on saturated carbon alpha to aromatic rings, or alpha hydrogen (H<sub>α</sub>); and hydrogen on other saturated hydrocarbon structures, or beta hydrogen (H<sub>β</sub>). Both Brown and Ladner<sup>2</sup> and Oth and Tschamler<sup>8</sup> were able to calculate structural parameters for pitch-like materials through the use of such PMR data.

For structural analysis, Brown and Ladner's<sup>2</sup> method appeared especially suitable for adaptation to coke-oven pitch. Details of the structure of the aromatic portion of their pitch-like materials were derived by subtracting the non-aromatic atoms from the whole. This introduced an uncertainty by requiring an estimate of the H/C ratio in the substantial fraction of non-aromatic structures. Nevertheless, the parameters of their distillates proved to be functions of the ranks of the parent coals. Coke-oven pitches in this analysis should enjoy the advantage of a very low proportion of non-aromatic structures.

Rao, Murty, and Lahiri<sup>6</sup> reported the use of the PMR spectrum in the characterization of the 65 weight per cent carbon disulfide-soluble fraction of a pitch that was evidently of coke-oven origin. Only 22% of the hydrogen was non-aromatic, and 70% of the non-aromatic hydrogen was of the alpha type. They concluded that the non-aromatic hydrogen was mostly present as methylene-, methyl-, and small alkyl-substituents on aromatic ring systems.

This paper describes the application of PMR spectrometric methods to the determination of certain aspects of the chemical structure of coke-oven pitches.

### Experimental

A series of coke-oven pitches representing a wide range of electrode-binder properties with a narrow range of softening points and, for comparison purposes, a low-temperature-carbonization pitch from a sub-bituminous B coal were selected. The analytical data for these pitches, together with the sources and methods of preparation, are summarized in Table I.

A.C.S. reagent-grade carbon disulfide was used to prepare the pitch extracts for the PMR determinations. The internal PMR standard was Anderson Chemical Division of Stauffer Chemical Company's "pure" grade of tetramethylsilane (TMS). The reference compounds were fluorene, m.p. 114-116° C (lit., 115-116° C), and acenaphthene, m.p. 93-94° C (lit., 95° C).

#### Carbon Disulfide-Soluble Fractions of Pitches

The carbon disulfide-soluble PMR spectra samples were prepared in the following manner: Samples of the pitch weighing 5.00 g. and sized to pass a 20-mesh sieve were added to 50 ml. of carbon disulfide in a 250-ml. beaker with stirring. The beaker was covered with a watch glass, and the magnetic stirring was maintained for 30 minutes. After collecting the insolubles on a 60-ml., medium-porosity fritted-glass funnel and washing with 25 ml. of carbon disulfide, the solids were air-dried and weighed. The filtrate and washings were concentrated on the steam bath (in a hood) to give a 60% weight/volume (w/v) solution. Samples of this solution and of dilutions made up as needed were placed in Varian A-60 Spectrometer sample tubes, and a trace of TMS was dissolved in each sample.

#### Determination of PMR Spectra

The PMR spectra were recorded on a 10 in. by 20 in. record sheet using a Varian A-60 Spectrometer. The samples were spun rapidly at room temperature, and the spectra were traversed slowly (sweep time 500 sec.) from 550 to 50 cycles per second (c.p.s.) below the TMS line (the increasing-frequency convention was observed). Radio-frequency (RF) power settings were intermediate—between 0.04 and 0.20 milligauss (mG.)—and filter bandwidth was usually set at 1 c.p.s.

#### Determination of the Integrals of the PMR Spectra

After plotting a spectrum, the integral of the curve was recorded electronically in a 10 in. by 20 in. area of chart, using the same sample and conditions,

with the exceptions and precautions noted below (see Figure 1). Care was necessary to insure both stability of the integral and non-saturation of any of the sample protons. To avoid saturating sample protons, the RF energy was kept below a setting of about 0.4 mG., while the sweep time was set down to 50 or 100 seconds. Saturation of a particular proton would result in an area under its absorption band less than proportional to the number of protons represented. Three factors were used to obtain stable integrals. The use of only the most concentrated, the 30 and 60% w/v, solutions for integrals was important. Also, the sweep time was reduced to 50 or 100 seconds, and finally, it was sometimes advantageous to increase the RF power.

#### Estimation of Hydrogen Types from PMR Integrals

Quantitative estimation of the hydrogen types involved measurement of the integral heights at the following frequencies (tau values; see Figure 1): for aromatic hydrogen together with phenolic hydrogen (H<sub>ph</sub>), approximately 4.5 tau; for alpha<sup>2</sup> hydrogen (H<sub>α<sup>2</sup></sub>; this is hydrogen on any carbon atom which joins two aromatic rings), 6.60 tau; for alpha hydrogen, approximately 8.1 tau; and for beta hydrogen, the end of the spectrum (about 9.2 tau). These boundary tau values were equivalent to the following frequencies in c.p.s. below TMS: about 4.5 tau, near 315 c.p.s.; 6.60 tau, 190 c.p.s. for 30% and 180 c.p.s. for 60% w/v solutions; and 8.1 tau, 110 c.p.s. for both 30 and 60% solutions. The considerations which led to the choice of these frequencies will be discussed in the following section.

#### PMR Frequencies (Tau Values)

The use of dissolved TMS eliminated volume susceptibility corrections<sup>10</sup> and interference by the standard in regions where the pitch components absorbed. It did not, however, prevent anomalous aromatic medium effects<sup>11</sup> from interfering. The spectra of different concentrations of pitch fractions in carbon disulfide showed frequency differences as great as 0.40 p.p.m. (tau units). To eliminate these effects, extrapolation to infinite dilution with the internal standard was necessary. This procedure with CS<sub>2</sub> extracts of pitches 1 and 2 gave smooth curves and infinite dilution frequencies for various absorption components of the spectra (see Figure 2).

The use of carbon disulfide provided a pitch solvent with Van der Waals deshielding effect about the same as that of carbon tetrachloride,<sup>12</sup> the tau solvent. Therefore, the infinite dilution frequencies should be very nearly true tau values,<sup>13</sup> in which form they are herewith reported. This was confirmed by the value of 6.68 tau thus obtained for the methylene line of acenaphthene in pitch (lit., 6.66 tau).

The choice of the frequencies listed in the preceding section to divide between the four types of hydrogen was made in the following manner: There was a broad region of zero signal between aromatic and non-aromatic bands, centering in the 4.5 tau region. The alpha<sup>2</sup> hydrogen, since it is close to two rather than one aromatic ring, is more deshielded than alpha hydrogen. Thus, the alpha<sup>2</sup> hydrogen absorption occurs at lower tau values (frequencies). The boundary was chosen just below the acenaphthene methylene peak at 6.66 tau because this is an intermediate type between alpha and alpha<sup>2</sup>, although it is formally alpha hydrogen. Conservatively, then, absorption below 6.60 tau was attributed to alpha<sup>2</sup> hydrogen. The anomalous shifts due to changes in pitch concentration necessitated the use of the two frequencies. For the boundary between alpha and beta hydrogen, the spectrum of pitch 7, which showed separate absorption maxima for beta and for alpha hydrogen types, was considered (see Figure 3). The minimum between these maxima occurred at about 8.2 tau. To avoid overestimating alpha hydrogen, a value near 8.1 tau was chosen. This includes types such as durene methyl groups (7.86 tau) and excludes such types as Me<sub>3</sub>CH (8.44 tau) and cyclohexane (8.56 tau).

Molecular Weight Determination

Molecular weight measurements were ebullioscopic with incremental addition of sample and extrapolation to infinite dilution. Solvents were benzene and freshly prepared chloroform, depending upon the solubility of the sample. Interference by foaming or incomplete solubility prevented determination of molecular weight in certain cases (see Table II).

Structural Parameters

From PMR and elementary analytical data, Brown and Ladner<sup>2</sup> were able to calculate the following average structural characteristics of their pitch-like materials:

$f_a$ , the ratio of aromatic carbon ( $C_{ar}$ ) to total carbon ( $C$ ),

$\sigma$ , the fraction of the total available outer-edge positions of the aromatic skeleton which is occupied by substituents, and

$H_{ar}/C_{ar}$ , the atomic H/C ratio that the average aromatic skeleton would have if each substituent were replaced by a hydrogen atom.

Brown and Ladner developed the following equations for calculating these parameters:

$$f_a = \frac{\frac{C}{H} - \frac{H_{\alpha}^*}{x} - \frac{H_{\beta}^*}{y}}{\frac{C}{H}} \quad (1)$$

$$\sigma = \frac{\frac{H_{\alpha}^*}{x} + \frac{O}{H}}{\frac{H_{\alpha}^*}{x} + \frac{O}{H} + H_{ar}^*} \quad (2)$$

$$\frac{H_{ar}}{C_{ar}} = \frac{\frac{H_{\alpha}^*}{x} + \frac{O}{H} + H_{ar}^*}{\frac{C}{H} - \frac{H_{\alpha}^*}{x} - \frac{H_{\beta}^*}{y}} \quad (3)$$

where  $C/H$  and  $O/H$  are the atomic ratios, obtained from elementary analysis;  $H_{\alpha}^* = H_{\alpha}/H$ , the ratio of alpha-type hydrogen to total hydrogen obtained from PMR spectrometric analysis;  $H_{\beta}^* = H_{\beta}/H$ , the ratio of beta-type hydrogen to total hydrogen from PMR analysis;  $x = H_{\alpha}/C_{\alpha}$  and  $y = H_{\beta}/C_{\beta}$ , the atomic ratios of hydrogen to carbon in the alpha and beta structures, both of which must be obtained by estimate;  $H_{ar}^* = H_{ar}/H$ , the ratio of aromatic hydrogen to total hydrogen obtained indirectly from PMR spectrometry with the help of elementary analysis, assuming 60% of the total oxygen to be phenolic. Since phenolic hydrogen ( $H_{ph}$ ) is included in the "aromatic" hydrogen ( $H_{ar} + ph$ ) seen in PMR spectra,  $H_{ar}^*$  was calculated by the following equation:

$$\frac{(\text{Har} + \text{ph})}{\text{H}} - 0.60 \frac{\text{O}}{\text{H}} = \frac{\text{Har}}{\text{H}} = \text{Har}^*$$

They assumed that every oxygen atom was present as a substituent on an aromatic nucleus in completing the development of the above equations.

Their method for the conversion of the hydrogen distribution in coal-like materials to carbon structure was adapted for use with coke-oven pitches. Changes were made in the assumptions and equations as described below. It is accepted that 60% of the total oxygen is phenolic, but Brown and Ladner's assumption that all of the oxygen occurred as substituents on aromatic nuclei could not be justified for coke-oven pitches. Instead, the remaining 40% oxygen is assumed to occur not as aromatic substituents but in other forms, among which heterocyclic oxygen must be included. Alpha<sup>2</sup> hydrogen is included in the equations separately as  $\text{H}\alpha^2$ , with  $z = 2$  the estimated ratio of hydrogen to carbon in such groups, and  $\text{H}\alpha^{2*} = \text{H}\alpha^2/\text{H}$ . Because the predominant alkyl substituent in known coke-oven pitch components is the methyl group, the value of  $x$  (estimated H/C ratio for alpha structures) is raised from the value of 2 to 2.5. The value of  $y = 2$  is retained.

Considering equation (1), a term for alpha<sup>2</sup>-type carbon is added to its numerator, the number of aromatic carbon atoms, giving  $\text{C} - \text{C}\alpha^2 - \text{C}\alpha - \text{C}\beta$ . The resulting equation for coke-oven pitches is the following:

$$f_a = \frac{\frac{\text{C}}{\text{H}} - \frac{\text{H}\alpha^{2*}}{2} - \frac{\text{H}\alpha^*}{2.5} - \frac{\text{H}\beta^*}{2}}{\frac{\text{C}}{\text{H}}} \quad (4)$$

Considering equation (2), it is necessary to add a term for the contribution of alpha<sup>2</sup> structures to the total number of substituents. Since each bridge represents two substituents, this added term must equal  $2 \times \text{C}\alpha^2$ , which is  $2 \text{H}\alpha^2/z$ . To replace (2) for determining the degree of substitution of coke-oven pitches, the following equation is used:

$$\sigma = \frac{\text{H}\alpha^{2*} + \frac{\text{H}\alpha^*}{2.5} + 0.6 \frac{\text{O}}{\text{H}}}{\text{H}\alpha^{2*} + \frac{\text{H}\alpha^*}{2.5} + (\text{Har} + \text{ph})^*} \quad (5)$$

Similarly, equation (3) is replaced by the following equation for the atomic C/H ratio of the hypothetical unsubstituted average aromatic nucleus of coke-oven pitches:

$$\frac{\text{Car}}{\text{Haru}} = \frac{\frac{\text{C}}{\text{H}} - \frac{\text{H}\alpha^{2*}}{2} - \frac{\text{H}\alpha^*}{2.5} - \frac{\text{H}\beta^*}{2}}{\text{H}\alpha^{2*} + \frac{\text{H}\alpha^*}{2.5} + (\text{Har} + \text{ph})^*} \quad (6)$$

This degree-of-condensation parameter is also the ratio of total aromatic carbon to aromatic edge-carbon.

Equations 4, 5, and 6 were used to calculate parameters for the carbon disulfide solubles of eight pitches and for the carbon disulfide-soluble, n-hexane-insoluble (resin) fraction of one of the coke-oven pitches. The parameters of low-temperature-carbonization pitch 7 were calculated by means of equations 1, 2, and 3. Data and results are listed in Table II.

## Results and Discussion

### PMR Spectra of Coke-Oven Pitches

The carbon disulfide-soluble fractions of coke-oven pitches, using the Varian A-60 Spectrometer, showed hydrogen distributions in keeping with the reputed high aromaticity of these pitches. From 80 to 90% of their hydrogen was aromatic. The higher molecular weight resin fraction of pitch 2 had an even higher (95%) aromatic hydrogen content. This is in sharp contrast with the 20% of aromatic hydrogen in the low-temperature-carbonization pitch carbon disulfide-soluble fraction.

There were only two absorption maxima in the coke-oven pitch spectra: the aromatic- and the alpha-hydrogen bands. Both indicate types closely associated with aromatic rings. Reports on other pitches<sup>2,3,8</sup> have shown an additional band due to hydrogen not associated with any aromatic ring (beta hydrogen). Low-temperature-carbonization pitch 7 also fell in the latter category (see Figure 3), exhibiting two maxima in the beta hydrogen region. The total alpha and alpha<sup>2</sup> hydrogen in coke-oven pitches was never less than 79% of the non-aromatic hydrogen. Thus, only 21% of the non-aromatic and only 4.2% of the total hydrogen failed to show a close proximity to an aromatic ring.

In addition to the above considerations, which are based on tau values, there was the sensibility of the non-aromatic protons of the coke-oven pitches to the anomalous aromatic medium shifts. This is a further indication that these protons are held close to aromatic rings, since paraffins were insensitive to these effects.

### Individual Components

Without fractionating the pitches, it was possible in four cases to identify acenaphthene, and in two, fluorene, as components of the pitch. There is a possibility that yet other of the more abundant components could thus be identified, since a number of sharp individual peaks appeared in each spectrum. Two factors combined to confirm the conclusions as to identity. The first factor was the identity of the peaks in question with those of the added authentic compound at one concentration. The second factor was repetition of the same results at another concentration of the pitch in the solvent. Thus, the aromatic medium effect was shown to be the same for the authentic compound and the pitch component.

### Structural Parameters

A Brown-Ladner type of analysis of the PMR and elementary analytical data, together with molecular weight data, permitted the following conclusions regarding molecular structure (see Table II):

#### Carbon Aromaticity ( $f_a$ )

The coke-oven-pitch carbon disulfide-soluble fractions were estimated to contain only 2.5 to 5.7% non-aromatic carbon atoms ( $f_a = 0.975$  to  $0.943$ ). A contrast between coke-oven pitch 2 and low-temperature-carbonization pitch 7 is available through their resin fractions, which by calculation contained 1 and 33% non-aromatic carbon ( $f_a = 0.987, 0.67$ ), respectively.

#### Degree of Substitution ( $\sigma$ )

Only from 6 to 12 of every 100 available sites for substitution around the average nucleus were occupied by substituents in these coke-oven-pitch fractions ( $\sigma = 0.063$  to  $0.116$ ). The value was 2 per 100 lower ( $\sigma = 0.048$ ) in the larger molecular weight fraction of pitch 2. Such trends to less substitution in larger

molecules of pitch have been reported by other workers using other methods.<sup>14,15</sup> Again, comparison with pitch 7 serves to emphasize the high aromaticity of the coke-oven pitches. Sixty five per cent ( $\sigma = 0.65$ ) of the edge aromatic carbons were bonded to substituents in pitch 7 resin fraction.

#### C/H of the Aromatic Nucleus (Car/Haru)

The atomic C/H ratios of the average hypothetical unsubstituted aromatic nucleus (Car/Haru values) of the coke-oven pitches were, for carbon disulfide-soluble fractions, 1.5 to 1.7, and for the resin fraction of pitch 2, 1.83 (Table II). The interpretation of these numbers depends upon the molecular weight of the materials. With the molecular weights, the degree of condensation of the average aromatic nucleus was shown to be nearly linear (of the benzene-naphthalene-phenanthrene series: each ring fusion involves only two carbon atoms).

The average molecular weight of the carbon disulfide-soluble fraction was about 400. As a result, an average aromatic nucleus of 7 to 8 rings with one substituent was indicated. The resin fraction of pitch 2 with molecular weight 660 would indicate an average aromatic nucleus with near 13 rings and about 1.3 substituents.

To illustrate this, for the fractions of pitch 2, a type molecule was chosen as a possible structure for the average molecule, as shown in Table III. This suggests that the higher molecular weight fractions of coke-oven pitch, such as the C-1 sooty material, do not approach graphite in structure but may be mostly linearly condensed aromatic ring systems.

#### PMR Solvent

Carbon disulfide proved to be a good solvent for PMR examination of coke-oven pitches. The soluble fraction represented a large proportion—60 to 84%—of the total material. Solutions of concentrations up to 60% were readily available in this non-protonic solvent, permitting accurate quantitative work, and the infinite dilution values were very nearly true tau values.

#### Summary

Proton magnetic resonance spectrometry proved a useful method for the characterization of coke-oven pitch. The estimation of aromatic and three types of aliphatic hydrogen by this means made possible the formulation of a structure for the typical molecule in the carbon disulfide-soluble fraction. This was a linearly condensed aromatic nucleus with 2 to 6% of the carbon atoms occurring as substituents which were predominantly methyl groups. The average molecular weight was near 400, which was equivalent to 7 or 8 fused aromatic rings. Fluorene and acenaphthene were identified in several of the pitches. It is hoped that these methods will prove to be of value in a search for correlations between the chemical and physical properties of a coke-oven pitch and its efficacy in a particular industrial end-use.

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Table I

Analytical Data, Sources, and Methods of Preparing  
Experimental Pitches

<u>Pitch Designation<sup>a)</sup></u>	<u>Softening Point, °C, C.I.A. <sup>b)</sup></u>	<u>Benzene Insoluble, Wt. %</u>	<u>Quinoline Insoluble, Wt. %</u>	<u>Atomic C/H Ratio</u>
1	89.0	33.2	13.1	1.80
2	90.2	32.6	12.8	1.93
3	93.5	29.7	10.58	1.87
4	94.9	28.0	9.13	1.76
5	90.6	17.5	6.87	1.78
6	88.2	13.0	2.44	1.61
A	102.3	25.5	12.4	1.84
C	95.0	25.0	4.2	1.73
7	59.5	—	—	0.95

a) 1. Thermal treatment of a 74° C pitch at 380° C for 24 hours and back-blending with 9.1% of starting pitch. 2. Laboratory distillation of soft pitch from a production tar. 3. Laboratory distillation of 36.2 wt. % from a production tar. 4. Blend of 88.55 wt. % 105° C pitch (produced by distillation of light tar at 50 mm. to 300° C) with 11.45% of coal-tar distillate oil (boiling 230° to 270° C). 5. A production pitch after removal of n-heptane solubles. 6. Laboratory distillation of a 69° C pitch from light tar. A. Produced by plant distillation of production tar. C. Produced by adding quinoline to the parent tar of A, centrifuging this mixture to remove insolubles, and then distilling. 7. A 60° C pitch produced by blowing at 120° C a tar from low-temperature carbonization of a sub-bituminous B coal.

b) Cube-in-air method.

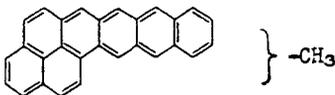
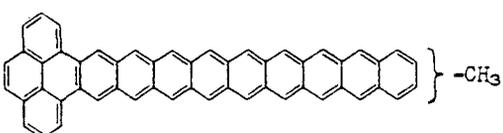
Table II  
Structural Parameters of Pitch Fractions

Pitch	2	3	A	5	C	4	1	6	7	
Pitch Analysis	93.41 4.07	93.31 4.18	93.22 4.24	92.55 4.38	93.29 4.52	92.88 4.44	93.34 4.36	91.35 4.77	76.94 6.81	
N, %								1.11	0.78	
S, %								0.73	0.29	
O (diff.), %	2.52	2.51	2.54	3.07	2.19	2.68	2.30	2.04	15.18	
Solvent Fraction*	2	2 + 3	2 + 3	2 + 3	2 + 3	2 + 3	2 + 3	2 + 3	2**	
Analysis of Fraction	92.87 4.34 2.79 1.80 0.040	92.92 4.69 2.42 1.66 0.032	93.09 4.88 2.02 1.65 0.026	92.70 4.72 2.57 1.58 0.034	92.50 4.91 2.58 1.58 0.033	92.48 4.83 2.68 1.61 0.035	91.80 4.90 3.30 1.57 0.042	92.00 5.18 2.81 1.49 0.034	91.10 5.13 3.61 1.49 0.044	75.84 6.12 18.04 1.04 0.186
Molecular Weight	660	386	370	---	421	459	---	379	455	
Yield of Fraction, Wt %	21.1	69.3	73.6	80.5	70.9	70.9	66.2	83.8	7.4	
Hydrogen Distillation	0.946 0.009 0.035 0.010	0.902 0.017 0.064 0.0146	0.902 0.017 0.068 0.0126	0.892 0.019 0.075 0.0136	0.903 0.016 0.074 0.014	0.890 0.018 0.082 0.011	0.864 0.022 0.098 0.017	0.856 0.025 0.096 0.024	0.802 0.024 0.1344 0.042	0.315 -- 0.382 0.303
Structural Parameters	fa σ Car/Maru	0.987 0.048 1.83	0.974 0.063 1.65	0.972 0.074 1.71	0.972 0.069 1.62	0.971 0.077 1.66	0.963 0.093 1.64	0.958 0.091 1.55	0.943 0.116 1.60	0.670 0.65 1.20

\* Solvent fraction 2 is the carbon-disulfide-soluble, n-hexane-insoluble fraction; fraction 2 + 3 is the carbon-disulfide-soluble fraction.  
 \*\* The original Brown-Ladner equations were used to calculate fu, σ, and Car/Maru for this low-temperature-carbonization pitch fraction.

Table III

Correlation of Structural Parameters in Pitch Fractions  
with Possible Type Molecules

PITCH #2 FRACTION or TYPE MOLECULE	PARAMETER VALUES FOR FRACTIONS AND TYPE MOLECULES				
	C/H	Mol. Wt.	fa	$\sigma$	Car/Haru
CS <sub>2</sub> -Soluble Fraction	1.66	386	0.975	0.066	1.71
 (C <sub>28</sub> H <sub>15</sub> -CH <sub>3</sub> )	1.61	364	0.965	0.062	1.75
Resin Fraction	1.80	660	0.987	0.048	1.83
 (C <sub>52</sub> H <sub>27</sub> -CH <sub>3</sub> )	1.77	666	0.981	0.036	1.86

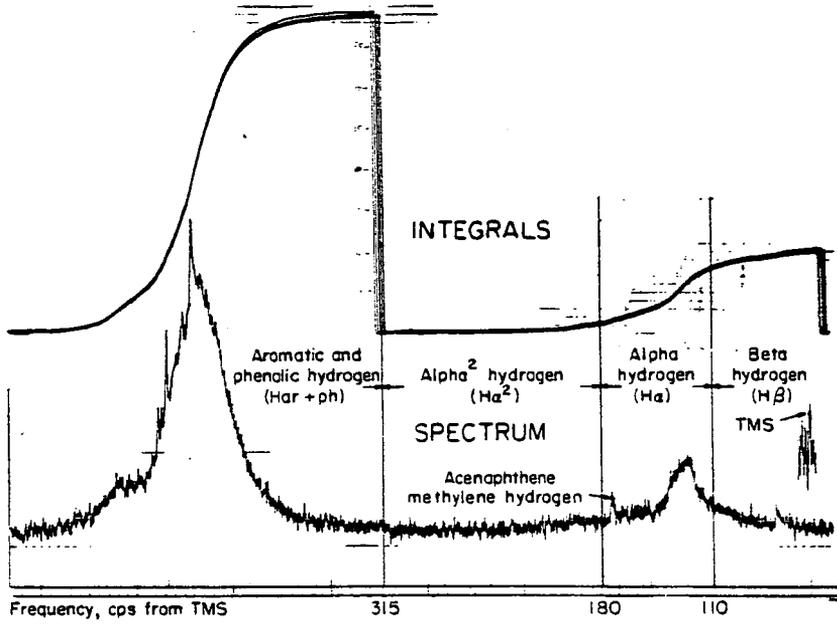


Figure 1. PMR Spectrum and Integrals: Pitch 6, Carbon Disulfide Solubles

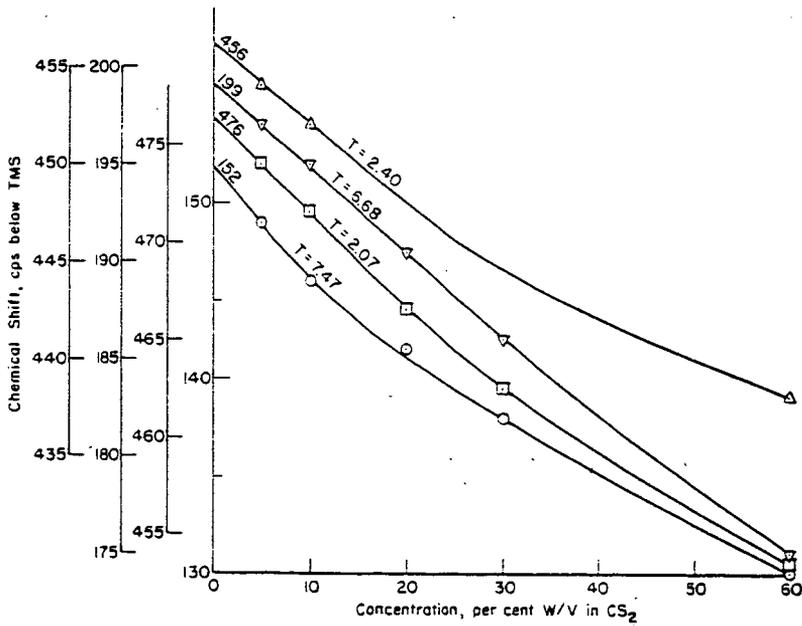


Figure 2. Extrapolation of PMR Frequencies to Infinite Dilution with an Internal Standard: Pitch 1 - CS<sub>2</sub> Extract

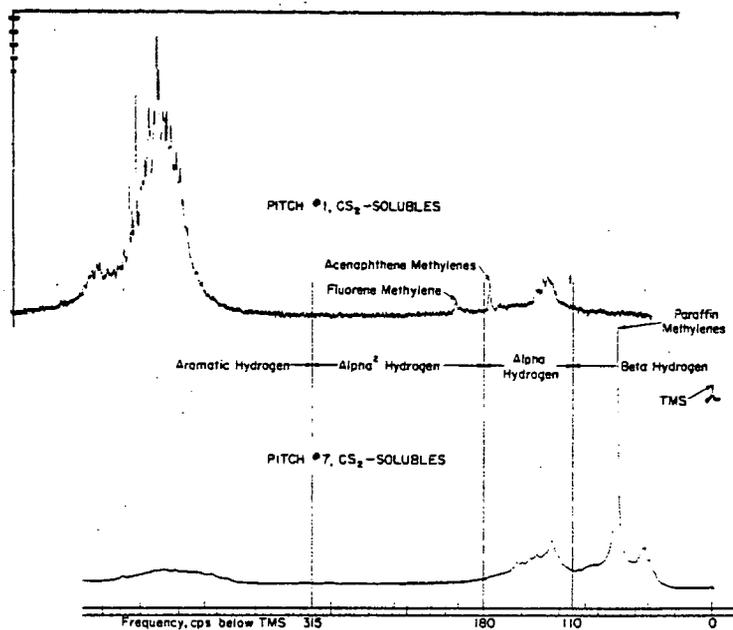


Figure 3. Comparison of PMR Spectra: Coke-Oven Pitch (No. 1) and Low-Temperature-Carbonization Pitch (No. 7); CS<sub>2</sub> Solubles, 60% w/v in CS<sub>2</sub>

THE USE OF THE BRABENDER PLASTOGRAPH IN STUDYING  
THE RHEOLOGY OF ELECTRODE MIXES

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Introduction

The performance of the continuous, self-baking Soderberg electrode, which is widely used in the production of primary aluminum, is closely related to the rheology of the carbon mix that is added to the top of the electrode. The fluidity must be sufficient to ensure an even distribution of the mix over the top of the electrode and to permit the mix to fill voids that are created when contact studs are removed. However, separation of the binder from the aggregate or difficulty in containing the mix in the sheet metal casing may result if the mix is excessively fluid.

Some investigators have attempted to obtain mixes with proper fluidity by studying the rheology of the binders with the assumption that the rheology of the mix is a function of the rheology of the binder.<sup>1)</sup>\* Others have investigated the rheology of the mix itself.<sup>2)</sup> The latter approach appears to be the more desirable because interactions between the binder and aggregate influence the rheological behavior of the mix.

A method in which a Brabender Plastograph is used for measuring the consistency of the Soderberg mix was described at a previous meeting of this division.<sup>3)</sup> In the development of the method at the Applied Research Laboratory of the U. S. Steel Corporation, a petroleum-coke aggregate was used that had a smaller size-consist than is commonly used in plant practice. The method has been extended to include the measurement of the consistencies (rheological measurements) of Soderberg mixes containing plant-scale aggregates.

The present paper presents typical results that were obtained in an investigation to (1) use the consistencies of mixes prepared with plant-scale aggregates to predict the optimum binder content for optimum electrode properties and (2) determine the influence of temperature and time in the Soderberg electrode on the consistency of the mix.

Experimental

The two electrode binders and the plant-scale petroleum-coke aggregate used in this investigation are representative of the materials in use at a carbon-paste plant. Some of the more common properties of the two binders are shown in

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\* See References.

Table I. The properties of the two binders are similar; however, Pitch B contains slightly more benzene- and quinoline-insoluble matter than Pitch A. Past-plant experience has shown that subtle but significant differences exist in the performance of the two binders: pastes prepared with Pitch B required the use of more binder for optimum electrode performance than Pitch A, and the electrodes produced with Pitch B performed better than the electrodes from Pitch A.

The plant-scale petroleum-coke aggregate was graded into the seven fractions shown in Table II. The appropriate weight of each fraction, corresponding to the percentage shown, was used in each binder-aggregate mix.

The major phases of the present investigation are as follows:

1. Determination of the maximum mix consistency for optimum binder concentration and optimum electrode properties. (The two binders were used in the preparation of mixes containing from 28 to 35 percent binder).
2. Investigation of the effect of mixing temperature and holding time on the mix consistency and electrode properties.

The Brabender Plastograph, shown in Figure 1, was used to prepare Soderberg mixes and measure their consistencies. A brief description of the operation of the instrument is given below. The sigma blades in the mixing head are driven by a dynamometer, which is suspended between floating bearings. The torque produced as the blades rotate in the mix at a constant rate of shear is transmitted to the dynamometer. The dynamometer translates the torque through a series of balance levers to a direct-reading balance, which is calibrated to indicate the torque in meter-gram units. A strip chart provides a continuous record of the consistency in terms of meter-gram units. Excessive movement of the lever system is dampened by an oil dash pot.

The mixing head has a working capacity of 650 milliliters. It is heated by recirculating hot oil from a constant-temperature bath through a jacket that surrounds the mixing head. A special insulated lid, not supplied by the instrument manufacturer, minimizes the loss of heat from the head and is an indispensable aid in maintaining the mix at a uniform temperature. Through a small opening in the lid, coke additions can be made without removing the lid.

In the determination of maximum mix consistency for optimum binder concentration and optimum electrode properties, mixes containing from 28 to 34 percent of Pitch A and mixes containing from 30 to 35 percent of Pitch B were prepared at 155 C. In all tests, the weight of the mix was held constant at 700 grams.

In the preparation of a typical mix, the calculated amount of binder is added to the preheated mixing head and is allowed to melt for eight minutes. The binder is then mixed for seven minutes to permit temperature equilibration. The 0.525-inch to 3-mesh fraction (preheated to 155 C) is then added through the opening in the insulated lid. The remaining fractions are added in the order of decreasing size at 5-minute intervals. This sequence of coke additions is used to (1) permit thorough wetting of the large coke particles before the addition

of fine particles to prevent uncoated fine particles from plugging the pores of the large particles and (2) minimize preferential absorption of binder by the fine particles. Mixing is continued for 30 minutes after the addition of the last coke fraction. The torque reading, in meter-grams, at the end of this mixing period is recorded as the consistency of the mix.

The temperature in the Soderberg electrode ranges from about 950 C at the lower working face to about 150 C at the top. As the electrode is consumed, it is lowered, and the unbaked mix in the upper end of the electrode is subjected to gradually increasing temperatures. To provide an indication of the effect of increasing temperature on the consistency of the mix and on the electrode properties, four mixes were prepared at temperatures between 155 C and 225 C. The optimum concentration of Pitch A was used with the mixing procedure previously described.

In the Soderberg electrode, temperature changes occur gradually, and a given portion of the unbaked mix may be subjected to a specific temperature for a relatively long period of time. The effect of time without mixing on the consistency of the mix was determined by repeating consistency measurements on the two mixes with the optimum concentration of Pitch A at 155 C and 225 C. At the conclusion of the normal mixing time, the mixer was stopped, and the mix was maintained at the mix temperature until the consistency approached the limit-of-scale value of 1000 meter-grams or 24 hours, whichever was shorter. Consistency measurements were recorded hourly.

All mixes were packed into perforated graphite molds and baked to 1000 C at a controlled rate of temperature rise in 24 hours. The baked electrodes were then tested for crushing strength and electrical resistivity. The procedure for baking and testing specimen electrodes has been described by Jones, Simon, and Wilt.<sup>4)</sup>

### Results and Discussion

The relationship between the mix consistency and electrode crushing strength at various binder concentrations is shown in Figure 2. To illustrate this relationship, the experimental data are plotted in bar-chart form. The lined bars represent the consistency of the mix at various levels of binder concentration, and the dotted bars show the crushing strength of specimen electrodes from those mixes. The number at the bottom of each bar represents the percentage of binder in the mix.

This chart indicates that the Plastograph is sufficiently sensitive to detect changes in binder concentration as small as 1 percent and that a good correlation exists between the mix consistency and the electrode crushing strength. As the percentage of binder increases within the limits shown, the consistency and crushing strength values pass through a maximum simultaneously. This relationship indicates that the mix-consistency measurement can be used to predict the optimum binder content for optimum electrode crushing strength. For Pitch A, the optimum binder content for optimum electrode crushing strength is 32 percent and for Pitch B, the optimum binder content is 34 percent. These results correlate well with carbon-paste-plant data on these two binders.

The relationship between the mix consistency and the electrical resistivity of specimen electrodes is shown in Figure 3. A good correlation also exists between these parameters. For each binder, as the consistency values pass through a maximum, the resistivity values pass through a minimum. This relationship further substantiates the premise that the mix-consistency measurement can be used to determine the optimum binder content for optimum electrode properties.

The effect of temperature on the mix consistency and electrode crushing strength is illustrated in Figure 4. The mixes, prepared with 32 percent of pitch A, show successive decreases in consistency as the temperature of the mix increases. The decreasing consistency results from increased fluidity of the binder at the higher temperatures. Simultaneously, the electrode crushing strength increases with higher mix temperatures and lower consistencies. The increase in strength is particularly pronounced between 200 C and 225 C. The higher crushing strengths apparently result from the increased fluidity of the mix. The method described here would provide a suitable means of determining the temperature susceptibility of mixes prepared with various binders.

A susceptibility index (SI) could be calculated with the following equation:

$$SI = \frac{(\text{Consistency at } 155 \text{ C}) - (\text{Consistency at } 225 \text{ C})}{\text{Consistency at } 175 \text{ C}}$$

A low value for the susceptibility index (approaching zero) is indicative of a mix that is not sensitive to temperature change, whereas a high susceptibility index would be obtained with a temperature-sensitive mix.

The effect of hold time without mixing at two temperatures on the mix consistency and electrode properties is shown in Table III. When the mix is maintained at 155 C for 7.5 hours, the mix consistency increases from 600 meter-grams to 1000 meter-grams. Substantial improvements in the electrode crushing strength and electrical resistivity are noted. Similarly, at 225 C, the mix consistency increases from 190 meter-grams to 600 meter-grams in 24 hours, with significant improvements in electrode properties. The increased consistency and improved electrode properties resulting from extended time at high temperatures may be due to an aging or curing of the binder that is initiated or accelerated by the presence of the carbon aggregate. Similar effects probably occur in the Soderberg electrode as the unbaked mix is subjected to elevated temperatures for extended periods of time.

The rheology of the mix in the upper portion of the Soderberg electrode is strongly influenced by temperature and by the length of time the mix is exposed to elevated temperatures. Increased temperature tends to decrease the mix consistency, whereas an extended holding time without mixing at elevated temperatures tends to increase the consistency. The over-all effect of both factors is to improve the electrode crushing strength and electrical resistivity.

#### Summary

Consistency measurements on Soderberg mixes containing a plant-scale aggregate have been made, with a Brabender Plastograph. The consistencies were

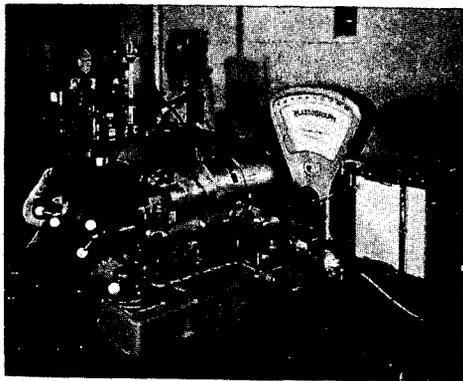
used to predict the optimum binder concentration for each of two binders. A different amount of each binder was required for optimum binder content and optimum electrode properties. This difference was verified by carbon-paste-plant data on the two binders. The effects of temperature and time on the mix consistency and electrode properties were also studied. Increased temperature tends to decrease the mix consistency, whereas consistency increases with an increase in holding time without mixing at elevated temperatures. The over-all effect of the two factors is to improve the electrode crushing strength and electrical resistivity.

#### Acknowledgment

The authors wish to express their appreciation to Aluminium Laboratories Limited of Canada, which supplied the samples used in this work.

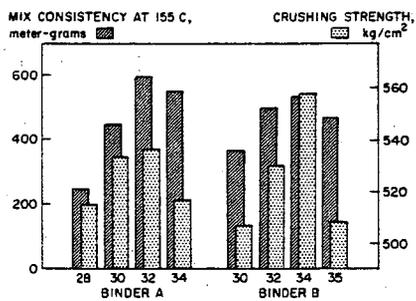
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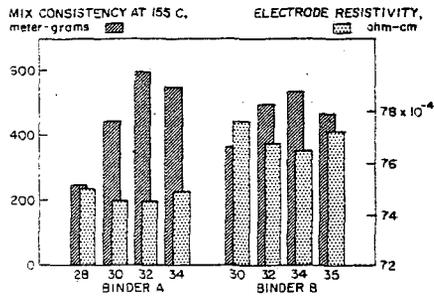
The Brabender Plastograph

Figure 1



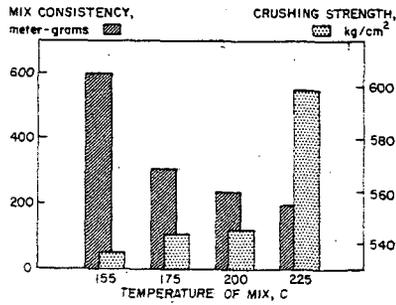
Relationship Between Mix Consistency and  
Electrode Crushing Strength

Figure 2



Relationship Between Mix Consistency and Electrode Resistivity

Figure 3



Effect of Mixing Temperature on Mix Consistency and Electrode Crushing Strength

Figure 4

## PROPERTIES OF PITCHES

	PITCH A	PITCH B
SOFTENING POINT (CIA), C	109.5	109.0
BENZENE INSOLUBLE, wt %	29.3	34.3
QUINOLINE INSOLUBLE, wt %	10.3	14.3
COKE VALUE (CONRADSON), wt %	58.5	58.3
SPECIFIC GRAVITY 60 F/60 F	1.32	1.29

Table I

PARTICLE-SIZE DISTRIBUTION  
OF PETROLEUM-COKE

TYLER MESH SIZE	FRACTION SIZE, weight percent
-0.525 in. +3 MESH	5.0
-3 +4 MESH	5.0
-4 +10 MESH	15.0
-10 +20 MESH	10.0
-20 +48 MESH	15.0
-48 +200 MESH	20.0
-200 MESH	30.0

Table II

EFFECT OF TIME ON MIX CONSISTENCY  
AND ELECTRODE PROPERTIES

TEMPERATURE, C	155		225	
	0	7.5	0	24
HOLD TIME, hours				
MIX CONSISTENCY, meter-grams	600	1000	190	600
ELECTRODE STRENGTH, kg/cm <sup>2</sup>	536	622	598	642
ELECTRODE RESISTIVITY, ohm-cm x 10 <sup>-4</sup>	74.5	63.2	73.9	63.0

Table III

RAPID TEST METHOD FOR THE DETERMINATION OF THE BENZENE-  
AND QUINOLINE-INSOLUBLE CONTENT OF PITCHES

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Introduction

Tests to determine the amount of benzene- and quinoline-insoluble matter in pitch are widely used by producers and consumers of pitch. For example, several thousand solvent-insolubles tests are performed annually at U. S. Steel's pitch-producing facilities. The present test method for determining the benzene-insoluble content of pitch is based upon a test that was developed by the Barrett Company (presently a division of Allied Chemical Corporation).

Briefly, the Barrett procedure involves digestion of the pitch sample in toluene, filtration, and then extraction of the residue in refluxing benzene. Because of the time-consuming extraction phase, the Barrett test requires in excess of 24 hours to complete. The undesirability of lengthy analytical procedures, especially in plant control work, prompted the Applied Research Laboratory of U. S. Steel to develop a rapid benzene-insolubles test that could be completed in about 6 hours.

This paper describes the salient features of the rapid method for determining the benzene-insoluble content of pitch. A rapid method for determining quinoline insolubles is also described and discussed briefly.

Experimental Work

The Barrett method for determining benzene insolubles is an empirical method that has been used throughout the industry over a number of years and has been accepted as a more or less standard procedure. To date, no ASTM (American Society for Testing Materials) test method for benzene insolubles has been devised. In developing a rapid method, the following objectives were fixed: (1) The time required to complete the test should be 8 hours or less. (2) The values obtained by the new method should be equivalent to those obtained by the Barrett method. (3) The general principles of digestion and extraction should be retained.

The rapid benzene-insoluble test closely duplicates the Barrett method in all phases except that the size-consist of the particles in the sample is controlled and the reflux extraction apparatus and technique are changed. A number of modifications have been made in the procedure and in the design of the apparatus. These changes provide the same degree of extraction as the Barrett method but in much less time. The apparatus used in each method is shown in Figure 1. In the new method, the special extraction flask and the filter paper thimble of the Barrett test are replaced with the more modern and versatile Soxhlet extraction apparatus and Soxhlet paper extraction thimble.

Important added features of the Soxhlet extraction apparatus are shown in Figure 2. The wire spacer, which rests on the bottom of the extraction cup of the Soxhlet apparatus, positions the thimble so that the middle of the thimble is at the top of the siphon tube. This provides an adequate liquid level in the thimble and at the same time prevents loss of sample through overflow. A reflux guide, built onto the bottom of the condenser, directs all of the refluxing stream into the thimble. Without the guide, considerable solvent by-passes the thimble.

The coal-tar pitches selected for use in this study represent a wide range (15 to 35 wt %) of benzene-insoluble contents. Table I shows some of the more common properties of these pitches. Three of the pitches were obtained from tars recovered during the high-temperature carbonization of bituminous coal. The fourth pitch was produced from tar from the low-temperature carbonization of sub-bituminous coal. The table shows the benzene-insoluble content of the pitches as determined by the Barrett method.

In the new rapid method, standard sampling procedures (ASTM D 140-55 and ASTM D 346-35) are followed to insure that the portion used for analysis is representative of the pitch sample. In addition, when the pitch is sufficiently hard it is ground to pass through a U. S. No. 60 sieve and the test sample is collected from material retained on a U. S. No. 100 sieve. This is done to obtain a sample with a particle size (0.0058-in. to 0.0082-in. diameter) that will insure good solvent contact. The particles should be sufficiently small so that the solvent can be rapidly absorbed, but not so small that agglomeration or packing of fines can prevent or retard solvent contact. The sample size is adjusted to yield approximately 0.25 gram of insoluble material (usually 1 or 2 grams). The sample is weighed into a beaker and digested in 60 milliliters (ml) of toluene for 30-minutes on a steam bath. The contents of the beaker are then transferred to a 30- by 77 mm (single weight) Soxhlet extraction thimble that has been previously tared in a weighing bottle. The thimble is placed in a crucible holder over a beaker and the insoluble matter is transferred to the thimble by the use of a brush and a small amount of toluene. Figure 3 shows this operation. When the liquid portion of the suspension has passed through the thimble, the thimble is washed with benzene and then placed into a 44-mm Soxhlet apparatus for extraction. Heat is applied gradually to the flask to avoid the possibility of liquid erupting into the extraction tube. The gradual heatup period requires approximately 15 minutes and the close attention of the operator. Once the desired throughput is achieved, the test will proceed practically unattended. The extraction is conducted for a total of 4 hours with a siphoning cycle of approximately three minutes. This approximates a solvent reflux rate of about 1800 ml per hour. At the end of this period the thimble is removed, air-dried for 15 minutes, oven-dried for 30 minutes at 105 C, cooled in a desiccator, and weighed. Six hours are required to complete the determination of the amount of sample insoluble in benzene.

### Results and Discussion

Several steps were involved in arriving at the proper operating conditions for the Soxhlet extractor. They were (1) determination of the permeability of the Soxhlet thimble relative to the filter-paper thimble, (2) establishment of the maximum throughput capacity for benzene in the Soxhlet apparatus, and (3) establishment of the throughput of benzene in the Barrett apparatus when operating at the recommended boilup rate.

That the Soxhlet thimble is no more permeable to the retained insoluble matter than is the filter-paper thimble was established by an experiment in which the Soxhlet thimble was used in the extraction apparatus of the Barrett method. This experiment showed that the use of the Soxhlet thimble gave results identical to those obtained in a test in which the filter-paper thimble was used.

The Soxhlet thimble was found to be capable of handling all the benzene returned to the siphon cup of the Soxhlet extraction apparatus at maximum boilup, which was 1800 ml per hour.

The average throughput of benzene in the Barrett test (about 80 drops per minute) is about 6600 ml in 24 hours. At maximum boilup, the Soxhlet apparatus required slightly less than 4 hours to reflux the same quantity of benzene.

Another matter that was considered concerned the temperatures to which the samples were subjected in the rapid test. Since the exterior of the thimble in the Soxhlet apparatus is partially immersed in the benzene condensate during a portion of the extraction cycle, it was conceivable that the condensate could lower the temperature of the contents of the thimble. In the Barrett apparatus, the thimble is constantly bathed by solvent vapors and refluxing solvent. To ascertain whether there was a temperature difference, an experiment was performed in which thermocouples were suspended in the liquid and vapor portions of the solvent in an operating Soxhlet extractor. After the first few siphon cycles, the temperature differential was within one degree Centigrade. A thermocouple was also suspended in the vapor portion of the Barrett apparatus and it was established that the vapor temperatures were the same in both apparatus.

The rapid benzene-insolubles test was performed by each of three operators, who conducted three duplicate tests on each pitch sample, to establish the repeatability of the test. The results of the tests are shown in Table II and plotted in Figure 4. The horizontal line across the center of the chart in Figure 4 represents a scale for benzene-insolubles values as determined by the Barrett test method. The points on the scale are the average of three duplicate determinations for benzene-insoluble contents of the four samples when tested by the Barrett method. The vertical scale represents the deviation, expressed in percentage of sample, from the values obtained by the Barrett method (the horizontal center line). The lines digressing from the horizontal center line represent the limits of reproducibility as established by the Barrett method. This is expressed in percentage of sample as  $0.1 + 0.05 \times$  percent insoluble matter in benzene. The points above and below the center line represent the values obtained by the rapid benzene-insolubles method. The different symbols represent different operators and each point represents a mean value as determined from the values of duplicate tests; as stated before, each operator performed three duplicate tests or six tests per pitch sample, to obtain three mean values for comparison with the standard value (center line).

As may be seen on the graph, most of the values obtained by the rapid procedure fall within the limits of reproducibility set for the values by the Barrett method.

Mean and standard deviation values for each of the pitches analyzed by the rapid method are shown in Table III.

Because of the exceptionally good reproducibility and the savings in time, we feel the rapid test method for benzene insolubles is a good replacement for the Barrett test method.

### Quinoline Insolubles

The less time-consuming a quality control test or specification test is, the more desirable it is. Even though the commonly used method for determining the portion of sample insoluble in quinoline requires only about 3 hours to complete, the possibility of shortening the time requirement was investigated. As in the investigation of the rapid benzene-insolubles test, the objectives included the limitation that the empirical values as obtained by the presently used procedure would be duplicated, and that the general principles of digestion and extraction should be retained.

A test meeting these requirements was developed which could be completed in less than 1 hour. The new rapid procedure differs little from the old procedure in principle. Time requirements were decreased by changing the techniques of extraction and drying.

### Experimental Work

The pitch samples tested were the same as those used in the benzene-insolubles study. Also, the same techniques of sample preparation were followed.

In the rapid quinoline-insolubles test, a weighed sample of sufficient size to yield 0.1 gram of insoluble material is digested with hot (170 C) quinoline for two minutes. The digested sample is then filtered with the aid of suction, as shown in Figure 5, through a Selas crucible (fine porosity) containing a quantity of diatomaceous filter aid. When substantially all of the material has been transferred from the beaker to the crucible, the beaker is rinsed with 20 ml of hot (170 C) quinoline; this material is also transferred to the crucible. Any particles that adhere to the beaker are washed into the crucible with benzene. The filter cake in the crucible is then washed with 80 ml of benzene and then with 80 ml of acetone. After the acetone wash, the filter cake is dried while still under suction by means of a 250-watt infrared lamp mounted about 12 inches above the crucible. This operation should be conducted in a well ventilated hood, to remove the small amount of acetone vapors that are evolved. When dry (about 15 minutes), the crucible is cooled in a desiccator and weighed.

### Results and Discussion

To develop a rapid quinoline-insolubles test method that would retain the basic principles of the old method, it was necessary to reduce the time requirement by altering the techniques of operation. One area studied was the conditions of digestion. It was determined that increasing the temperature of the quinoline from 80 C to 170 C and shortening the time of digestion from 20 to 2 minutes did not alter the end result. Adding an acetone wash to the procedure shortened the drying process. The acetone removes benzene, which is more difficult to vaporize, from the quinoline-insoluble matter. Subsequent removal of the acetone was quickly accomplished by the application of heat from a heat lamp. Further time savings were derived by using previously dried crucibles and filter-aid material. The sum of these time savers resulted in a rapid method that required less than 1 hour to complete as opposed to the 3 hours for the old method.

Table IV and Figure 6 show the results of rapid quinoline-insolubles tests as determined by three operators. The horizontal line across the center of the chart represents a scale for quinoline-insolubles values as determined by the old method of test. The points on the scale are the average of three sets of duplicate determinations of quinoline-insoluble contents of the four samples tested by the old method. The vertical scale represents the deviation, expressed in percentage of sample, from the values by the old method (the horizontal center line). The lines digressing from the center line represent the limits of reproducibility as established by the old method. This is expressed in percentage of sample as  $0.10 + 0.02 \times$  percent insoluble matter in quinoline. The points above and below the center line represent the values obtained by the rapid quinoline-insolubles method. The different symbols represent different operators and each point represents a mean value as determined from the values of duplicate tests. Each operator performed three duplicate tests, or six tests per pitch sample, to obtain three mean values for comparison with the standard value or center line.

As was true with the benzene-insolubles values, nearly all the quinoline-insolubles values obtained by the rapid method fall within the limits of reproducibility set for the values obtainable by the old method for quinoline insolubles.

Mean and standard deviation values for each of the samples analyzed by the rapid method are shown in Table V.

#### Summary

Methods have been developed for the rapid determination of benzene- and quinoline-insolubles in pitches. The rapid benzene-insolubles test requires 6 hours to complete as compared to the 24 hours necessary for the generally used Barrett method. The rapid quinoline-insolubles test requires 1 hour to complete as opposed to 3 hours for the old method. Results obtained with the rapid test methods correlate well with those of the standard methods. It is hoped that the time advantages gained warrant the consideration of these rapid tests as acceptable methods for analysis of benzene- and quinoline-insoluble matter.

Table I  
Properties of Pitches

	Pitch			
	A	B	C	D
Benzene Insolubles, wt %	14.73	22.57	33.94	35.42
Quinoline Insolubles, wt %	2.25	9.98	12.23	28.99
Softening Point, C	78.3	105.5	117.5	64.9
Coke Value, wt %	42.5	56.0	58.9	35.8

Table II  
Results of Benzene-Insolubles Determinations

Rapid Method		Pitch, wt %							
		A		B		C		D	
Operator	Run No.								
I	1	14.17		21.72		32.60		36.09	
	2	14.26	14.22*	21.80	21.76	32.39	32.50	35.60	35.85
	3	14.50		21.61		34.62		36.01	
	4	13.85	14.18	22.46	22.04	34.39	34.56	36.10	36.06
	5	14.82		21.41		33.70		34.90	
	6	15.22	15.02	22.40	21.92	33.50	33.60	34.82	34.86
II	1	13.86		22.50		33.55		37.29	
	2	14.13	14.00	23.44	22.97	33.33	33.54	36.63	36.96
	3	13.89		21.61		33.53		36.84	
	4	13.37	13.63	21.41	21.51	33.59	33.55	36.56	36.70
	5	14.52		22.57		32.92		36.33	
	6	14.69	14.50	23.22	22.90	33.17	33.04	36.53	36.43
III	1	14.40		22.06		32.20		36.36	
	2	14.37	14.39	22.02	22.04	33.83	33.02	36.91	36.64
	3	15.40		23.38		33.77		36.19	
	4	15.31	15.35	23.64	23.51	34.24	34.00	35.83	36.01
	5	15.08		22.56		35.05		35.74	
	6	15.97	15.53	21.85	22.20	34.94	35.00	35.14	35.44
<u>Barrett Method</u>		14.73		22.57		33.94		35.42	

\* Mean values

Table III

Statistical Data for the Rapid Benzene-Insolubles Test

	Pitch			
	A	B	C	D
Number of Runs	18	18	18	18
Mean	14.53	22.31	35.57	36.10
Standard Deviation	0.663	0.718	0.912	0.682

Table IV

Results of Quinoline-Insolubles DeterminationsRapid Method

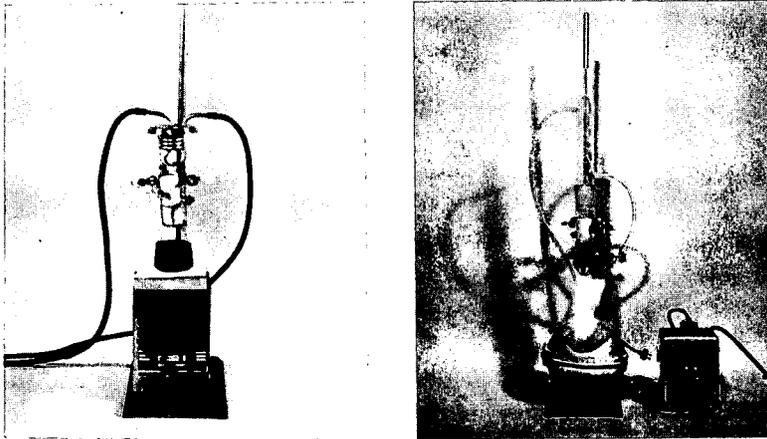
Operator	Run No.	Pitch, wt %							
		A		B		C		D	
I	1	2.20		10.21		12.16		29.46	
	2	2.22	2.21*	10.26	10.24	12.17	12.17	29.98	29.22
	3	2.31		10.23		12.20		28.07	
	4	2.33	2.32	10.23	10.23	11.99	12.10	28.41	28.24
	5	2.17		10.15		12.11		28.50	
	6	2.15	2.16	10.16	10.16	12.23	12.17	28.54	28.52
II	1	2.33		10.26		12.17		28.99	
	2	2.30	2.32	9.74	10.00	12.18	12.18	28.86	28.94
	3	2.28		10.20		12.93		28.95	
	4	2.30	2.29	10.23	10.22	12.79	12.86	28.90	28.93
	5	2.28		10.24		11.93		28.92	
	6	2.27	2.28	10.17	10.20	12.94	12.44	28.85	28.89
III	1	2.33		9.84		12.31		28.47	
	2	2.45	2.39	10.05	9.95	13.27	12.79	28.76	28.62
	3	2.22		10.13		12.13		28.64	
	4	2.35	2.29	10.11	10.12	12.69	12.41	28.79	28.72
	5	2.45		10.29		12.27		28.38	
	6	2.32	2.40	10.32	10.30	12.23	12.25	28.33	28.36
<u>Barrett Method</u>		2.25		9.98		12.23		28.99	

\* Mean values

Table V

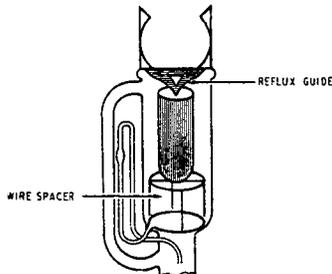
Statistical Data for the Rapid Quinoline-Insolubles Test

	Pitch			
	A	B	C	D
Number of Runs	18	18	18	18
Mean	2.29	10.16	12.38	28.71
Standard Deviation	0.081	0.150	0.377	0.325



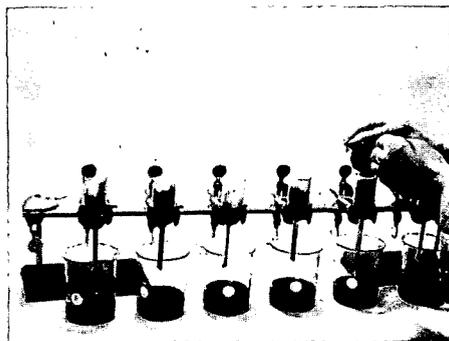
Extraction Apparatus for Benzene-Insolubles Tests

Figure 1



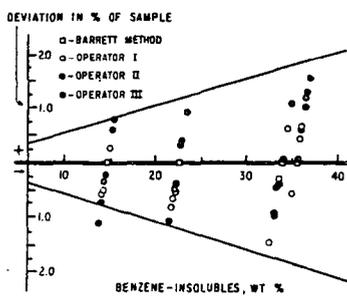
Modifications of Soxhlet Extractor  
for Rapid Benzene-Insolubles Test

Figure 2



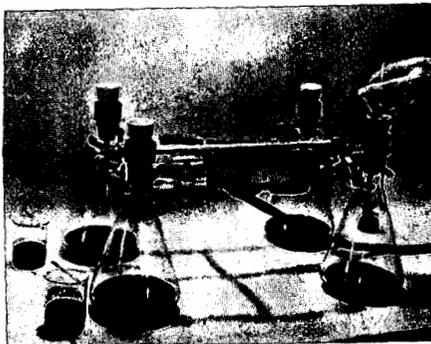
Transferring Insoluble Matter to Thimbles in  
Rapid Benzene-Insolubles Test

Figure 3



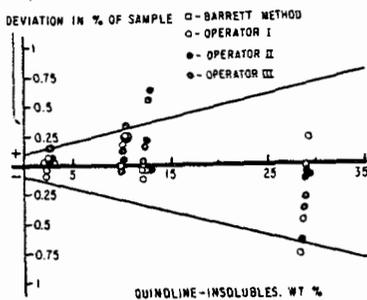
Statistical Data for Benzene-Insolubles Test

Figure 4



Quinoline-Insolubles Filtering Apparatus

Figure 5



Statistical Data for Quinoline-Insolubles Test

Figure 6