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CARBON-CARBON COMPOSITE MATRIX REACTIONS AND DENSIFICATION RESP--ETC(U)

1979 J P POPE F49620-78-C-0002

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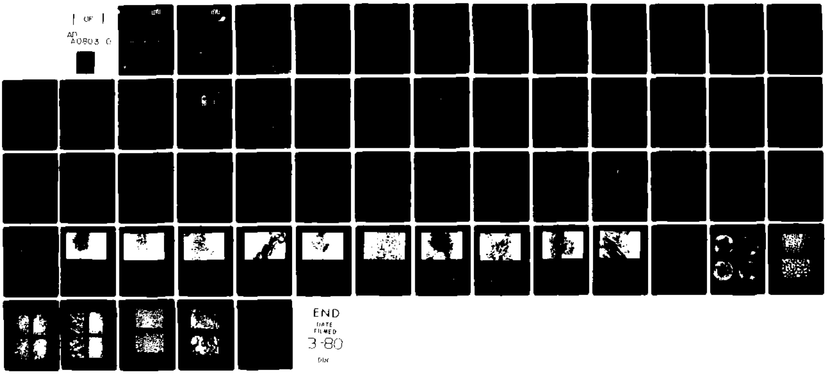

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REACTIONS AND DENSIFICATION RESPONSE.

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Air Force Office of Scientific Research (AFOSR)
Bolling Air Force Base, Washington, D.C. 20332

(11) 1979

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CARBON-CARBON COMPOSITE MATRIX
REACTIONS AND DENSIFICATION RESPONSE

Contract No. F49620-78-C-0002

I. SUMMARY

A small research hot isostatic pressure (HIP) autoclave was purchased with Science Applications, Incorporated (SAI) funds for use in this program. The research vessel, an Autoclave Engineers, Inc. hot wall vessel is rated for reaction pressures up to 15,000 psi and 700°C internal temperatures and has experimental load dimensions of 3 inch diameter by 10 inch length. Again using SAI Corporate funds, the HIP unit was modified to a Material Sciences Operation (MSO/SAI) design by Conaway Pressure Systems, Inc. (CPSI), Columbus, Ohio. The modification included providing access to the internal regions for the installation of diagnostic equipment by which to monitor thermal and thermochemical events during processing, and for real time analysis of gaseous effluents emanating from the decomposition of coal tar pitch.

Due to schedule and technical problems at CPSI, the modified research HIP facility was not returned until August 1978. Further technical problems with the unit delayed operational status until late September 1978. Since then, decomposition reactions have been studied at 3000, 5000, 10,000, and 15,000 psi imposed carbonization pressures on Allied Chemical CP 277-15V coal tar pitch. Carbonization cycles based upon the Air Force's Equivalent Industrial Standard Process (EISP) has been conducted for the full time-temperature-pressure schedule as well as for process runs interrupted in the liquid-solid transformation temperature range of the pressure decomposition of coal tar pitch (450°-490°C).

A technique for the hot recovery of liquid pitch from these interrupted runs was developed. This procedure provides material for the determination of properties and chemical and compositional changes of previously unmeasured pitch conditions of the process environment. These material measurements of pitch recovered at or near 470^{o}C have provided significant information regarding chemical and compositional variances between the still liquid state and transformed solid forms of pitch.

Characterization of basic compositional and chemical differences between manufacturing dates of lots of Allied 15V pitch, between samples within the same lot, and between the Allied material and Koppers Chemical, Incorporated's version of the Air Force's 15V specifications were made. The effect of preconditioning the precursor before impregnation has been studied and a correlation between heat treatment time and mesophase formation was derived.

The use of high pressure liquid chromatography (HPLC), and gel permeation (GP) techniques to resolve compositional and chemican structural differences between precursors and partially processed liquid states of pitch has been implemented. Analysis of the HPLC and GP data are being compared to thermogravimetric analysis data to establish key features of the pitch precursors which respond distinctively to process parameters.

Fiber studies in which Hercules HM yarns (PAN) and Union Carbide VSB-32 pitch yarns are included in the decomposition experimental packages were initiated in the weeks of this years effort. Significant structural changes in fully carbonized yarns impregnated with Allied 15V were observed as a result of processing according to an EISP schedule at 10,000 and 15,000 psi.

Yarns included in runs interrupted at 470°C and rapidly quenched were strikingly different from fully carbonized yarns processed at the same pressure.

Other significant results to date include the discovery of a large concentration of hydrogen in pitch removed from EISP processed pitch at 10,000 and 15,000 psi carbonization pressures. Similarly, material recovered from interrupted runs showed that only a minor reduction in the hydrogen content of Allied 15V had occurred by 470°C in contrast to calculated equilibrium decomposition rates. At the same time, the oxygen weight content of recovered material is significantly higher than the precursor in material removed from the carbonization runs interrupted at 470°C, and increasingly higher yet for fully carbonized (EISP) material.

II. OBJECTIVES AND STATEMENT OF WORK

The Air Force Office of Scientific Research (AFOSR) and the Air Force Materials Laboratory (AFML) have initiated mutually supporting programs designated as Processing Science Programs to develop models which can reliably predict the response of the carbon-carbon material generic class through processing. The objective of this AFOSR program is to provide experimentally derived understanding of the time-temperature-pressure relationships imposed upon the pitch matrix during carbonization and to provide reaction related compositional information on candidate Air Force matrix precursors. Experimental data and processing information regarding in-situ thermochemical reactions, anomalies, and significant environmental events are systematically developed in a manner which is of useful input to the analytical model development effort as well as carbon-carbon processors.

To achieve the objectives of this program, a two-year research study is being conducted in five tasks as follows:

(1) Characterization of raw materials and setup and calibration of high pressure pyrolysis autoclave and diagnostic instrumentation.

(2) The definition of reaction rates in pitch decompostion without the presence of fibers, powders, or mechanical constraints.

(3) The decomposition of pitch as modified by the presence of active surfaces such as fibers and utilization of fluid dynamics and heat conduction consideration in the design of experimental decomposition packages.

(4) The utilization of various characterization techniques to evaluate the form of solids produced as a result of matrix decomposition reactions.

(5) Analysis of pitch composition with consideration of fluid flow, viscosity, and microstructural effects.

III. BACKGROUND

Carbon-carbon composites have emerged over the past decade as the baseline high temperature structural material for selected critical components of advanced Air Force exit (launch) and reentry systems. An Air Force commitment to the use of carbon-carbon composites as integral throat and entrance (ITE) rocket nozzles and combined clear air and aggravated encounter reentry nosetips has justified concern regarding the reliability and reproducibility of the carbon-carbon processing technology base upon which future national defense systems will rely. The complex processing environment can be described in the most general applicable terms as severe, stochastic, and aggressively damaging. The multifarious phenomena of the process environment governing the formation of constituent properties and the final composite attributes are poorly understood. Existing models are, in most cases, misceral correlation of post-process properties and carbon-carbon microstructure to imposed external parameters of the process cycle and supposed internal events (which are not supported by internal diagnostic evidence). Models, such as they exist, have been derived essentially from a decade of empirical development by processors at several facilities in which equipment, materials, and process parameters are at extreme variance.

The principal reason behind the lack of a decent process environment model is the lack of basic information regarding coal tar pitch precursor properties and behavior during the impregnation and carbonization cycles of the process sequence. The purpose of this program is to provide some of the basic information by conducting unique and innovative processing experiments.

IV. STATUS OF RESEARCH EFFORT

1. Experimental Approach

The research approach is based upon completeness of precursor characterization and unique experimental packages and analysis techniques. Early in the program, it was recognized that the contribution of this program to the Air Force's Processing Science objectives could best be met by expanding the data base to include pitch precursors from different vendors and manufacturing dates as well as including experimental pitches which may be of interest to the Air Force over the next decade. For this reason, the program was expanded to include Koppers Chemical, Inc. pitches such as their 15V Equivalent of the Allied 15V baseline material and several experimental pitches. Although not planned for study until 1979, the Koppers pitches were integrated into the processing and characterization phases in late 1978 to provide additional data for resolution of compositional issues.

Midway through the first year's effort, it became apparent that additional chemical analysis techniques were required to completely characterize pitch precursors and to model the thermophysical and thermochemical response of pitch material to imposed pressure and temperature schedules. For this reason, two techniques, high pressure liquid chromatography and gel permeation were incorporated into the measurement methods exercised. Results obtained on various pitches and conditions of the same pitch material were received in later 1978 and early 1979 and are reported later in this section.

Table 1 presents a summary of the experimental approach to the research effort underway. Table 2 is a presentation of the pitch material which has been obtained for this program.

2. Equipment and Experimental Package Designs

The basic equipment used in conducting decomposition reaction experiments is shown schematically in Figure 1. The research HIP

Table 1

REACTION STUDIES

MATRIX TYPE	CONDITION AND EFFECT	TECHNIQUES	OBSERVABLES/MEASUREMENTS
Allied-15V	As Received	Microscopy	● Temp. Dependent Viscosity
Lot-501	Heat Treatment . Time . Temperature	Chemical Analysis	● Softening Point
Lot-701		TGA/Derivaties	● Benzene Insolubles
Koppers "15V Equivalent"	. Mechanical Agitation	Bulk Physical Properties	● Quinoline Insolubles
Koppers KCP	. Bubble Percolation	. Post Heat Treatment	● Temp. Dependent Weight Loss
Koppers Exp. Pitches	Carbonization Cycle . Heat Rate . Pressure . Temperature . Modified Loads - Pore Volume - Surface Area . Interrupted Runs	Experimental Packages	● Temp. Dependent Decomposition Rates ● Hydrogen/Carbon Ratio ● Bulk & Apparent Density ● Mesophase Formation ● Pitch Density/Porosity . Bulk . Apparent ● Surface/Volume Effect on Impregnation Efficiency ● Pyrolysis Gas Rates ● High Pressure Liquid Chromatography ● Gel Permeation

Table 2

PITCH MATERIALS TO BE INVESTIGATED

IMPREGNATING PITCH	MANUFACTURING DATE	SOFTENING[1] POINT, $^{\circ}C$
Allied 15V - Lot 501	1975	85°
Allied 15V - Lot 701	1977	93°
Koppers "15V Equivalent"	1977	95°
Koppers "15V Equivalent" 3275-1	1978	N/A
Koppers KCP Impregnating Pitch	1978	115°
Koppers Experimental Pitch/78-252-524	1978	110°-120°[2]
Koppers Experimental Pitch/78-524	1978	110°-120°[2]
Koppers Carbon Impregnating Pitch Y/78-480	1978	110°-120°[2]

(1) As determined by SAI
(2) Telecon: Koppers/SAI

facility was modified to provide access to the inner region of the autoclave for implementation of diagnostic apparatus for monitoring on a real time base the events and thermal profiles of decomposing pitch. External monitoring of input power and heat transfer is also continuously recorded to provide for evaluation of the heat conduction of the reacting mass in the load. The modification to the HIP vessel was based upon requirements to measure variables of the process environment as shown in Figure 2. Experimental packages are designed uniquely for isolation of precursor response to imposed process parameters. Figure 3 shows schematically a typical experimental package for the Research HIP facility and the types of process parameters and package variables employed. Figure 4 is a reproduction of the recorded history of a typical decomposition run.

3. Coal Tar Pitch Characterizations

The basic compositional and decomposition characteristics of Allied 15V, Koppers 15V, and two experimental impregnating pitches obtained from Koppers are presented in Table 3, and Figures 6 through 16. Included in that data are the variation in properties and composition of lots of Allied 15V manufactured in 1975 and 1977 (Lot 501 and Lot 701, respectively). Three barrels from each lot were analyzed for chemical elements of the composition, benzene and quinoline insolubles (B.I. and Q.I.), softening point, and ash content (Table 3). A significant increase in the average of the oxygen content was determined for Lot 701 along with increases in B.I. and Q.I. content and softening point. The significance of these changes on the decomposition reactions has not been determined. However, the increase in oxygen content of

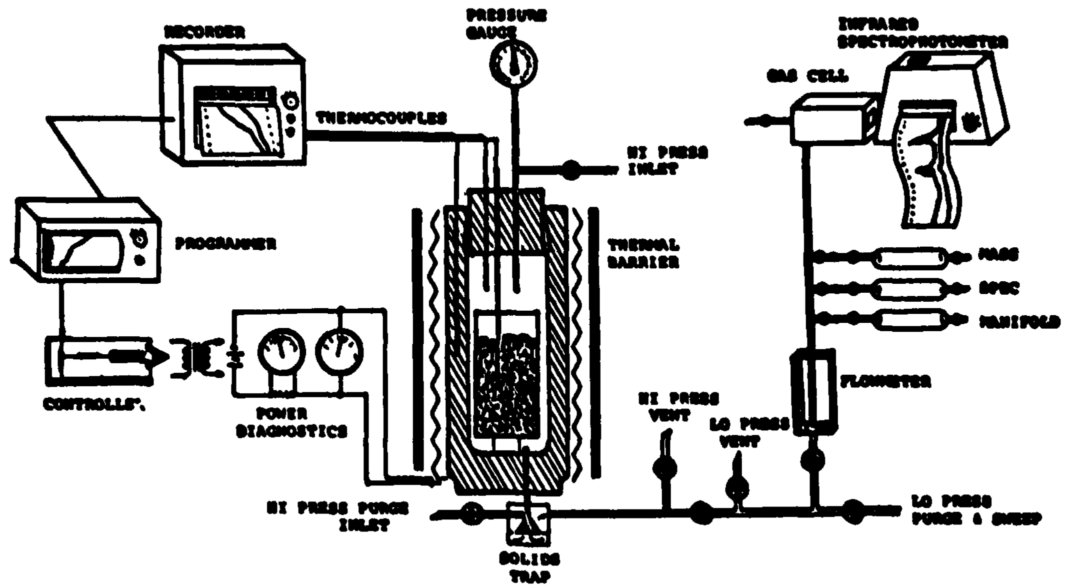


Figure 1. Schematic of Research HIP Facility

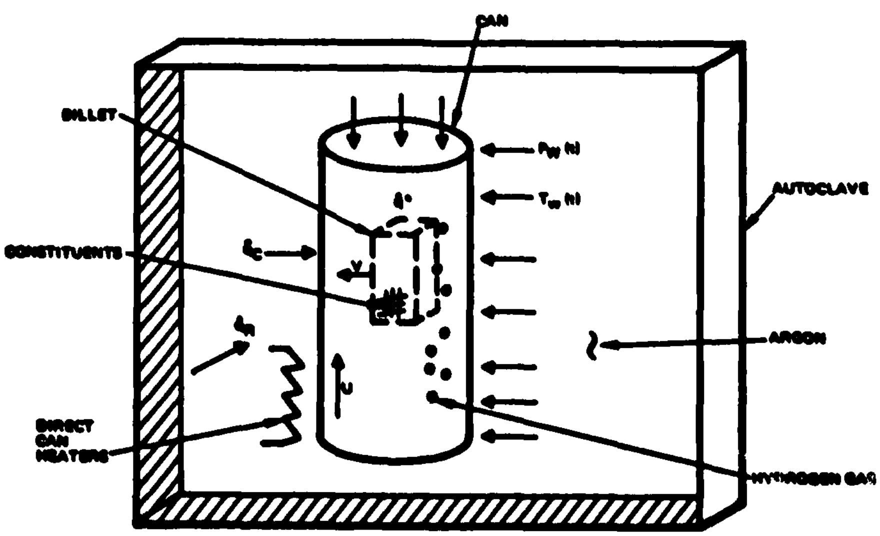


Figure 2. Process Environment Model

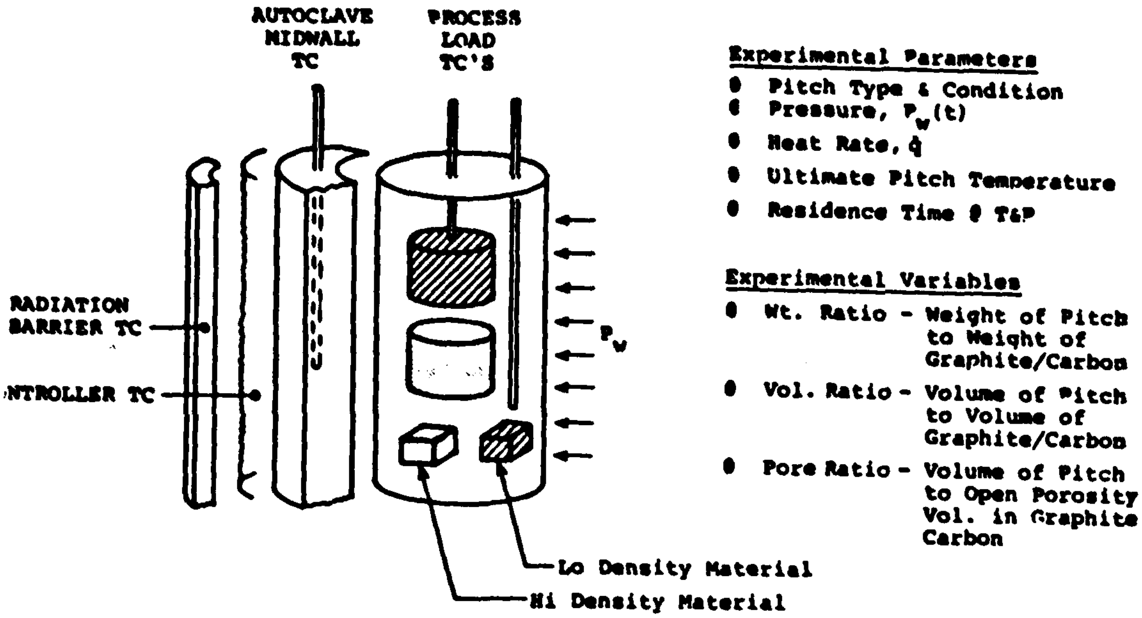


Figure 3. Schematic of Typical Experimental Package

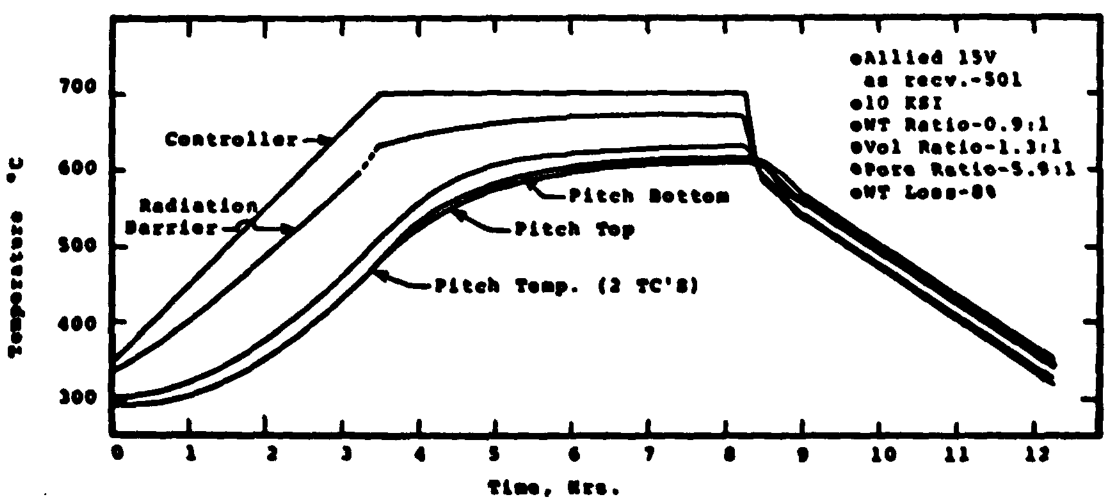


Figure 4. Reproduction of Recorded History of 10 KSI Carbonization Reaction Experiment

the precursor pitch material is of specific interest because of measured increases in the oxygen content of fully carbonized pitch to be discussed in Paragraph 4.

Table 3

PROPERTIES OF ALLIED 15V FOR TWO
MANUFACTURING DATES (AVERAGE OF THREE DRUMS PER LOT)

LOT NO.	MFG. DATE	SOFT. PT. °C	VISCOSITY @ 200°C CENTIPOSIE	B.I. W/O	Q.I. W/O	ELEMENTAL COMPOSITION, W/O					
						C	H	N	S	O	Ash
501	1975	87.5	27.0	14.50	2.50	92.42	4.83	1.07	0.53	1.03	0.15
701	1977	91.1	47.5	17.74	4.05	91.49	4.53	1.03	0.61	2.23	0.10

Important compositional difference between Lot 501 and Lot 701 (Allied 15V) are shown in the gel permeation data of Figure 5, and the TGA data of Figures 6 and 7. Of particular interst is the apparent shift of distribution and increase in total complex molecular compounds found in Lot 701 when compared to the earlier manufacturing date of Lot 501 (Figure 5). At the same time, Lot 701 appears to be less uniform as shown in typical TGA data in Figures 6 and 7 wherein the data obtained for Lot 501 was much more reproducible than Lot 701.

TGA data, high pressure liquid chromatography measurements, and gel permeation data are presented in Figures 8, 9, 10 and 11 to contrast the composition and basic decomposition of Koppers 15V Equivalent pitch material with Allied 15V. Figures 12, 13, 14 and 15 present the same type of signature for two Koppers experimental pitches designated (by Koppers) as 78-252-480, and 78-480. The viscosity of these pitches are compared in Figure 16 with viscosities measured for Allied 15V; Lot 501 and Lot 701, and Koppers 15V Equivalent.

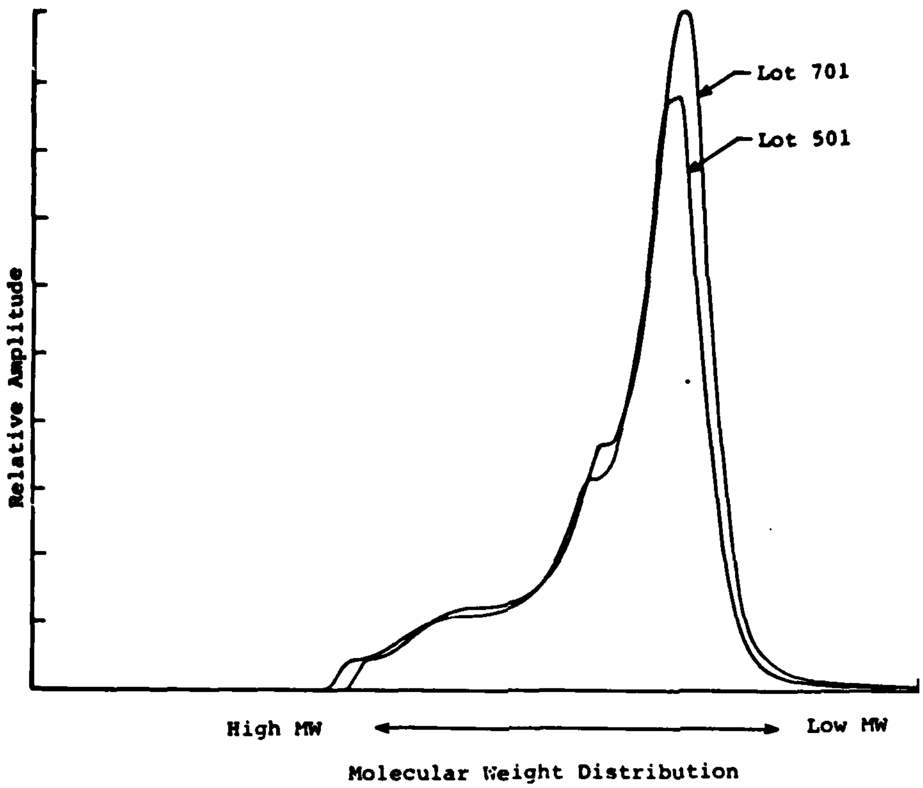


Figure 5. Molecular Weight Distribution Differences Between Lots of Allied 15V

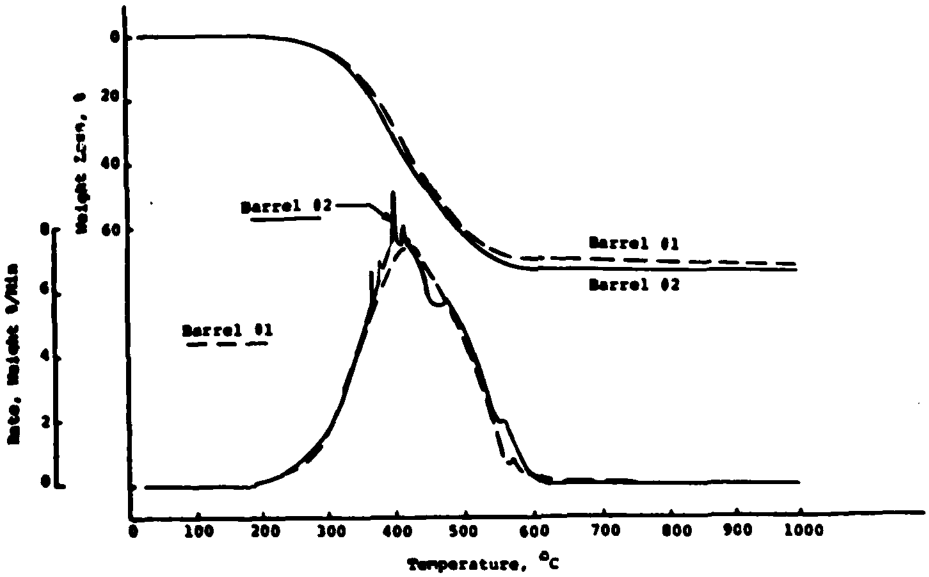


Figure 6. TGA of Two Barrels of Allied 15V - Lot 501

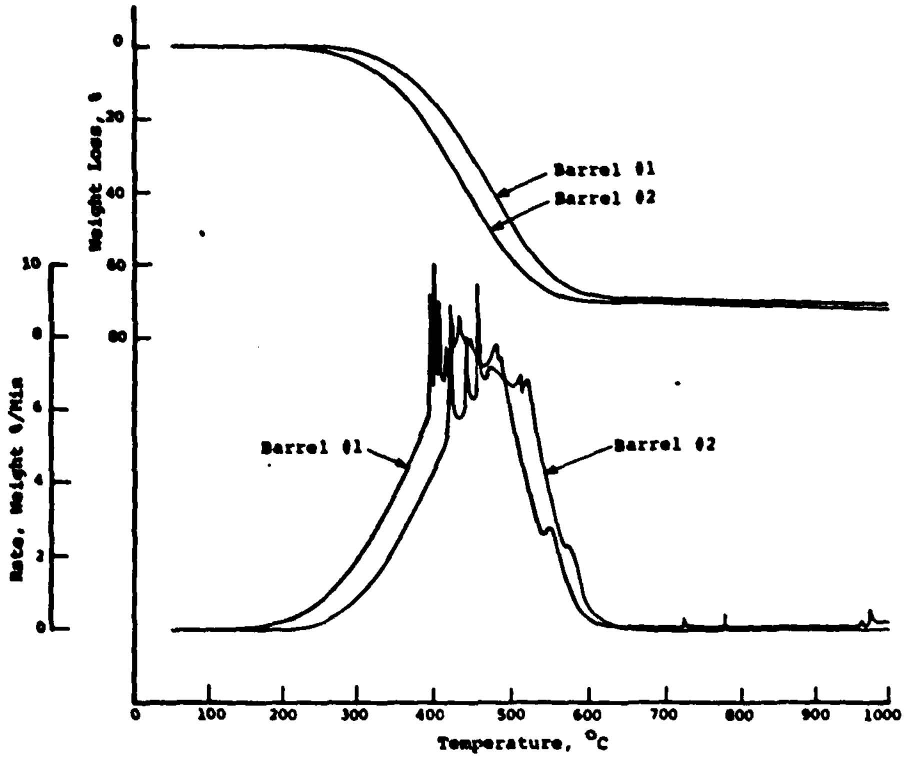


Figure 7. TGA of Two Barrels of Allied 15V - Lot 701

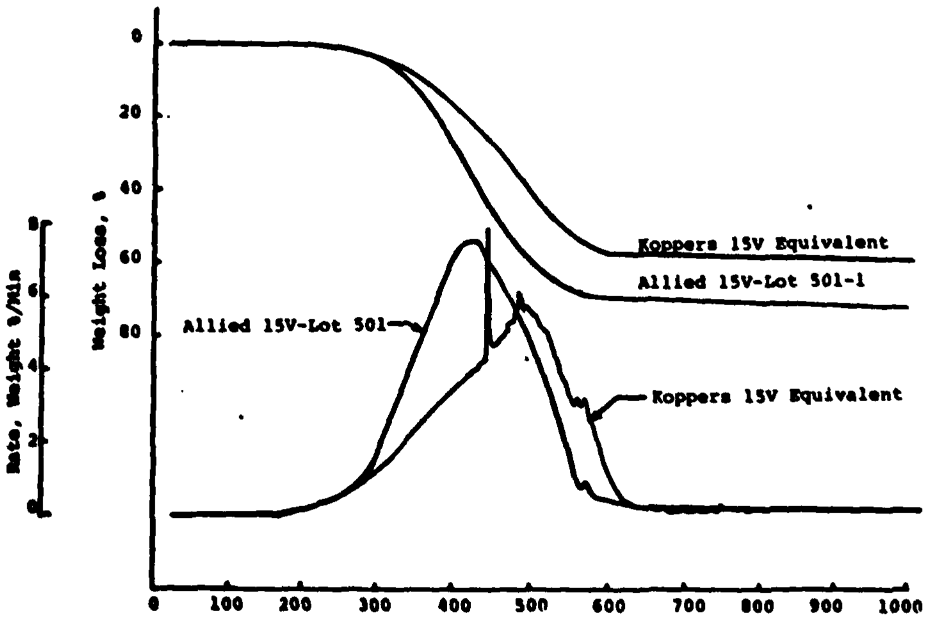


Figure 8. TGA Differences Between Koppers and Allied 15V

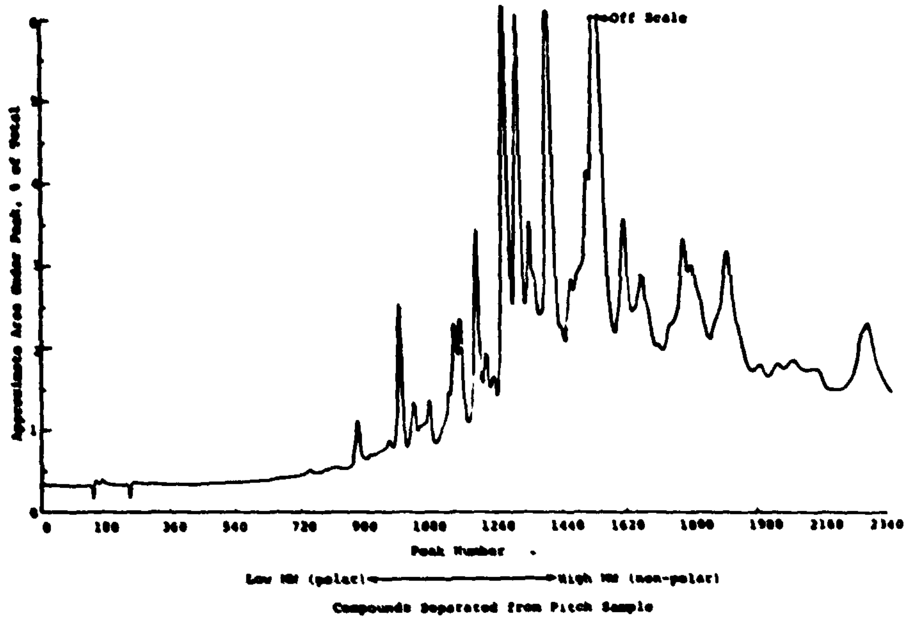


Figure 9. High Pressure Liquid Chromatogram of Allied 15V - Lot 701 Coal Tar Pitch

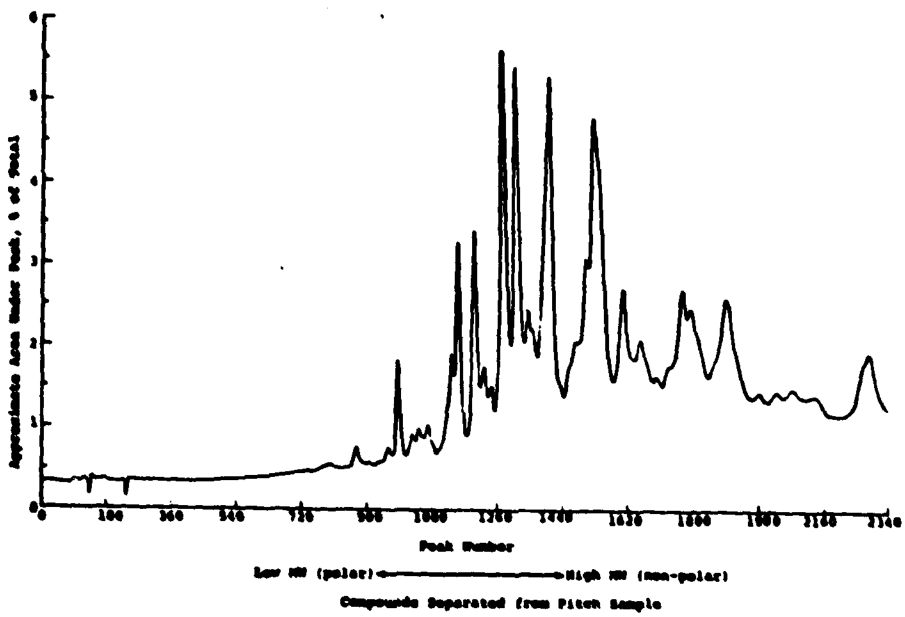


Figure 10. High Pressure Liquid Chromatogram of Koppers 15V Equivalent Coal Tar Pitch

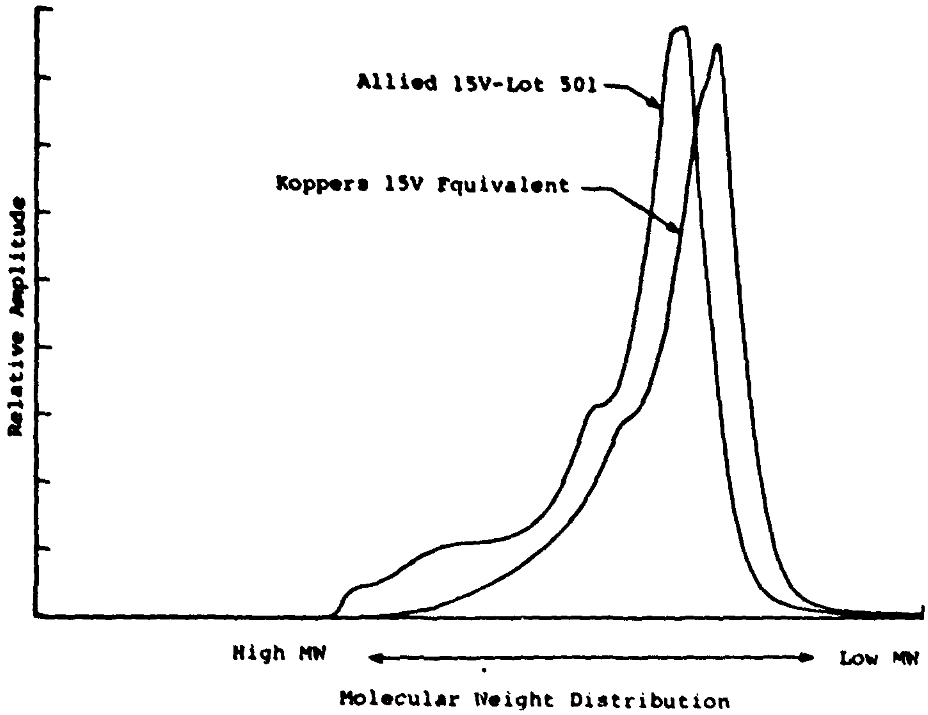


Figure 11. Compositional Differences Between the Allied and Koppers Version of 15V Pitch

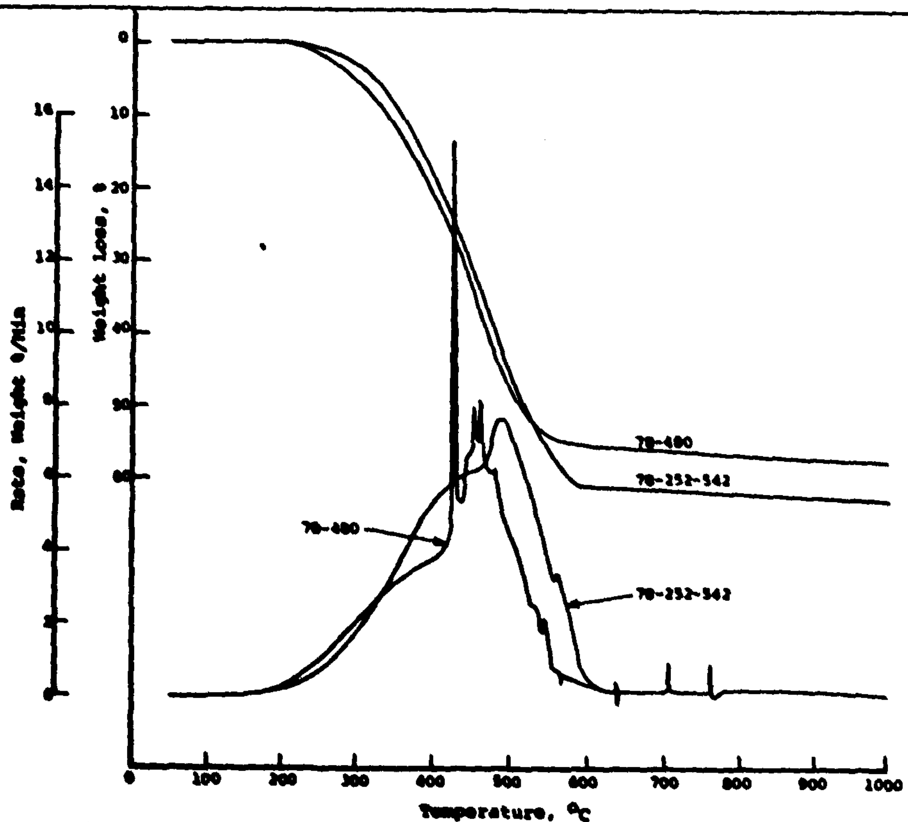


Figure 12. TGA of Koppers Experimental Pitches

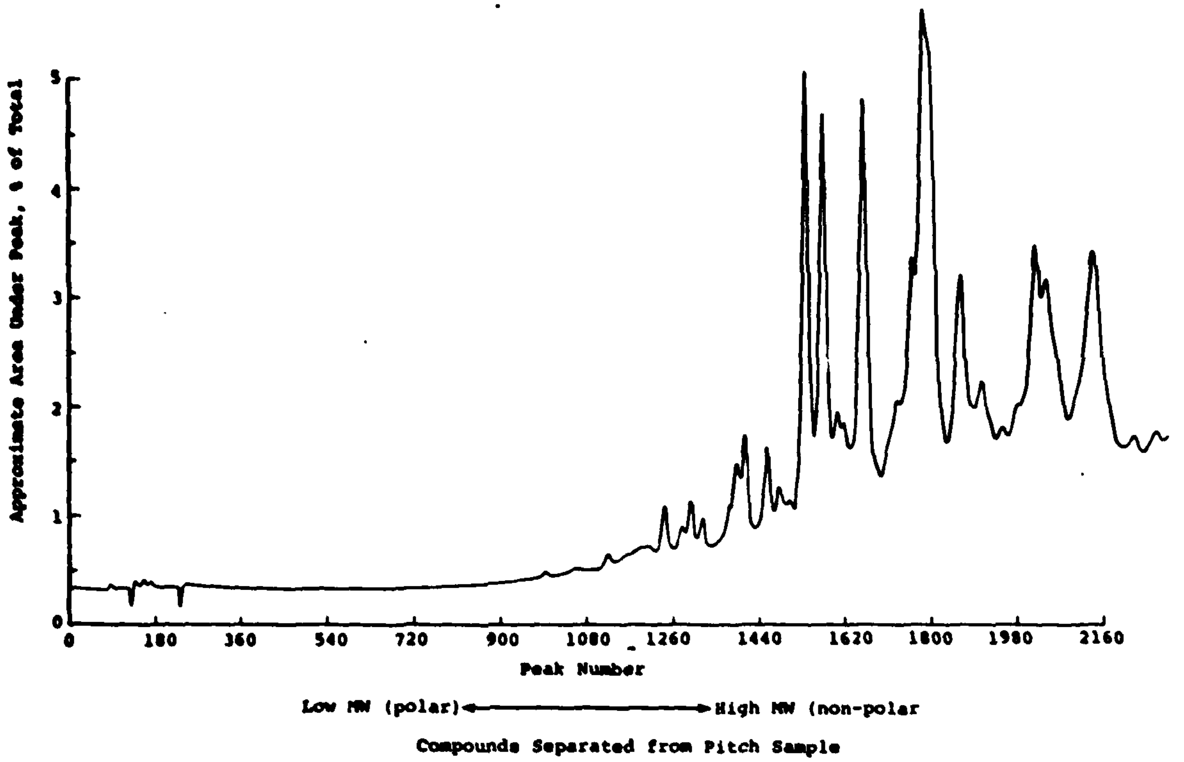


Figure 13. High Pressure Liquid Chromatogram of Koppers Experimental Impregnating Pitch #78-252-480

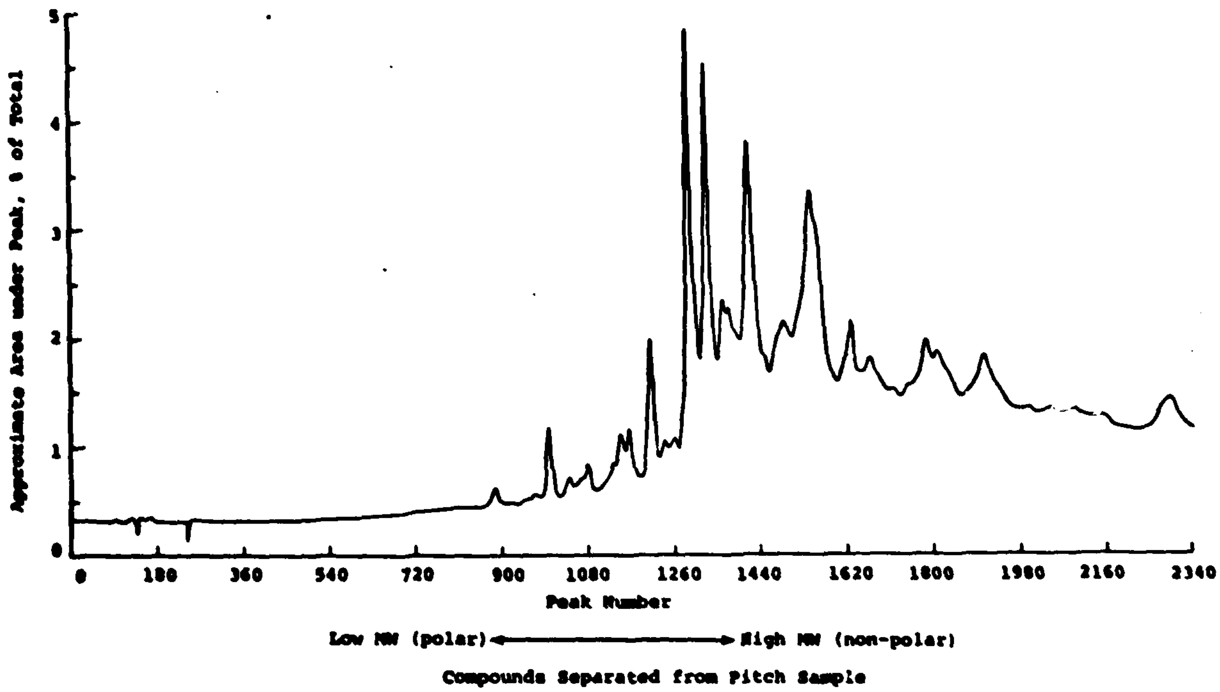


Figure 14. High Pressure Liquid Chromatogram of Koppers Experimental Impregnating Pitch #78-480

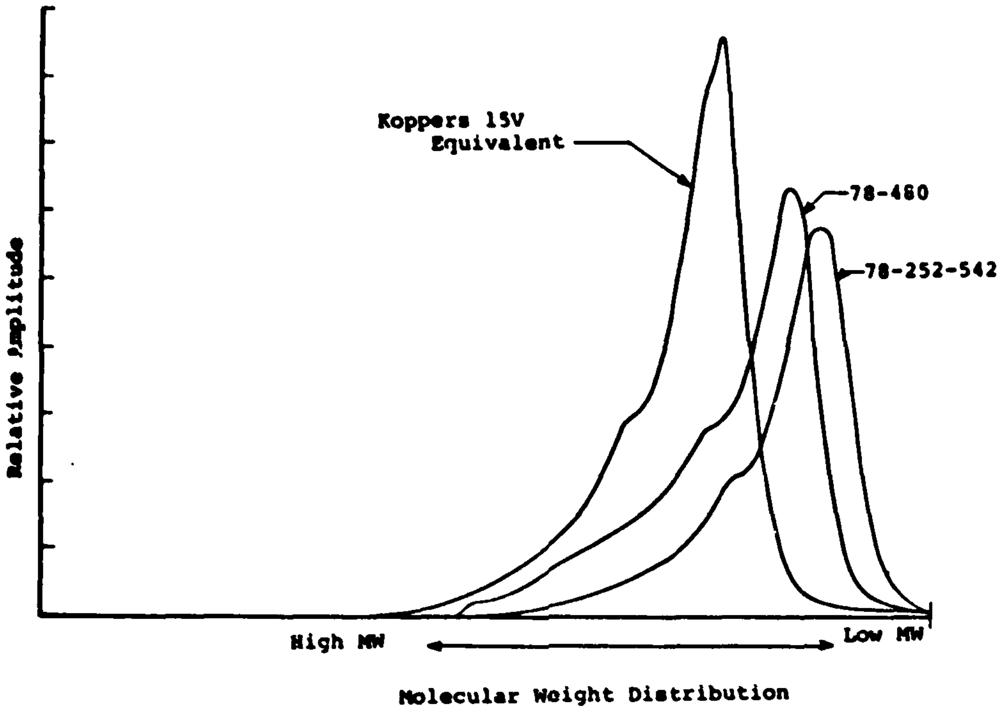


Figure 15. Compositional Differences of Three Koppers Pitches

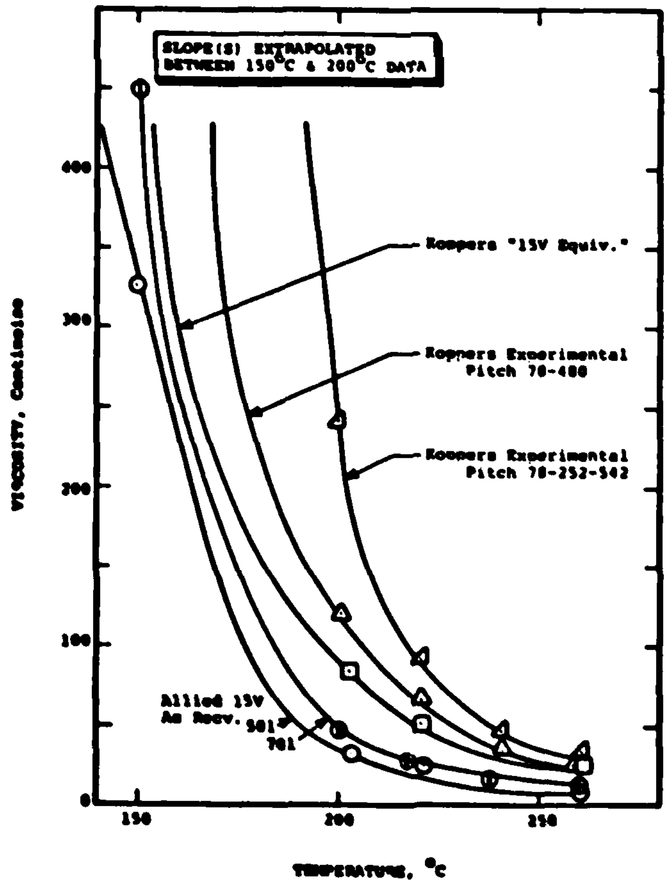


Figure 16. Viscosities of 15V Pitches and Two Experimental Koppers Pitches

4. Heat Treatment of Coal Tar Pitch

The effect of heat treating to improve the char yield of as received Allied 15V pitch was thoroughly investigated. The dependance upon the temperature, residence time, and the effect of mechanically agitating (mixing) the liquid mass of pitch undergoing conditioning were parametrically analyzed. Table 4 shows the quinoline insoluble content of several conditions of pitch (as received and pre-treated).

Table 4

QUINOLINE INSOLUBLE CONTENT OF TREATED PITCH

IMPREGNATING PITCH	CONDITION	QUINOLINE INSOLUBLES, %
Allied 15V	As Recv. - Lot 501, Bbl #1	2.2
Allied 15V	As Recv. - Lot 501, 861 #7	3.0
Koppers "15V Equiv."	As Recv. - 1977 Distilled	7.1
Allied 15V	HT @ 405°C-14 hrs-w/o Agitation	6.3
Allied 15V	GT @ 405°C-14 hrs-with Agitation	8.8
Allied 15V	HT @ 405°C-20 hrs-w/o Agitation	10.8

Because the treating of pitch to increase the carbon yield upon impregnation and carbonization is an ancillary task undertaken to understand basic composition characteristics, the data has been placed in Appendix 1 (TGA and viscosity) and Appendix 2 (Mesophase Formation).

5. Decomposition Reactions

Experimental packages with and without fiber modifications have been conducted according to the Air Force's EISP schedule to provide material for chemical and physical measurements and analysis. Carbonization runs at 3, 5, 10, and 15 ksi have been carried out to the completion of the EISP schedule, and have been interrupted

(Figure 17) and rapidly quenched to freeze in properties and the composition of liquid pitch prior to transformation of the pitch to a solid state. Figures 18, 19, 20, 21, and 22 compare the properties and compositional characteristics of as received Allied 15V and partially carbonized (at 15 ksi) Allied 15V recovered by the hot recovery technique developed specifically for retrieving liquid pitch samples. Figure 23 compares the distribution of the molecular weights of recovered liquid pitch from a 15 ksi run with the molecular weight signature of Koppers 15V Equivalent. Figures 24 and 25 present the high pressure liquid chromatogram from fully completed EISP carbonization schedules at 10 ksi and 15 ksi, respectively.

The elemental analysis of Allied 15V pitch material as a function of the degree of processing is presented in Tables 5 and 6. The properties of carbonized pitch for several process conditions and degree of completeness is presented in Table 7. It is important to note in Table 7 that while the bulk density of pitch carbonized to 470^{o}C and then rapidly quenched (Run No. 005/SE) is similar to bulk properties of the material processed at higher temperatures, the true density (apparent) and porosity of the recovered material is significantly different. These differences can be accounted for if it is assumed that the material recovered had not completed, or was in the initial stages of transformation from a liquid to a solid.

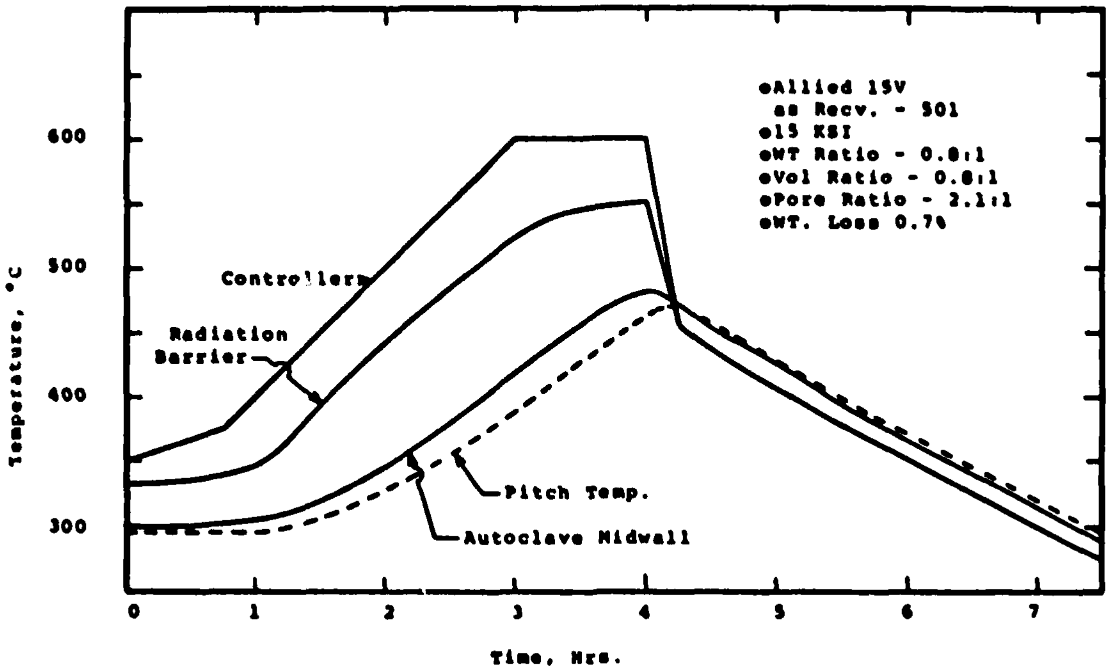


Figure 17. Time-Temperature-Pressure History of Interrupted 15 KSI Carbonization (EISP Schedule)

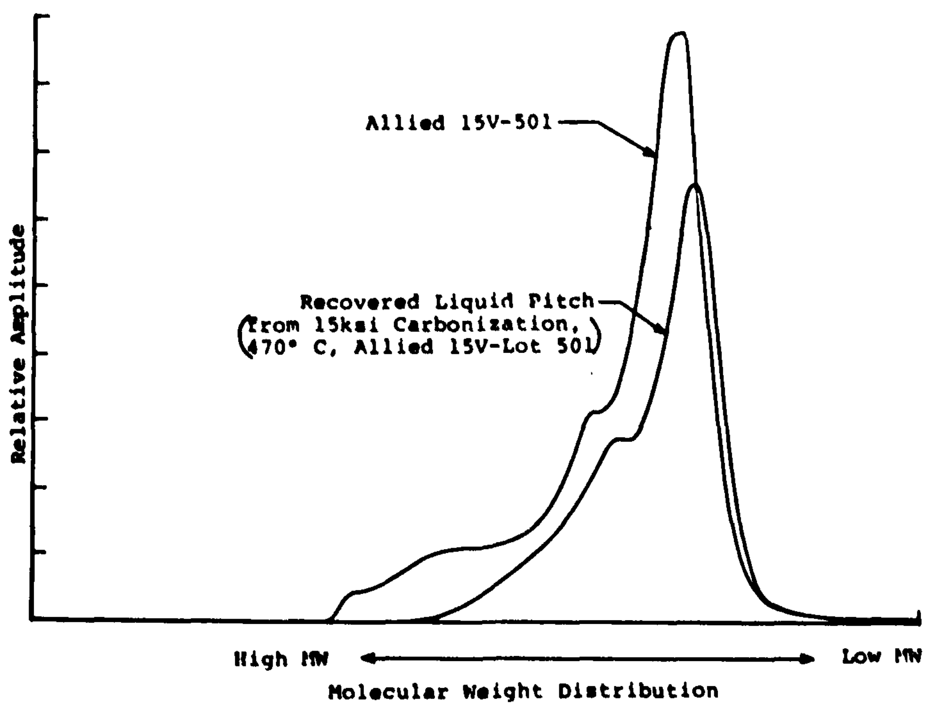


Figure 18. Gel Permeation Data Showing Shift in Molecular Weight Distribution Due To Partial Carbonization of 15 KSI

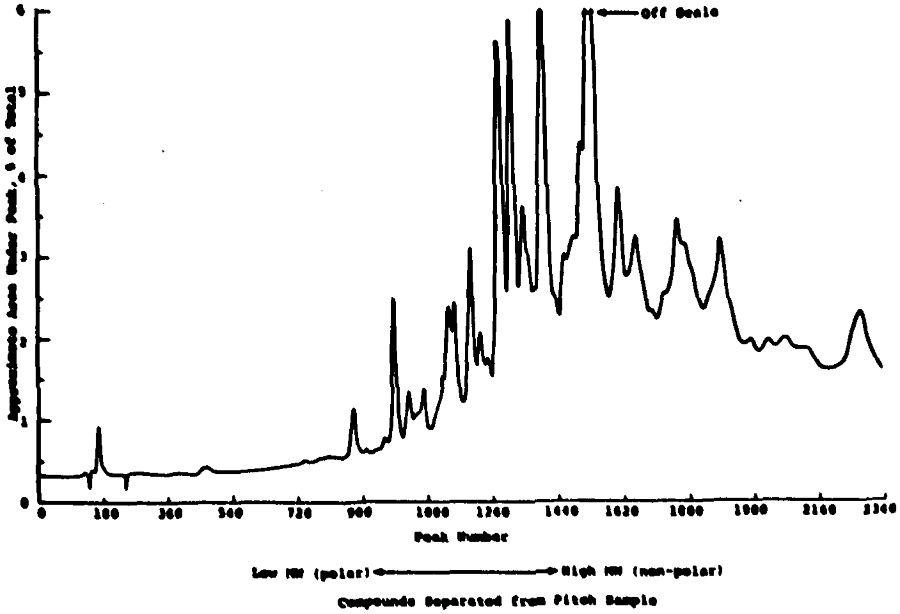


Figure 19. High Pressure Liquid Chromatogram of Allied 15V - Lot 501 Coal Tar Pitch Precursor

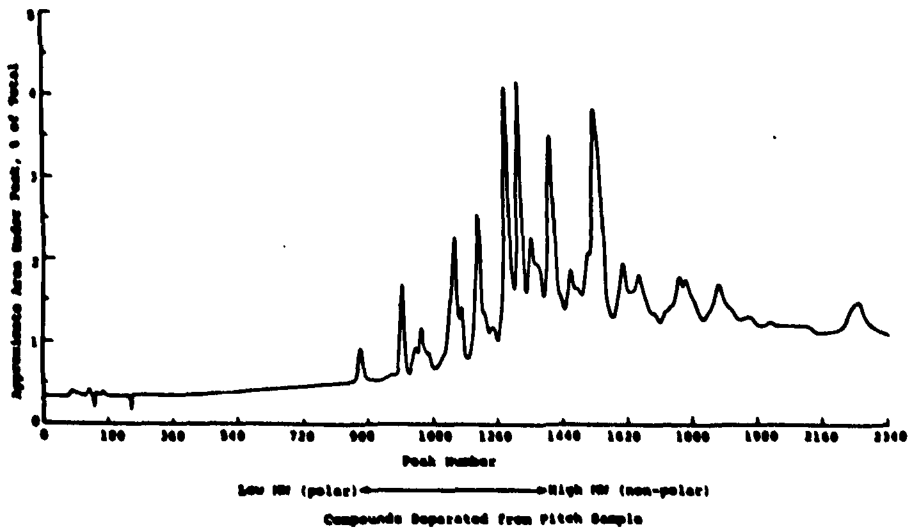


Figure 20. High Pressure Liquid Chromatogram of Hot Recovered Liquid Pitch (Allied 15V - Lot 501) from Interrupted (470°C) 15 KSI Carbonization

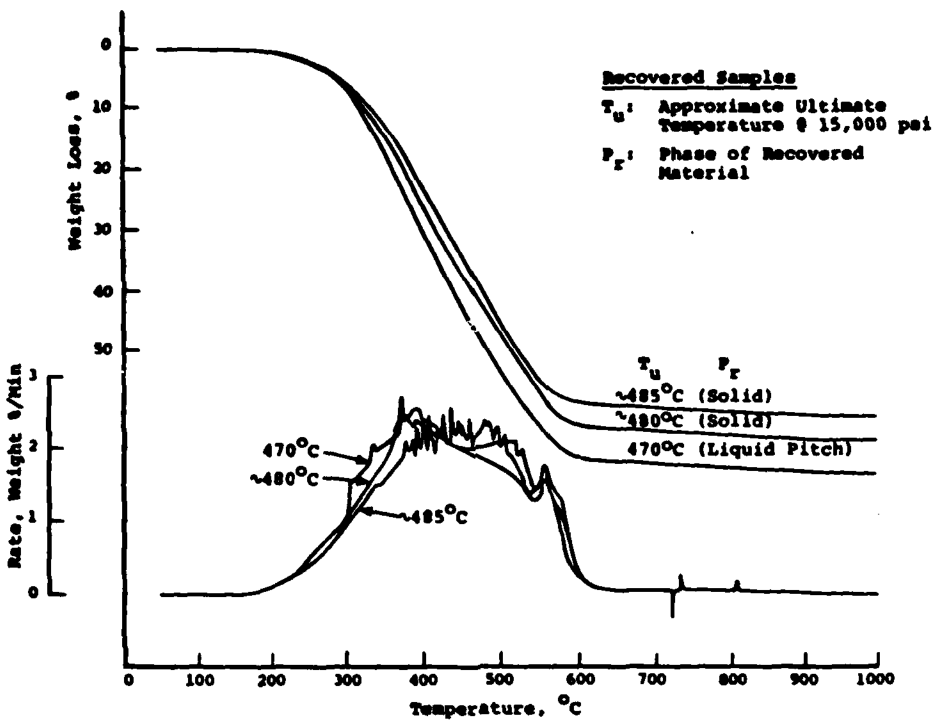


Figure 21. Weight Loss Comparison Between Liquid Pitch and Solid Pitch Recovered Hot from Interrupted 15 KSI Carbonization Cycle (TGA Data)

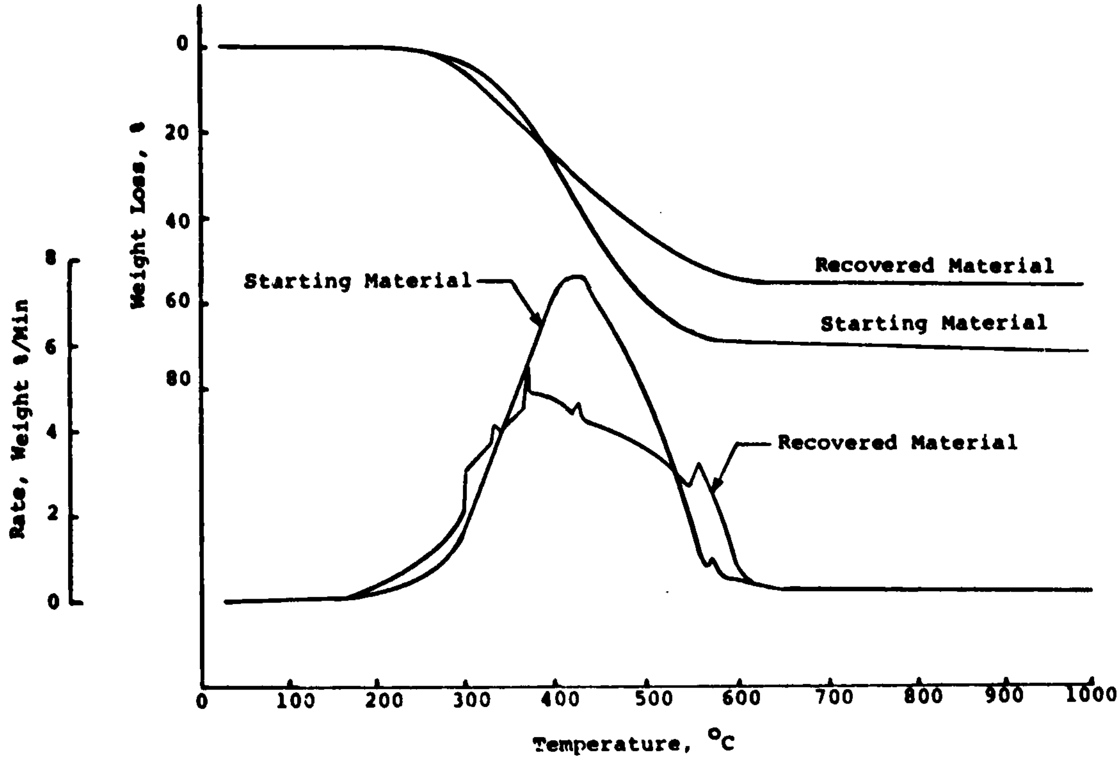


Figure 22. TGA Data Comparing Weight Loss Characteristics of Recovered Liquid Pitch from Interrupted Run with Starting Material

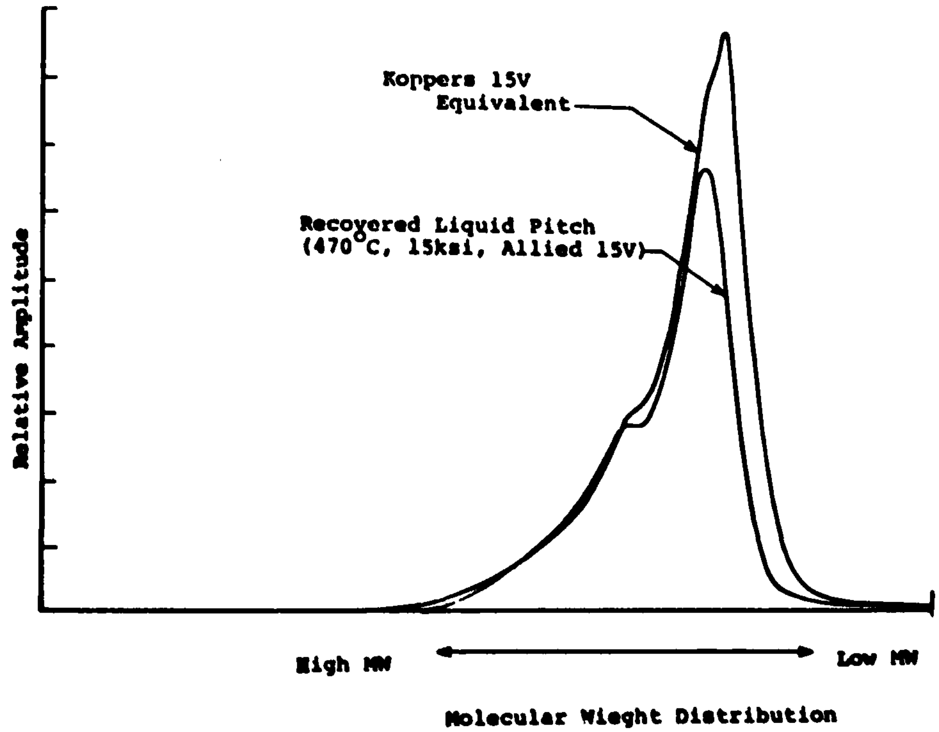


Figure 23. Gel Permeation Data Showing Compositional Similarity Between Partially Carbonized Allied 15V and Koppers 15V Equivalent (As Received)

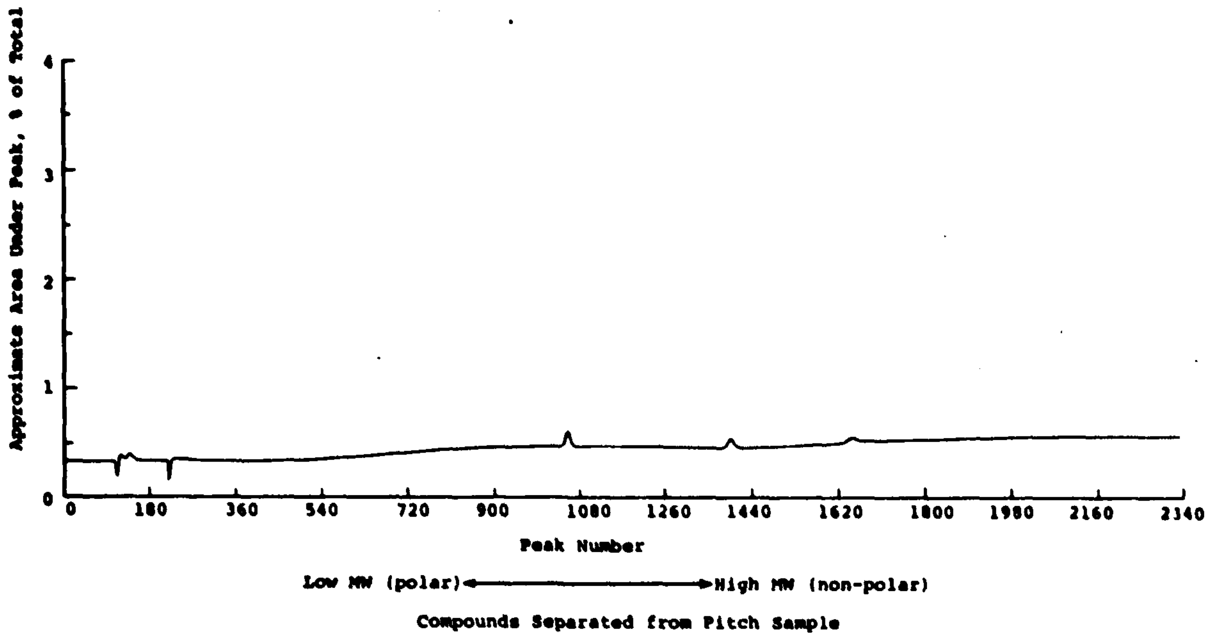


Figure 24. High Pressure Liquid Chromatogram of Allied 15V Carbonized to Completion via EISP Schedule at 10 KSI

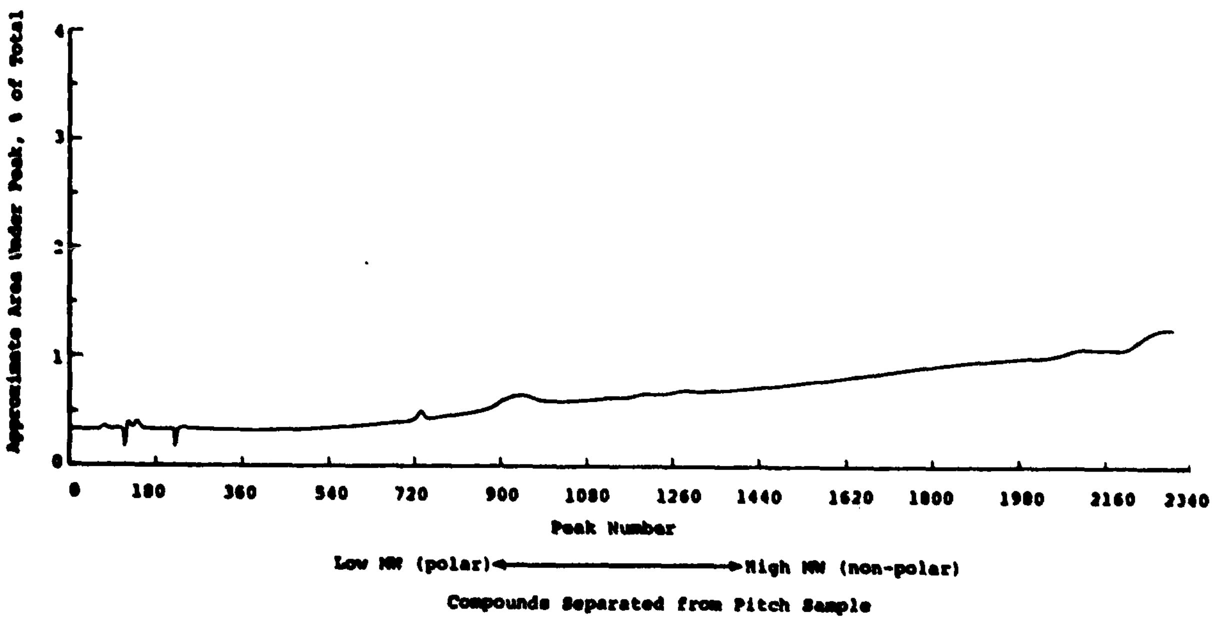


Figure 25. High Pressure Liquid Chromatogram of Allied 15V Carbonized to Completion via EISP Schedule at 15 KSI

Table 5

ELEMENTAL ANALYSIS OF ALLIED 15V-LOT 501
AS FUNCTION OF DEGREE OF CARBONIZATION AT 15,000 PSI

	COMPOSITION BY WEIGHT PERCENT					
MATERIAL CONDITION	C	H	N	S	O	Ash
As Received	92.42	4.83	1.07	0.55	1.03	0.15
Carbonized to 470°C	92.33	4.54	0.96	0.40	1.49	0.29
Full Carbonization	93.07	2.72	0.92	0.50	2.69	0.10

Table 6

ELEMENTAL ANALYSIS OF ALLIED 15V-Lot 501
AS FUNCTION OF PRESSURE FOR FULL CARBONIZATION* RUNS

	COMPOSITION BY WEIGHT PERCENT					
CARBONIZATION PRESSURE	C	H	N	S	O	Ash
10,000 psi	92.43	2.36	0.83	0.44	3.93	0.34
15,000 psi	93.07	2.72	0.92	0.50	2.69	0.10

* Identical carbonization cycles with exception of pressure - EISP schedule to 615°C pitch temperature, then held 5 hours.

Table 7

PROPERTIES OF CARBONIZED PITCH
FOR SEVERAL PROCESS CONDITIONS

RUN NO.	PRESSURE KSI	MAX PITCH TEMP., °C	RESIDENCE TIME HRS.	AUTOCLAVE LOCATION	BULK* DENSITY gm/cc	APPARENT* DENSITY gm/cc	POROSITY %
CARBONIZED ALLIED 15V							
002/SE	10	615°	1	Top	1.15	1.47	21.8
				Bottom	1.09	1.51	27.8
003/SE	10	615°	4	Top	1.13	1.52	25.7
				Bottom	1.00	1.59	37.1
004/SE	15	605°	4	Top	1.20	1.62	25.9
				Bottom	1.06	1.63	35.0
005/SE	15	470°	<0.25	Top	1.10	1.25	12.0
IMPREGNATED POROUS CARBON							
003/SE	10	615°	4	Middle	1.46	1.85	21.0
				Bottom	1.48	1.94	23.7
004/SE	15	605°	4	Top	1.51	1.85	18.4
				Middle	1.52	1.86	18.3
				Bottom	1.52	1.86	18.3
005/SE	15	470°	<0.25	Top	1.44	1.62	11.1
				Middle	1.52	1.69	10.1
				Bottom	1.51	1.67	9.6

*ASTM C-20

A P P E N D I X 1

THERMOGRAVEMETRIC ANALYSIS (TGA) AND VISCOSITY DATA FOR HEAT TREATED COAL TAR PITCHES

(Figures)

MATRIX/CONDITION	TEMP. °C	MAX RATE % PER MIN
• AS RECEIVED		
15V-Barrel 1	412°	7.66
15V-Barrel 2	420°	7.48
HOPPERS	480°	6.15
• HEAT TREAT @ 405°C W/O AGITATION		
15V-12 hrs.	472°	6.85
-14 hrs.	490°	7.13
-14.5 hrs.*	495°	7.36
-16 hrs.	495°	7.92
-18 hrs.	480°-495°	6.60
-20 hrs.	490°-505°	6.87
-20+cool+2 hrs.	488°	7.26
• HEAT TREAT @ 405°C WITH AGITATION		
15V-14 hrs.	495°	5.06

*Batch cooled then rapidly returned to 405°C

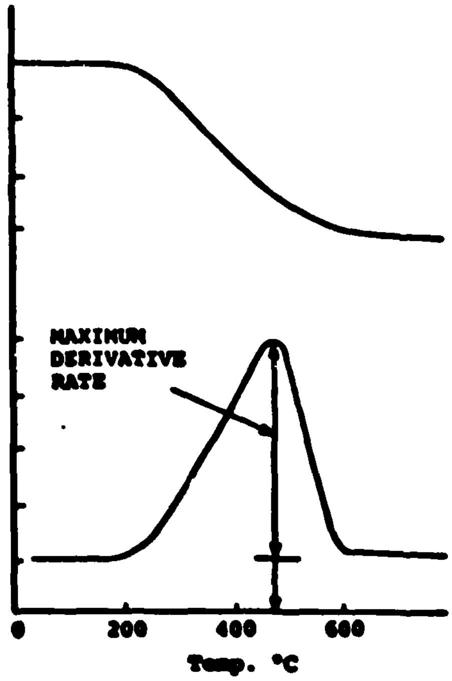


Figure 1-1. Maximum Decomposition Rates and Temperatures

MATRIX/CONDITION	REMAINING WEIGHT (%) 600°C	1000°C
• AS RECEIVED		
15V-Barrel 1	28.7	26.9
15V-Barrel 2	33.0	29.9
HOPPERS	41.7	39.9
• HEAT TREAT @ 405°C W/O AGITATION		
15V-12 hrs.	37.9	35.1
-14 hrs.	37.6	35.5
-14.5 hrs.*	38.7	36.2
-16 hrs.	38.5	36.8
-18 hrs.	40.6	38.3
-20 hrs.	39.5	37.7
-20+cool+2 hrs.	40.3	38.5
• HEAT TREAT @ 405°C WITH AGITATION		
15V-14 hrs.	49.7	47.2

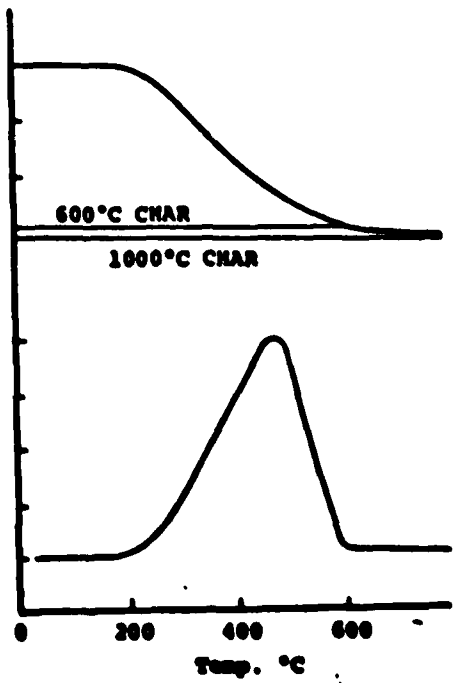


Figure 1-2. Comparative Weight Loss at 600°C and 1000°C

MATRIX/CONDITION	TEMPERATURE, °C		
	LOWER	UPPER	Δ
● **AS RECEIVED**			
15V-Barrel 1	370°	475°	105°
15V-Barrel 2	373°	479°	106°
HOPPERS	385°	510°	125°
● **HEAT TREAT @ 405°C W/O AGITATION**			
15V-12 hrs.	394°	498°	104°
-14 hrs.	408°	505°	97°
-14.5 hrs.*	405°	509°	104°
-16 hrs.	408°	508°	100°
-18 hrs.	403°	505°	102°
-20 hrs.	407°	511°	104°
-20+cool+2 hrs.	397°	502°	105°
● **HEAT TREAT @ 405° WITH AGITATION**			
15V-14 hrs.	396°	503°	107°

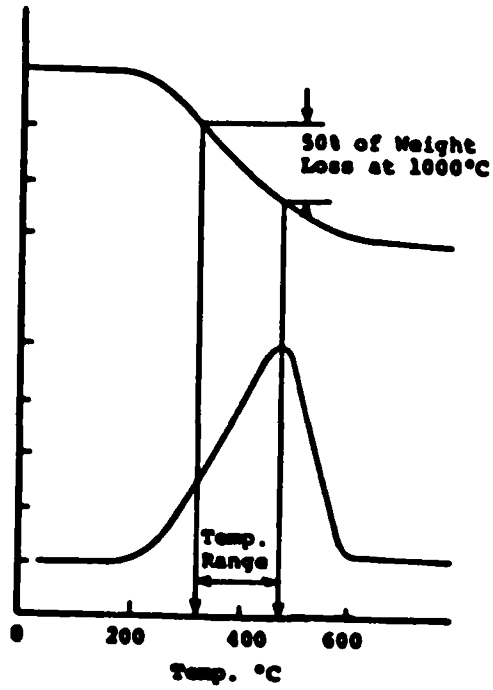


Figure 1-3. Median Temperature Range for Fifty Percent (50%) Weight Loss

MATRIX/CONDITION	TEMP. RANGE °C	dy' [10^{-4}(w/o).min^{-1}.°C^{-1}]
● **AS RECEIVED**		
15V-Barrel 1	316°-400°	6.08
15V-Barrel 2	295°-405°	5.30
HOPPERS	280°-465°	2.53
● **HEAT TREAT @ 405°C W/O AGITATION**		
15V-12 hrs.	338°-454°	3.93 Ave.
-14 hrs.	350°-475°	3.57 Ave.
-14.5 hrs.*	340°-485°	3.29 Ave.
-16 hrs.	367°-490°	3.79 Ave.
-18 hrs.	330°-470°	3.46 Ave.
-20 hrs.	360°-493°	3.63 Ave.
-20+cool+2 hrs.	363°-480°	3.65
● **HEAT TREAT @ 405°C WITH AGITATION**		
15V-14 hrs.	310°-460°	2.44 Ave.

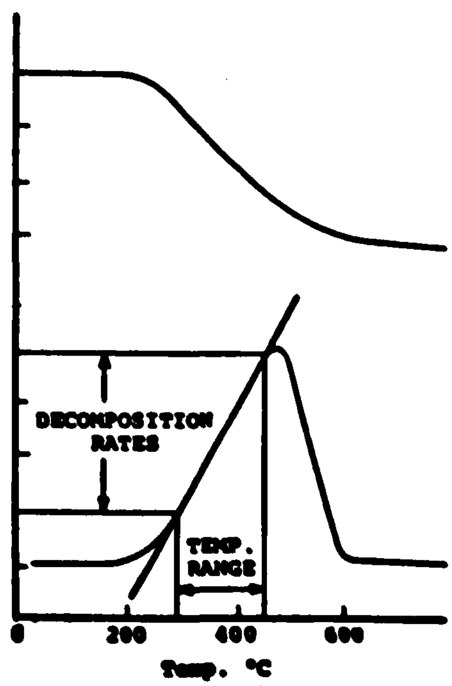


Figure 1-4. Derivative Rate of Change (dy') of Initial Decomposition

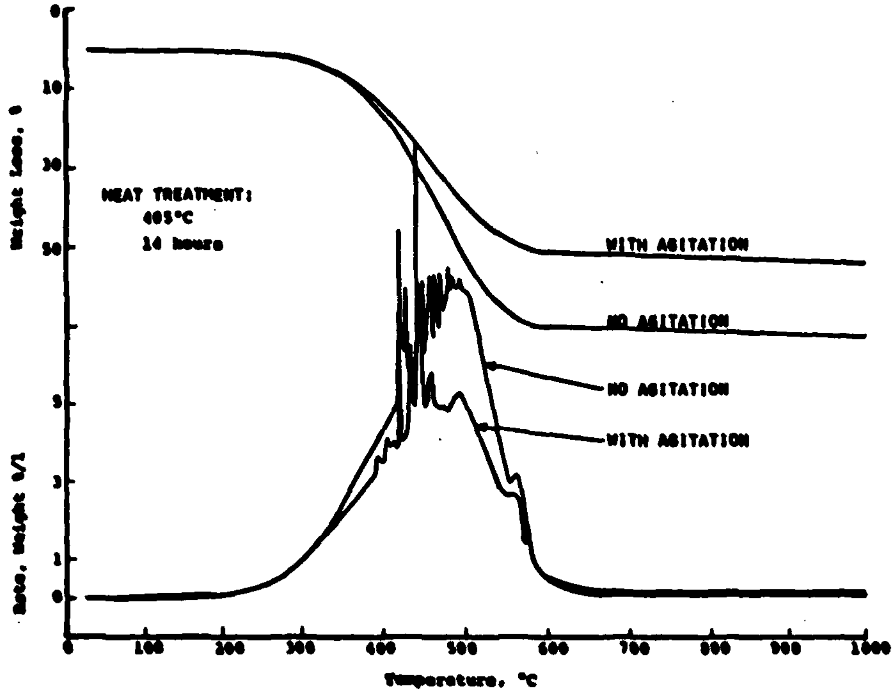


Figure 1-5. Effect of Mechanical Agitation on Weight Loss of Similarly Heat Treated Allied 15V Pitch (TGA Data)

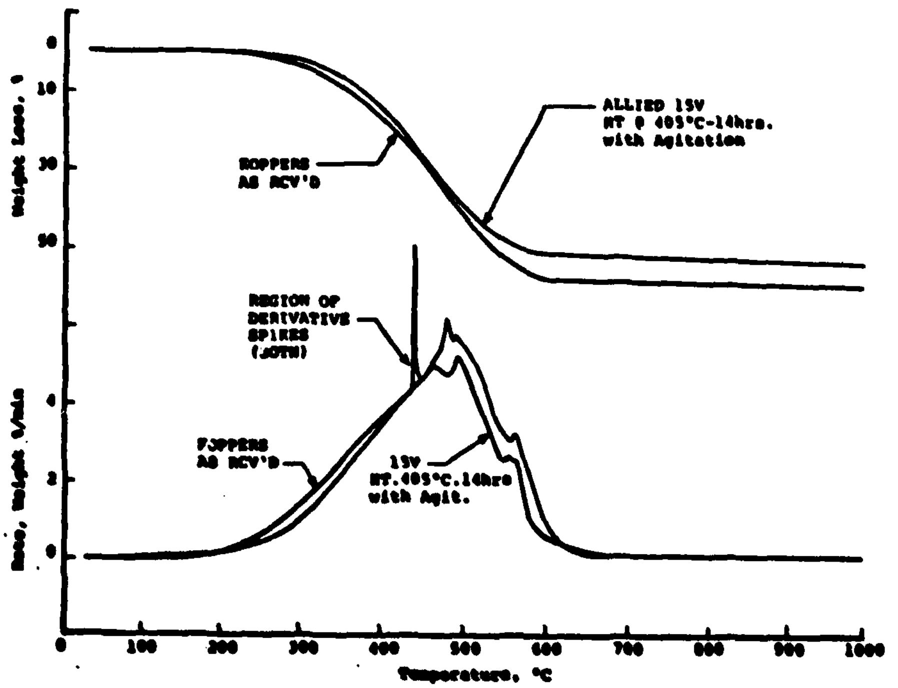


Figure 1-6. Weight Loss Similarity Between Mechanically Agitated and Heat Treated Allied 15V with "As Received" Koppers 15V (TGA Data)

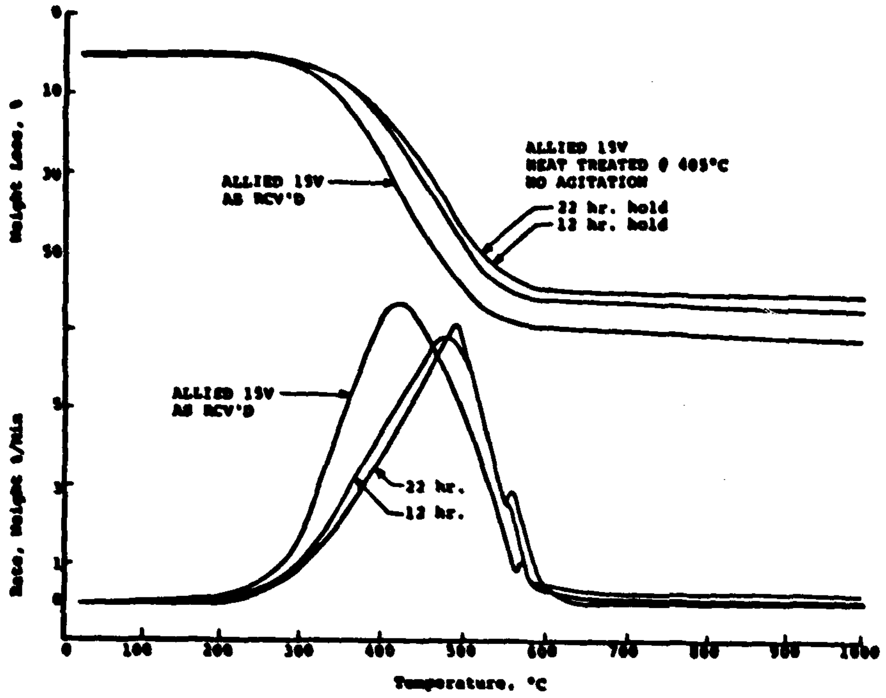


Figure 1-7. Effect of Heat Treatment Residence Time on Weight Loss of Allied 15V (TGA Data)

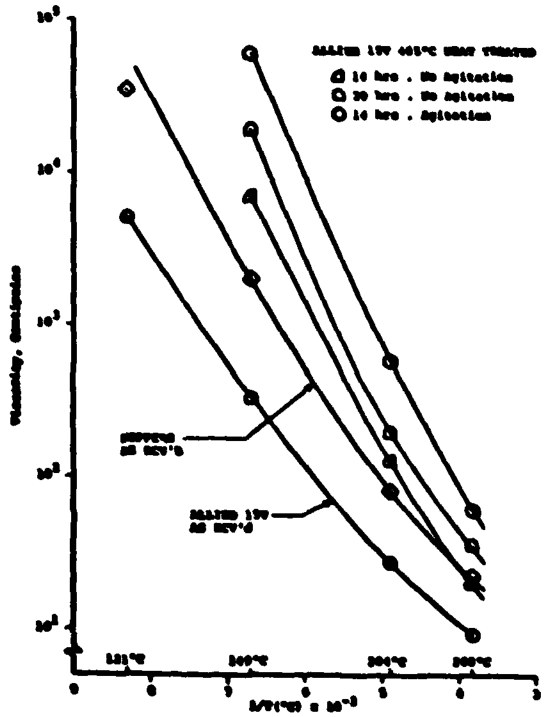


Figure 1-8. Viscosity of Allied 15V, Koppers 15V, and Heat Treated Allied 15V

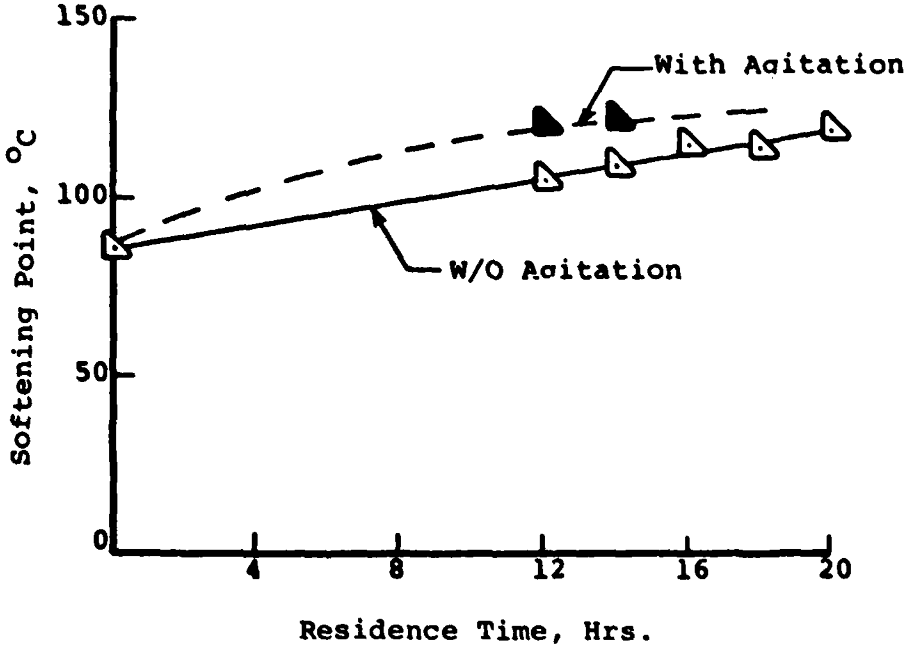


Figure 1-9. Softening Point of Heat Treated Allied 15V

APPENDIX 2

MESOPHASE FORMATION STUDIES

(Figures)

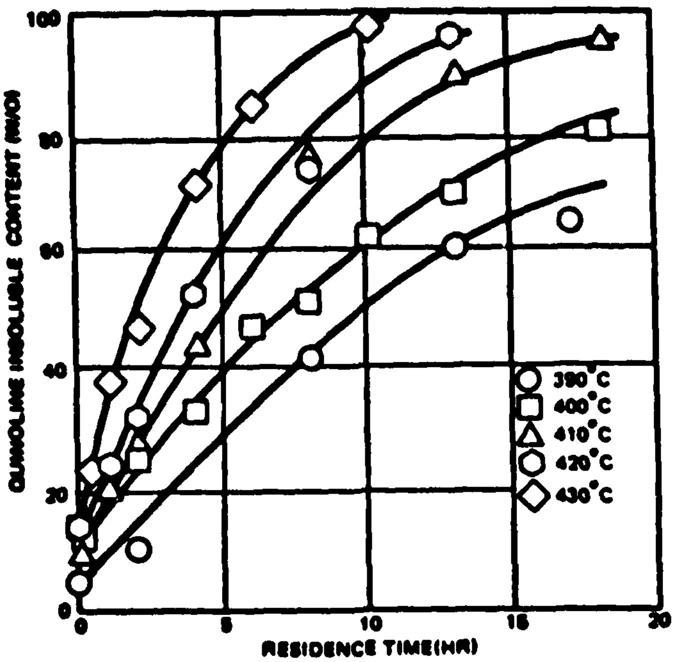


Figure 2-1. Mesophase Formation Rate (From Honda, H., Kimura, H., Sanada, Y., Sugawara, S. and Fusuta, T. Carbon, Vol. 8, 1970, p. 181)

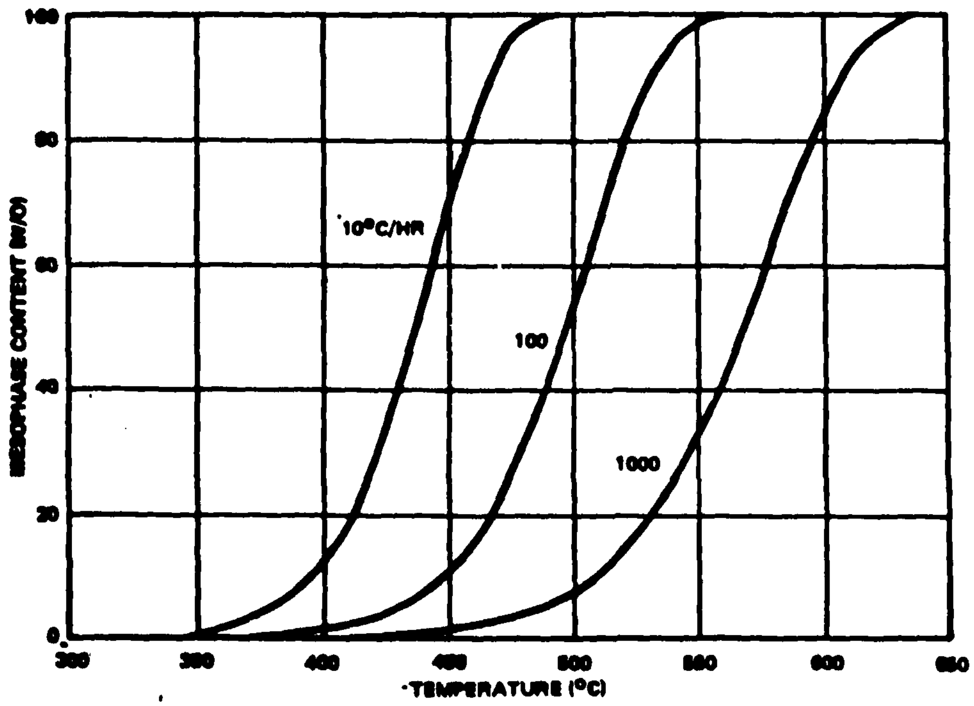
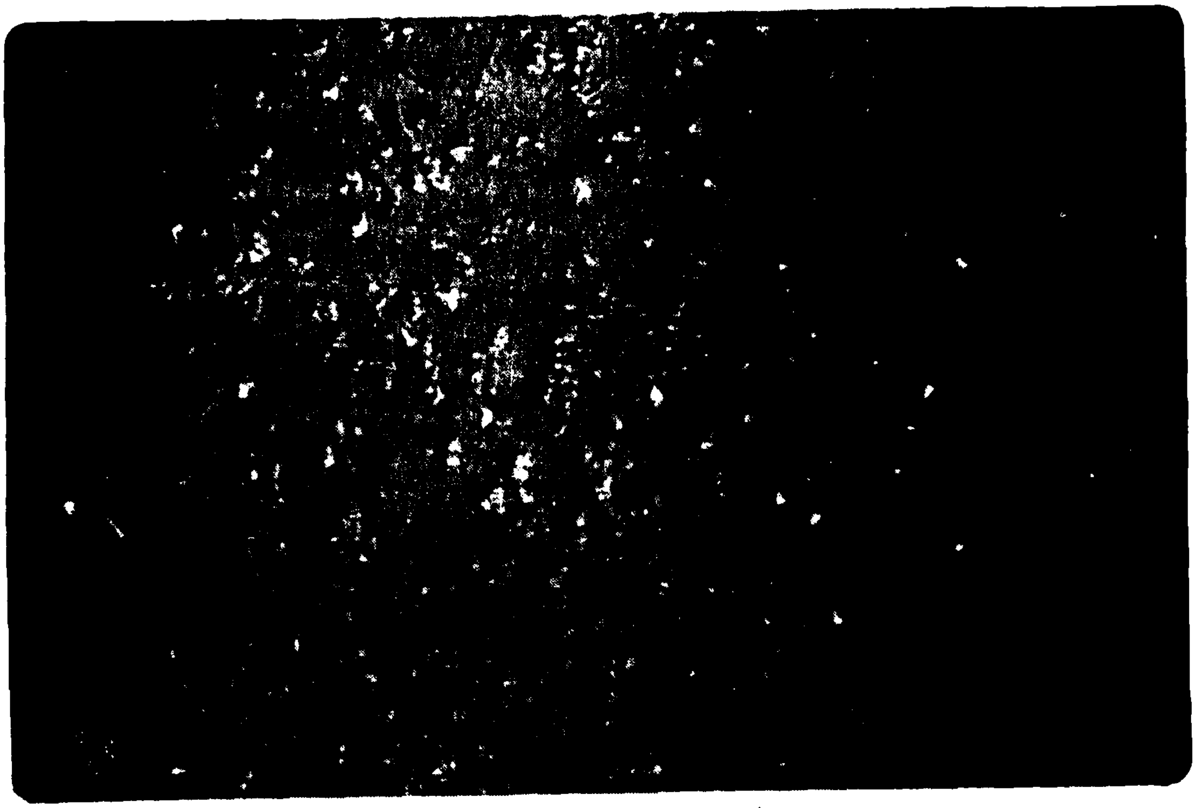


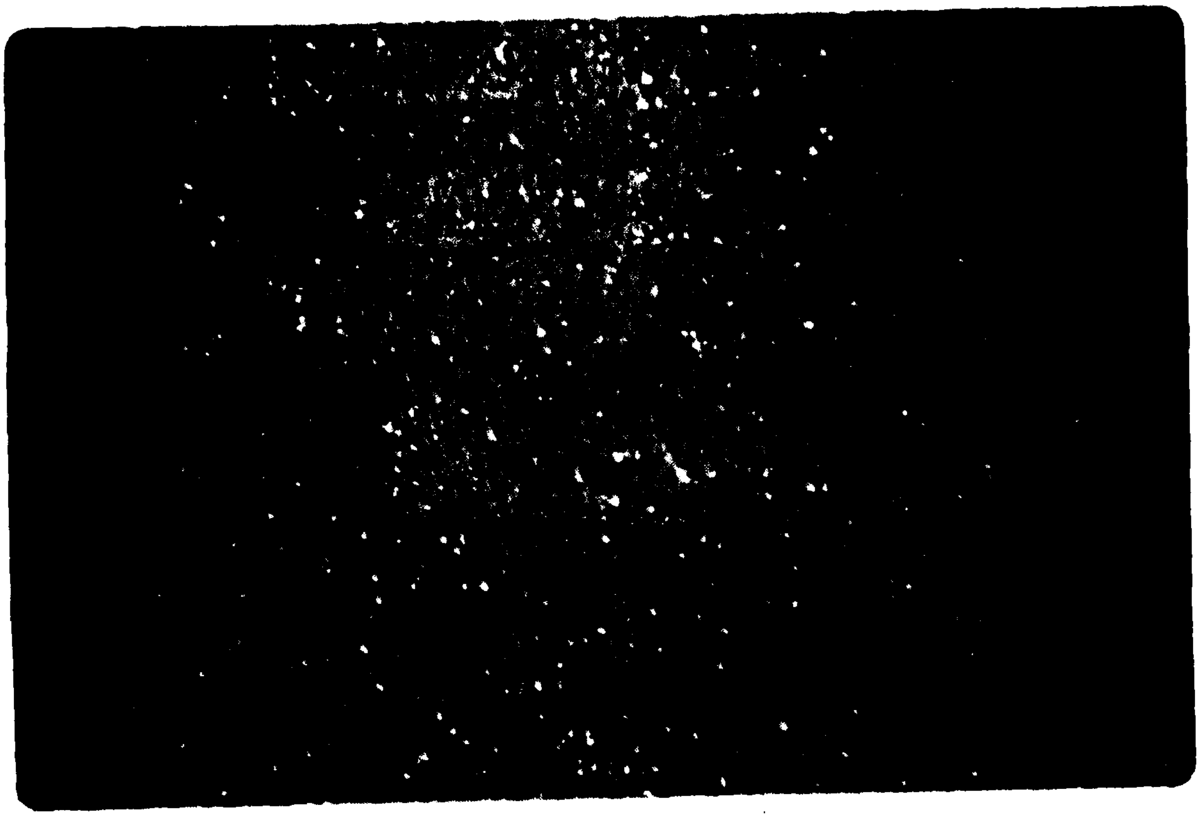
Figure 2-2. Mesophase Conversion for Constant Temperature Rise Rate (Calculated from Data in Figure 2-1)



500x

22 HOURS WITHOUT MECHANICAL AGITATION

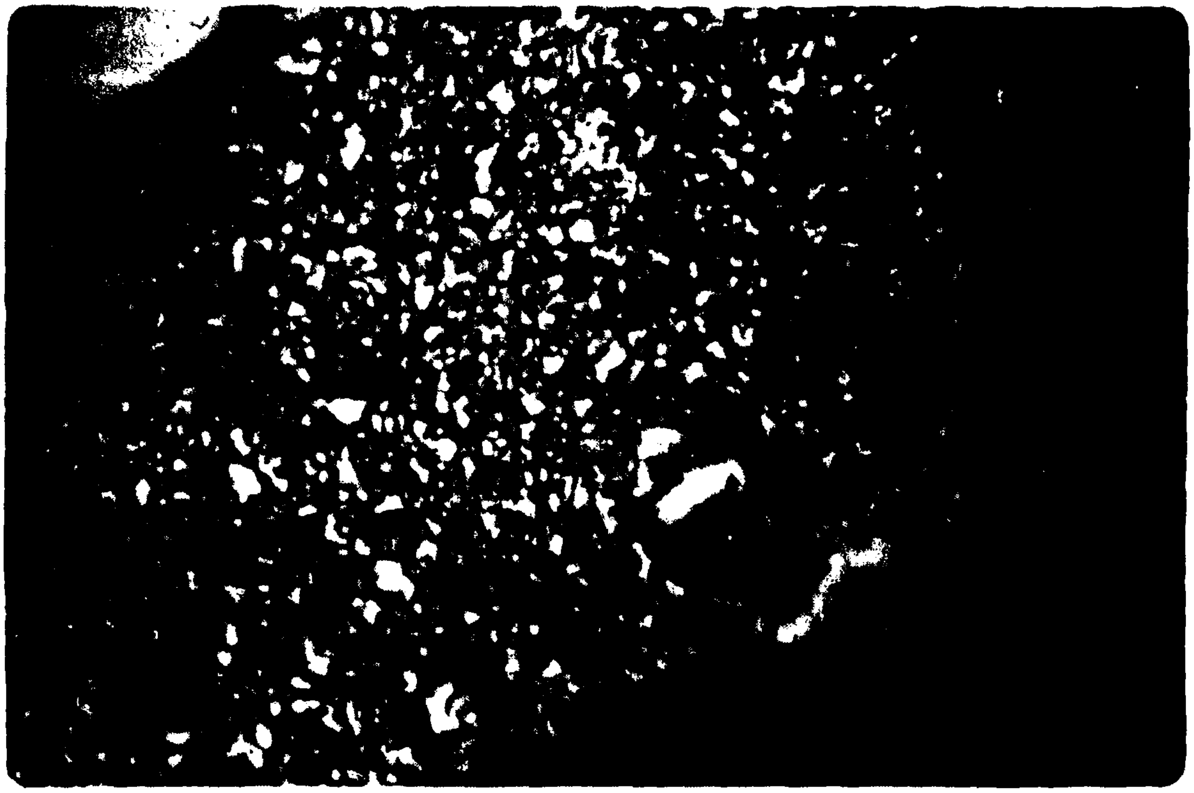
FIGURE 2-3 EFFECT OF AGITATION (MIXING) OF HEAT TREATMENT (@ 405°C) CONDITIONING OF AS RECEIVED ALLIED 15V COAL TAR PITCH



80x

14 HOURS WITH MECHANICAL AGITATION

FIGURE 2-4 EFFECT OF AGITATION (MIXING) OF HEAT TREATMENT (@ 405°C) CONDITIONING OF AS RECEIVED ALLIED 15V COAL TAR PITCH



500x

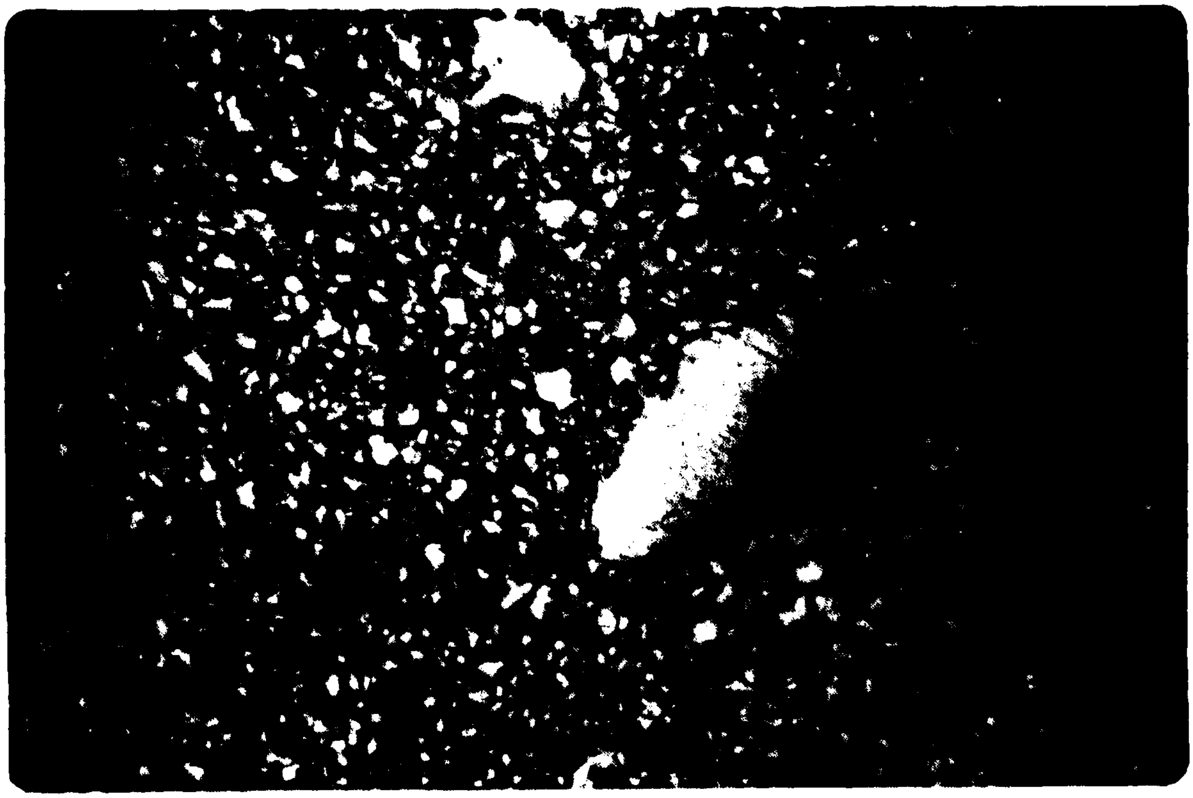
INTERRUPTED RUN-470°C/RAPID COOL

FIGURE 2-5 MESOPHASE COALESCENE DUE TO INTERRUPTED CYCLE AT 3000 PSI FOR ALLIED 15V COAL TAR PITCH

500x

FULL CARBONIZATION-615°C/HELD 4 HOURS

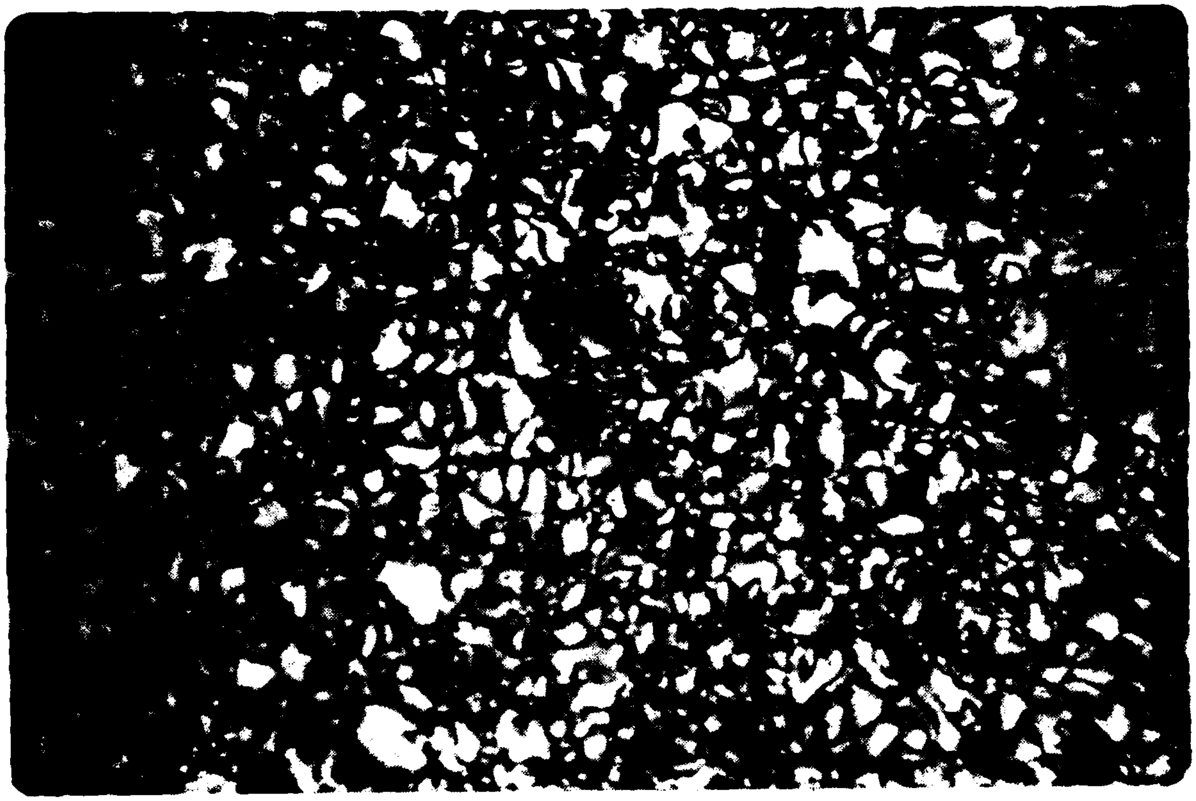
FIGURE 2-6 MESOPHASE COALESCENCE DUE TO FULL CARBONIZATION CYCLE



500x

INTERRUPTED RUN-470°C/RAPID COOL

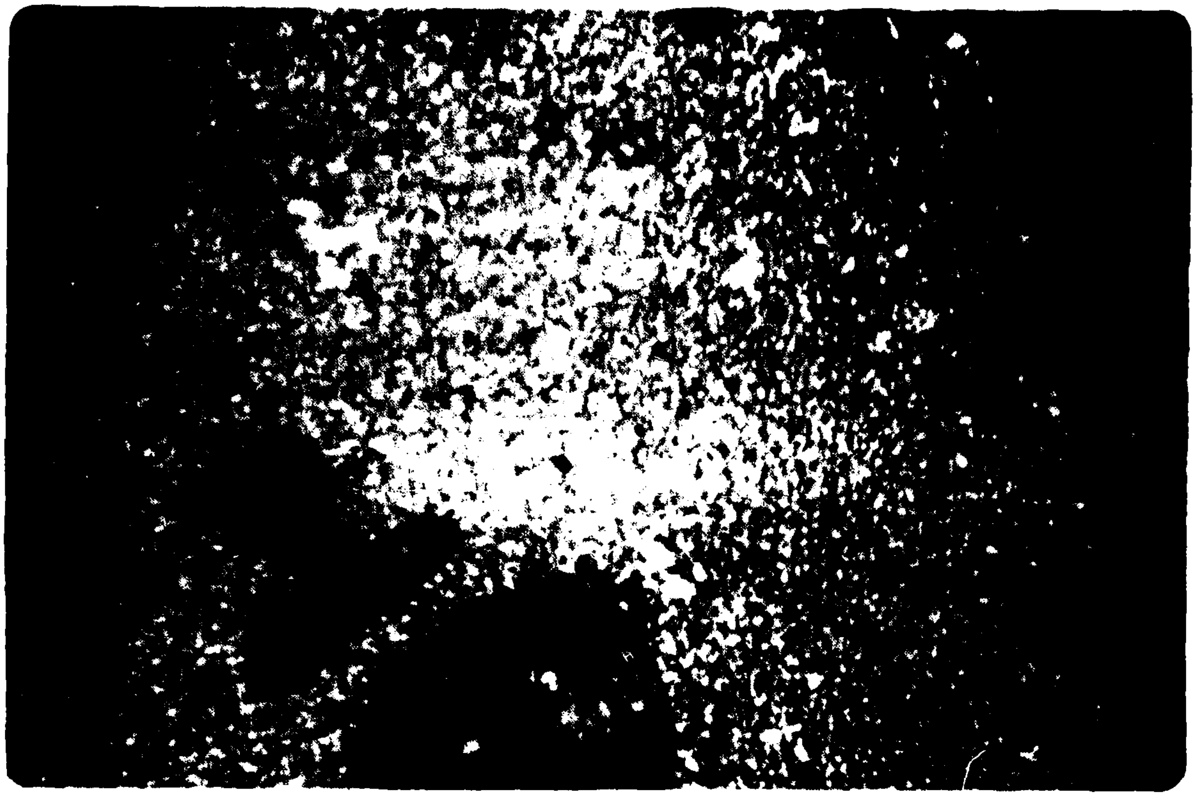
FIGURE 2-7 TYPICAL MESOPHASE PARTICULATE SIZE DUE TO DEGREE OF CARBONIZATION OF ALLIED 15V COAL TAR PITCH.



500x

FULL CARBONIZATION - 615°C/HELD 4 HOURS

FIGURE 2-8 TYPICAL MESOPHASE PARTICULATE SIZE DUE TO DEGREE OF CARBONIZATION OF ALLIED 15V COAL TAR PITCH.



80x

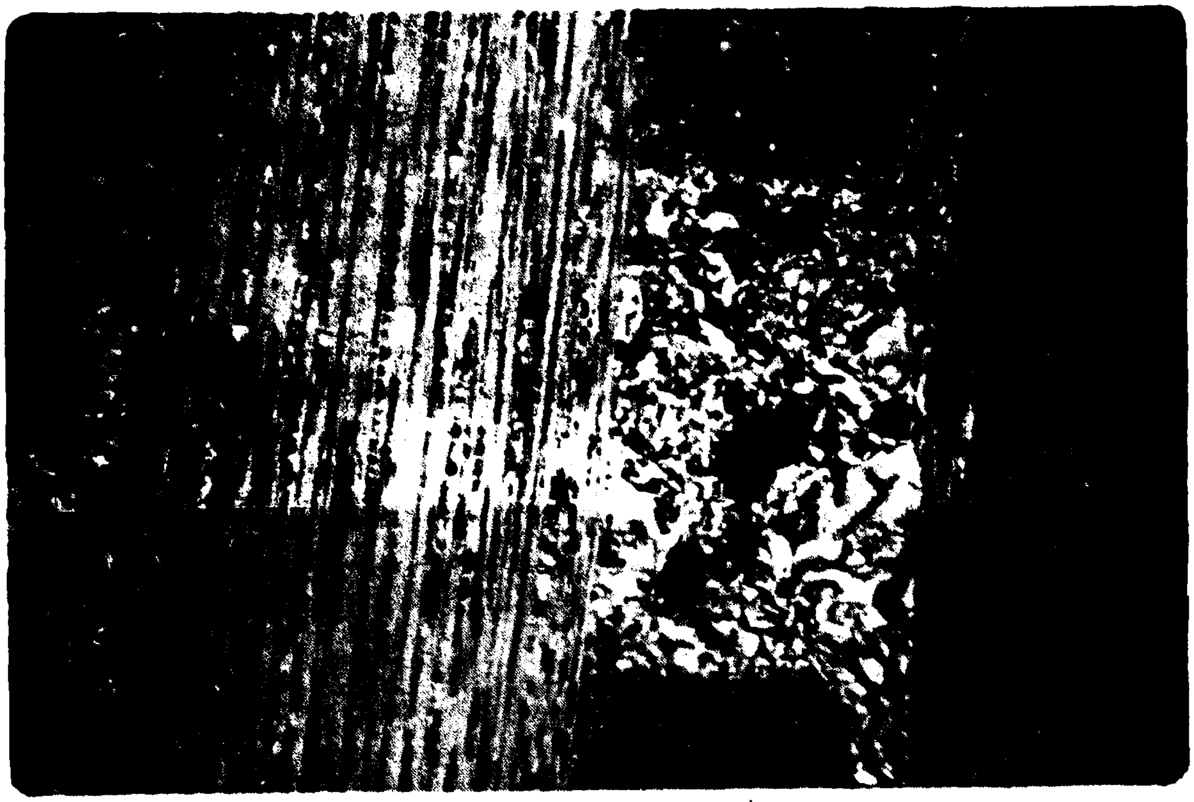
INTERRUPTED RUN - 470°C / RAPID COOL

FIGURE 2-9 TYPICAL MESOPHASE/POROSITY INTERFACES SHOWING EFFECT OF GASEOUS PERCOLATION AND DEGREE OF CARBONIZATION AT 3000PSI FOR ALLIED 15V COAL TAR PITCH.

500x

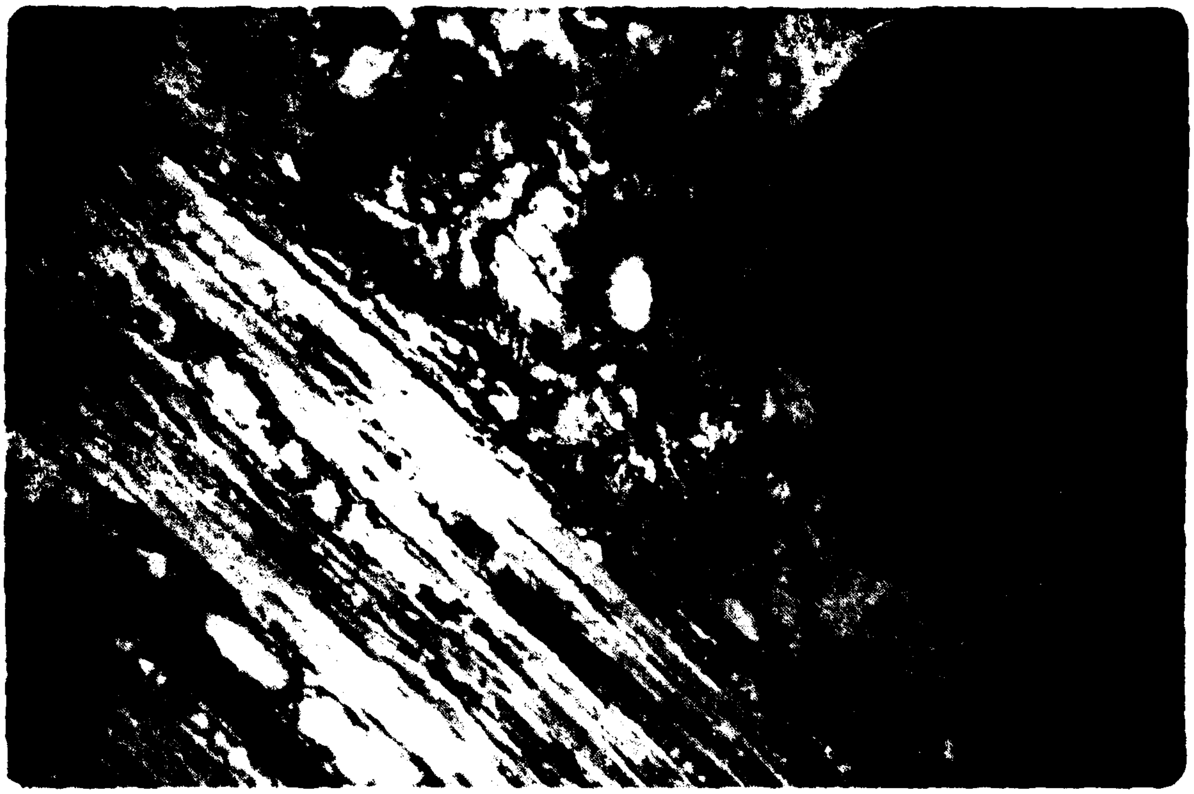
FULL CARBONIZATION - 615°C/HELD 4 HOURS

FIGURE 2-10 TYPICAL MESOPHASE/POROSITY INTERFACES SHOWING EFFECT OF GASEOUS PERCOLATION AND DEGREE OF CARBONIZATION AT 3000PSI FOR ALLIED 15V COAL TAR PITCH.



80x-FULL POL

FIGURE 2-11 MESOPHASE COALESCENCE IN GE 2-2-3, BILLET 408 R-2



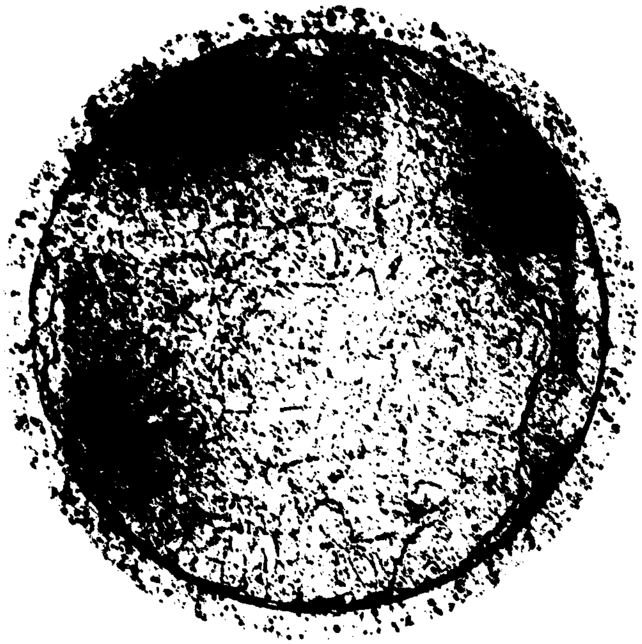
500x-POLARIZER ROTATED 15°

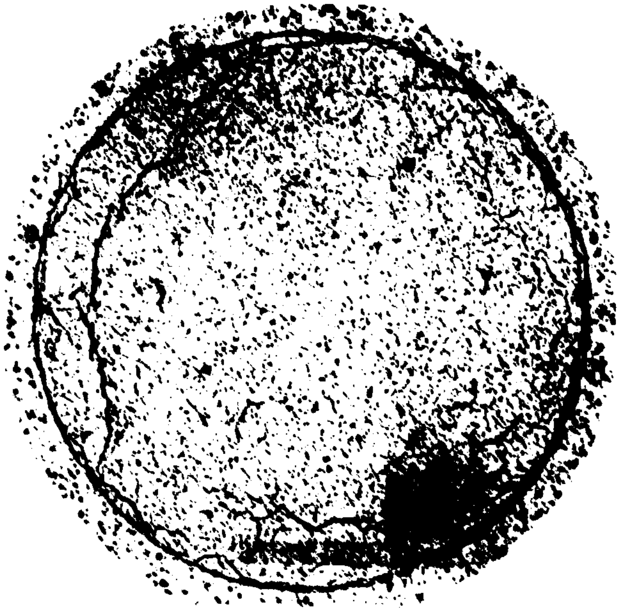
FIGURE 2-12 MESOPHASE COALESCENCE IN GE 2-2-3, BILLET 408 R-2 AT YARN/MATRIX INTERFACE

APPENDIX 3

FIBER/CARBONIZATION STUDIES

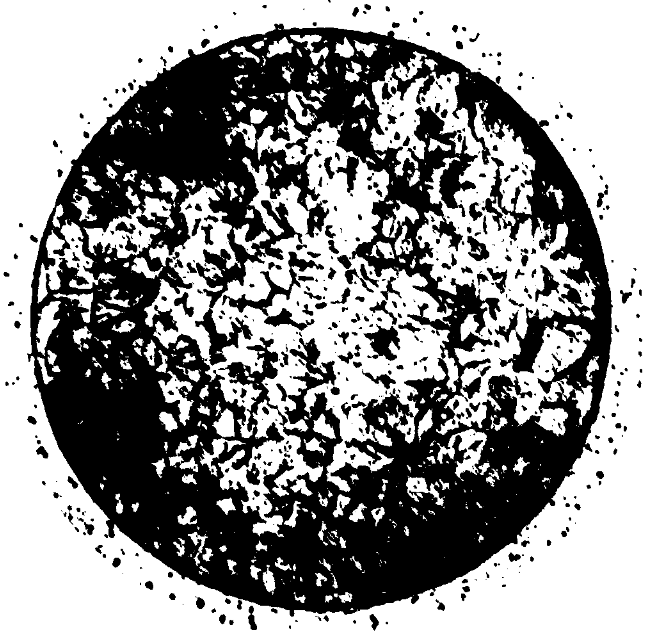
(Figures)

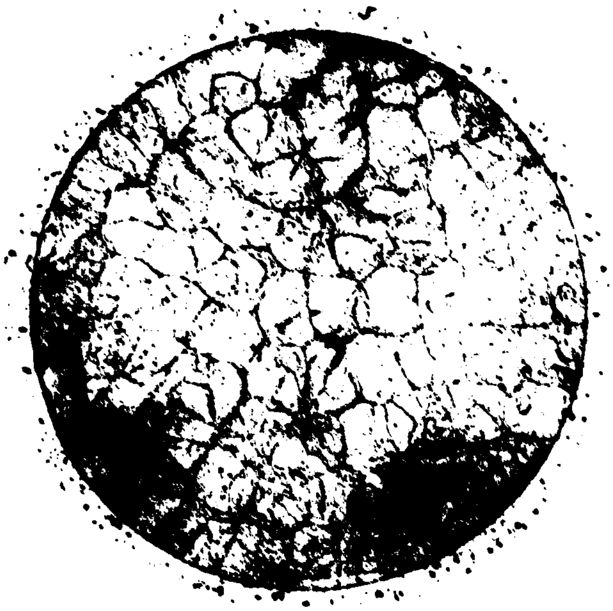




a. VSB-32 FULLY CARBONIZED

HM-10,000 FULLY CARBONIZED





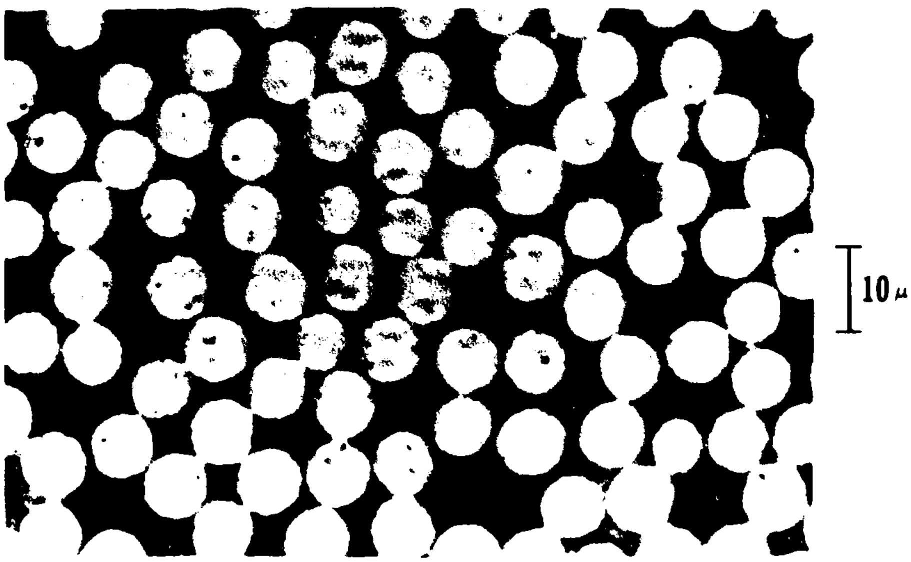
b. VSB-32 INTERRUPTED AT 470°C

HM-10,000 INTERRUPTED AT 470°C

FIGURE 3-1 TRANSVERSE VIEW OF 70 YARN BUNDLE PACKS SHOWING RESTRUCTURING DUE TO DEGREE OF CARBONIZATION AT 10,000 PSI (10x)

1280x

a. FULL CARBONIZATION CYCLE

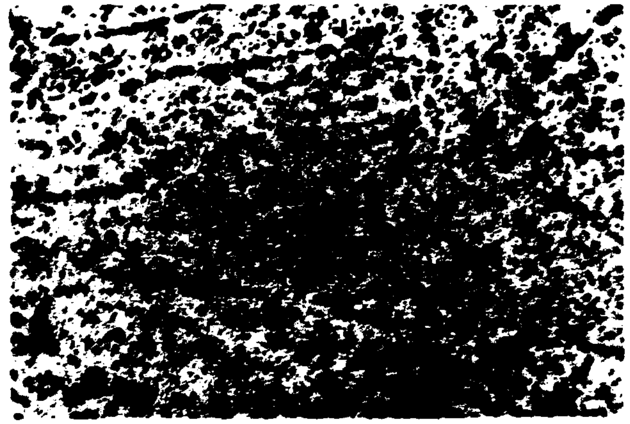


1280x

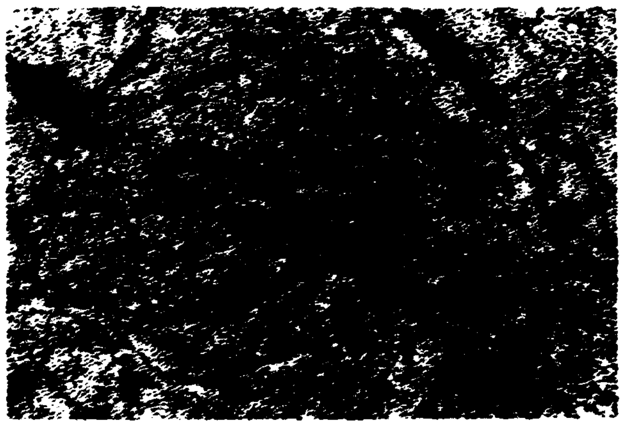
b. INTERRUPTED CARBONIZATION CYCLE

FIGURE 3-2 COMPARISON OF FILAMENT SHAPE AT 470°C (INTERRUPTED CYCLE) AND 650°C (FULL CYCLE) IN 10,000 PSI CARBONIZATION AT 100°C/HOUR HM YARN

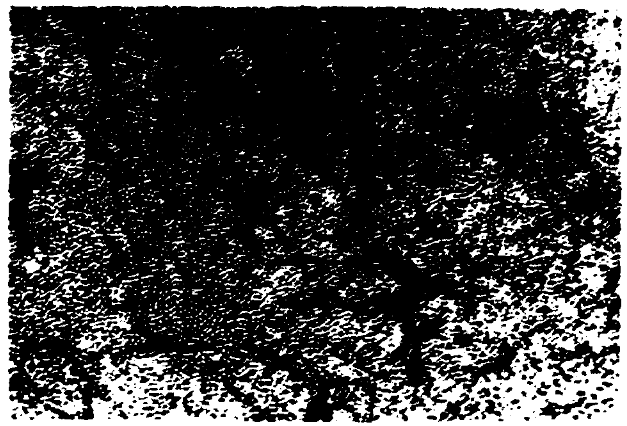
a. HM PAN FILAMENTS-FULL CARBONIZATION



b. VSB-32 PITCH FILAMENTS-FULL CARBONIZATION

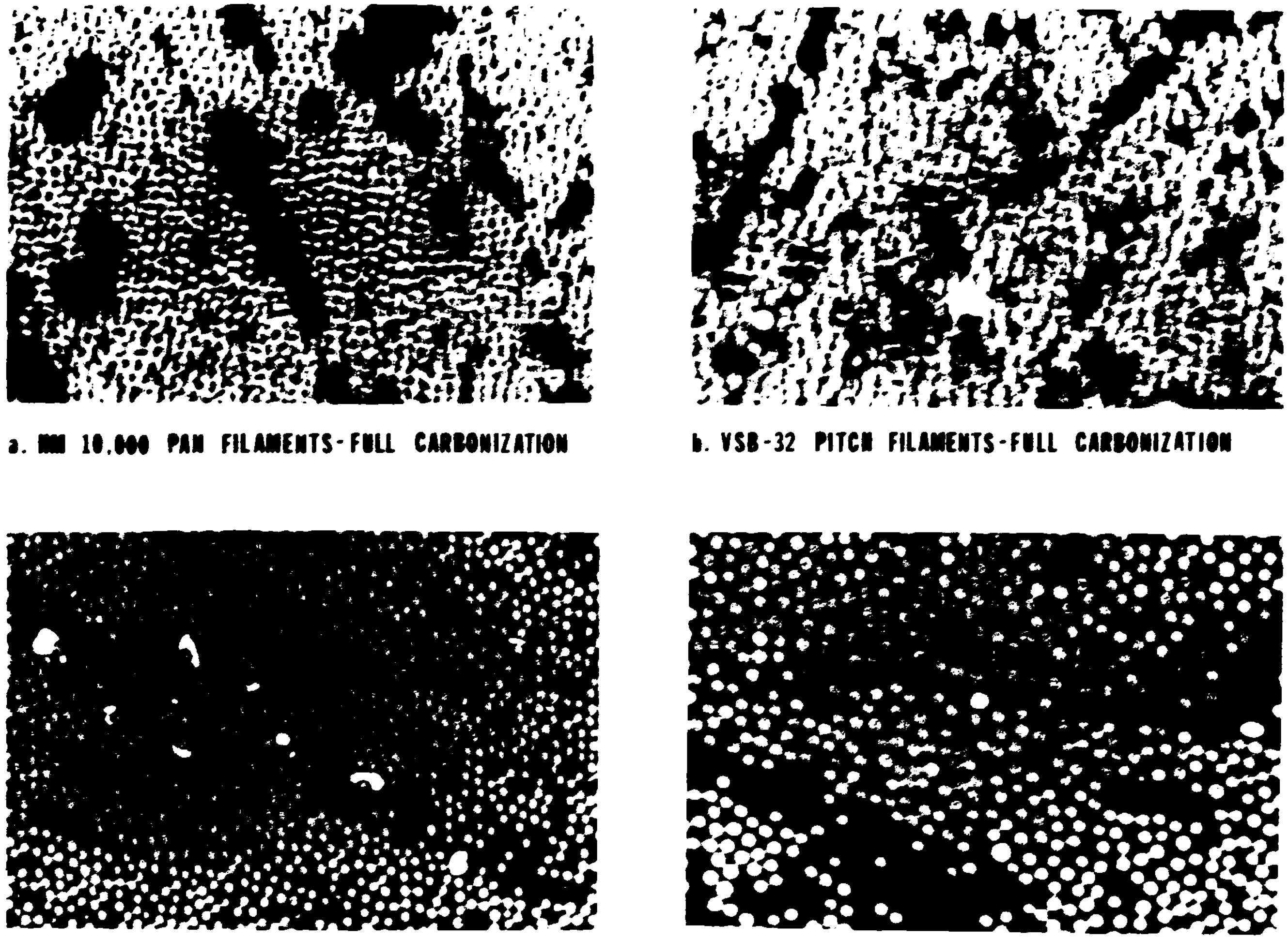


c. HM PAN FILAMENTS-INTERRUPTED CARBONIZATION



d. VSB-32 PITCH FILAMENTS-INTERRUPTED CARBONIZATION

FIGURE 3-3 EFFECT OF DEGREE OF CARBONIZATION AT 10,000 PSI AND 100°C/HOUR ON HM PAN FILAMENTS AND VSB-32 PITCH FILAMENTS - 90x



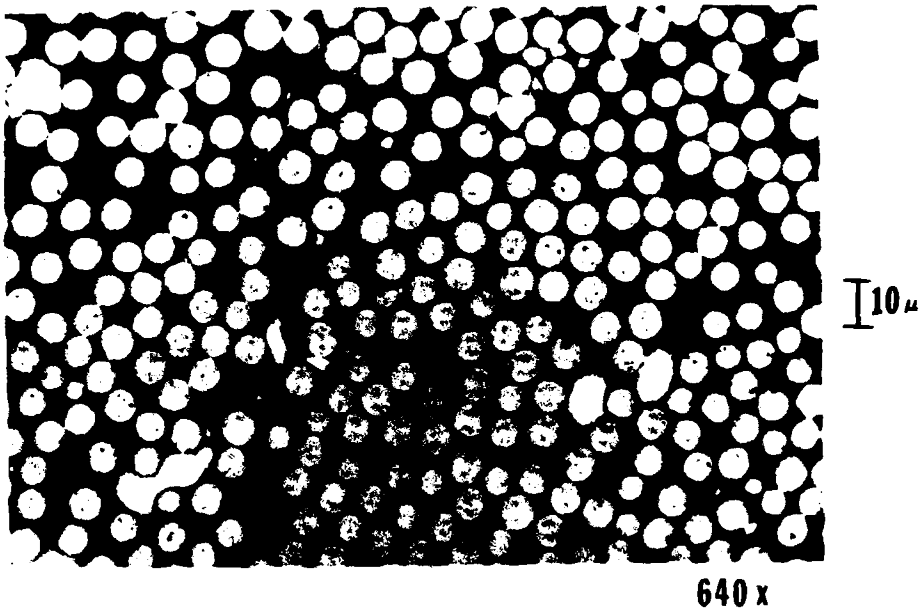
a. HM 10,000 PAN FILAMENTS-FULL CARBONIZATION

b. VSB-32 PITCH FILAMENTS-FULL CARBONIZATION

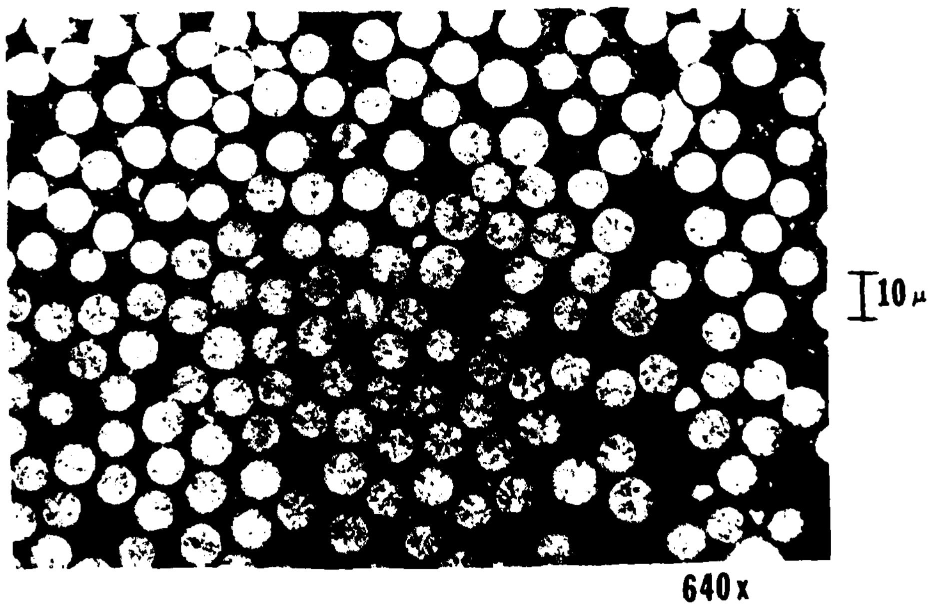
c. HM 10,000 PAN FILAMENTS-INTERRUPTED CARBONIZATION

d. VSB-32 PITCH FILAMENTS-INTERRUPTED CARBONIZATION

FIGURE 3-4 RESTRUCTURING OF FILAMENT/YARN BUNDLE DUE TO DEGREE OF CARBONIZATION AT 10,000 PSI AND 100°C/HOUR FOR HM PAN FILAMENTS AND VSB-32 PITCH FILAMENTS-320x



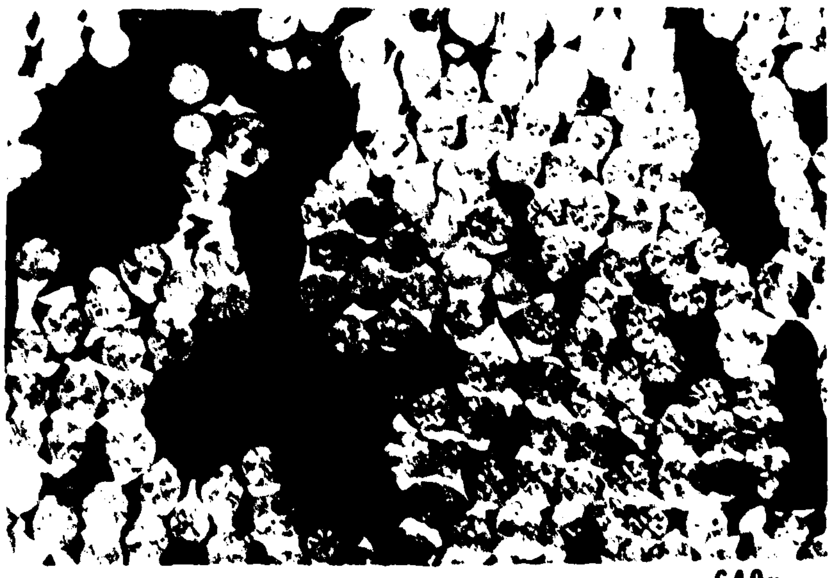
a. HM 10,000 PAN FILAMENTS



b. VSB-32 FILAMENTS

FIGURE 3-5 10,000 PSI CARBONIZATION HEAT RAMP INTERRUPTED AT 470° AND RAPIDLY COOLED.

a. HM 10,000 PAN FILAMENTS



b. VSB-32 FILAMENTS

FIGURE 3-6 10,000 PSI CARBONIZATION TO 650°C AT 100°C/HOUR HEAT RAMP