213
2-29-70
C

AEC RESEARCH AND DEVELOPMENT REPORT

DWR 1479

Y-1724

Metals, Ceramics,
and Materials

O/R
8/3/70

PITCH, POLYFURFURYL ALCOHOL RESIN, AND
STYRENE-DIVINYLBENZENE COPOLYMERS
AS CARBON BINDERS

C. R. Schmitt

MASTER

THIS DOCUMENT CONFIRMED AS
UNCLASSIFIED
DIVISION OF CLASSIFICATION
BY J.H. Kahn/amb
DATE 8/4/70

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE Y-12 PLANT

operated for the ATOMIC ENERGY COMMISSION under U. S. GOVERNMENT Contract W-7405 eng 26

UNION
CARBIDE

OAK RIDGE Y-12 PLANT
P. O. Box Y
OAK RIDGE, TENNESSEE 37830

P6153

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Printed in the United States of America. Available from Clearinghouse for Federal
Scientific and Technical Information, National Bureau of Standards,
U.S. Department of Commerce, Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.65

— LEGAL NOTICE —

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Date Issued: July 20, 1970

Document Y-1724

TID-4500

UNION CARBIDE CORPORATION
Nuclear Division

OAK RIDGE Y-12 PLANT

Operated under Contract W-7405-eng-26
With the US Atomic Energy Commission

PITCH, POLYFURFURYL ALCOHOL RESIN, AND
STYRENE-DIVINYLBENZENE COPOLYMERS AS CARBON BINDERS

C. R. Schmitt

Material for this report has been compiled and edited from earlier Y-12 Technical Progress Reports (1963). The work is being reported at this time because of renewed interest in the general field of graphite binder chemistry and applications.

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Oak Ridge, Tennessee

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

fy

Document Y-1724

TID-4500

DISTRIBUTION

Atomic Energy Commission

Keller, C. A.
Zachry, D. S.

Lawrence Radiation Laboratory

Cady, W. E.
Dorough, G. D., Jr
Kury, J. W.
Rubin, B.

Los Alamos Scientific Laboratory

Dickinson, J. L.
Smith, M.
Taub, J. M.
Wewerka, E. M.

Oak Ridge Gaseous Diffusion Plant

Jordan, R. G.
Wilcox, W. J., Jr

Oak Ridge National Laboratory

Coobs, J. H.
Eatherly, W. P.
Hamner, R. L.
Pollack, C.
Strehlow, R. A.

Oak Ridge Y-12 Plant

Ardary, Z. L.
Ballenger, H. F. (2)
Beeson, H. C.
Benton, S. T.

Bernander, N. K.
Briscoe, O. W.
Burkhart, L. E.
Cook, J. L.
Dobbins, A. G.
Dodson, W. H.
Dorsey, G. F.
Evans, G. W.
Haeusler, K. R.
Harper, W. L.
Hemphill, L. F.
Kahl, K. G.
Keith, Alvin
Kite, H. T.
Lambdin, F.
Marrow, G. B.
McLendon, J. D.
McWhorter, W. C.
Mitchel, G. W.
Napier, J. M.
Phillips, L. R.
Schmitt, C. R. (15)
Schreyer, J. M.
Smith, R. D.
Smith, W. E.
Tench, F. M.
Waters, J. L.
Wesley, R. L.
Williams, R. D.
Yaggi, W. J.
Y-12 Central Files (5)
Y-12 Central Files (route)
Y-12 Central Files (Y-12RC)

Paducah Gaseous Diffusion Plant

Winkel, R. A.

Sandia-Albuquerque

Berry, L. M.
Frye, E. R.
Rainhardt, R.

Sandia-Livermore

Adolphson, D. R.
Brierly, J. M.
Frost, C.
Scholer, G. L.

In addition, this report is distributed in accordance with the category Metals, Ceramics, and Materials, as given in the "USAEC Standard Distribution Lists for Unclassified Scientific and Technical Reports", TID-4500.

ABSTRACT

Various types of pitch from vegetable, petroleum, and coal-tar origins were characterized analytically and pyrolyzed. Carbon compact formulation and density studies were made using a polyfurfuryl alcohol resin binder, and polymerization and coking-yield studies were made with various copolymers of styrene and divinylbenzene.

CONTENTS

SUMMARY	6
INTRODUCTION	7
STUDIES OF CARBON BINDERS	9
Pitch Characterization and Pyrolysis Studies	9
Carbon Compact Formulation and Density Studies Using Polyfurfuryl Alcohol Resin	18
Styrene-Divinylbenzene Copolymers	22
Polymerization Studies	22
Caustic Treatment for Inhibitor Removal	23
Knoop Hardness Studies	25
Uranium Dicarbide Oxidation Studies	25
Coking Yield Studies	26
Effect of Curing on the Coking Yield	30
Effect of the Divinylbenzene Content	30
<u>Meta</u> -Divinylbenzene and <u>Para</u> -Divinylbenzene Isomers	33
Various Divinylbenzene Copolymers	36
Isoprene Polymerization	39
REFERENCES	41
ACKNOWLEDGEMENTS	42

SUMMARY

Analytical data were obtained on the carbon, hydrogen, sulfur, nitrogen, oxygen, and ash content of various commercial vegetable, petroleum, and coal-tar pitches. The pitches were also characterized by gel permeation chromatography, thermogravimetry, and molecular weight studies.

Carbon compact formulation and density studies were made using a polyfurfuryl alcohol resin binder. The compacts were made by pressing isostatically at 30,000 psi and coking at 950 and 1,500° C under a flowing helium atmosphere.

Preparation of styrene-divinylbenzene copolymers was studied by heating a mixture of the monomers of styrene and divinylbenzene in corked test tubes suspended in a mineral oil bath at a controlled temperature. The effect of temperature on the polymerization of caustic-washed monomers was determined. Extent of the oxidation of uranium dicarbide by the pyrolysis of the styrene-divinylbenzene copolymer and solidified polyfurfuryl alcohol resin was also compared. Coking-yield studies on various styrene-divinylbenzene copolymers showed that the coking yield was proportional to the divinylbenzene content, and that the highest coking yields were obtained using one weight percent p-toluene-sulfonic acid as a catalyst.

INTRODUCTION

Tars and pitches are now in general use commercially both as a carbon-base material and as a binder for various industrial carbon and graphite products.^(1 - 3) Two of the general requirements of a carbonaceous binder material for use in the fabrication of high-strength graphite bodies are that: (1) it should be a fluid or thermoplastic material to permit uniform mixing with the filler material, and (2) it should have a high carbon content so that a major portion of the carbon remains as a coke residue upon pyrolysis in a nonoxidizing atmosphere, forming a minimum of volatile gaseous decomposition products.

In the manufacture of graphite bodies, the binder used in the mix is an important ingredient since it has a profound effect on the physical and mechanical properties of the final carbon or graphite structure obtained. One of the materials widely used at the present time as a binder for graphite is coal-tar pitch. The nature and properties of the coal-tar pitch are dependent upon the conditions of the carbonization of the coal, and pitches having a wide range of softening points, coking values, and inorganic impurities are available. Samples of the various types of commercial pitches were, therefore, obtained so that these could be characterized and compared with regard to such factors as their physical and chemical properties, coking yield, and purity.

In preparing a carbon compact, the pitch binder is mixed thoroughly with the other ingredients, such as carbon flour, coke, or powdered graphite, and heated under pressure. The volatile portion is driven off and the carbonized pitch forms a bond between the filler particles.⁽¹⁾

In the fabrication of uranium-bearing graphite fuel elements, uranium dioxide or uranium dicarbide powder is usually blended with carbon and/or graphite filler powders, mixed with a carbonaceous binder, extruded into the desired configuration, and then heated to high temperatures to drive off volatile materials, graphitize the carbon, and carburize the uranium. Satisfactory carbonaceous binders that have been used for this purpose include: pitch, phenolic, polyfurfuryl alcohol, and other resins. All of these binders, however, contain oxygen in their molecular structure so that their pyrolysis products upon subsequent heat treatment cause appreciable oxidative degradation of the uranium dicarbide to uranium dioxide. It was believed that the substitution of an oxygen-free resin, such as a styrene-divinylbenzene copolymer, for these oxygen-containing resin binders should reduce the possibility of oxidative

pyrolysis products. Accordingly, an experimental program was initiated at the Oak Ridge Y-12 Plant^(a) for preparing and evaluating such oxygen-free copolymers and for determining their effect on uranium dicarbide during pyrolysis.

(a) Operated for the US Atomic Energy Commission by the Union Carbide Corporation's Nuclear Division.

STUDIES OF CARBON BINDERS

PITCH CHARACTERIZATION AND PYROLYSIS STUDIES

A total of eleven pitch samples, nine of coal-tar origin and one each of vegetable and petroleum origin, were procured from five different commercial vendors, and analytical data on the carbon, hydrogen, sulfur, nitrogen, oxygen, and ash content of these pitches were obtained. Table 1 lists the chemical composition of these pitches. As Table 1 shows, the vegetable and petroleum pitches possess a significantly lower carbon content than any of the coal-tar pitches, the vegetable pitch has the lowest sulfur content (0.03%), and the petroleum pitch contains the highest sulfur content (1.75%).

Table 1
CHEMICAL COMPOSITION OF COMMERCIAL PITCH SAMPLES

Pitch Type	Vendor(1)	Softening Point (° C)	Chemical Composition (%)					Ash
			Carbon	Hydrogen	Nitrogen	Oxygen	Sulfur	
Vegetable	Crowley	50	68.61	6.77	0.69	23.73	0.03	0.17
Petroleum	Trotter	60	87.82	8.78	0.48	0.99	1.75	0.18
Coal Tar	Barrett - Type 1	63 - 68	93.40	4.49	0.76	0.87	0.45	0.03
Coal Tar	Barrett - Type 2	98 - 103	92.31	4.59	0.93	1.66	0.43	0.08
Coal Tar	Barrett - Type 3	126 - 132	92.27	4.96	0.78	1.45	0.44	0.10
Coal Tar	Koppers - Type 1	98 - 103	91.44	4.42	0.81	2.89	0.34	0.10
Coal Tar	Koppers - Type 2	105 - 115	91.74	4.775	0.83	2.18	0.40	0.10
Coal Tar	Koppers - Type 3	138 - 156	91.93	4.71	0.85	2.04	0.40	0.07
Coal Tar	Koppers - Type 4	128 - 138	91.0	4.3	0.75	2.6	0.34	1.0
Electrode	Reilly - Type 1	84	92.44	4.74	0.74	1.60	0.42	0.06
Electrode	Reilly - Type 2	100	92.78	4.45	0.63	1.61	0.44	0.09

- (1) Crowley Tar Products Company, New York, New York
 E. T. Trotter and Company, Great Neck, New York
 Barrett Division, Allied Chemical Corporation, New York, New York
 Koppers Company, Pittsburgh, Pennsylvania
 Reilly Tar and Chemical Corporation, Indianapolis, Indiana

The ash obtained from these pitches by burning them in air at 800° C was analyzed spectrochemically. Results, as given in Table 2, show that aluminum, calcium, chromium, copper, iron, silicon, and zinc are the major impurities, with considerable variation in the various pitch types.

Seven of the pitch samples were pyrolyzed to determine their coking yields and coke densities. Each sample was placed in a quartz boat contained in a

Table 2
SPECTROCHEMICAL ANALYSES OF ASH FROM VARIOUS PITCH SAMPLES
(All Values in Percent)

Element	Vegetable Pitch(1) Vendor A, 50	Petroleum Pitch Trotter, 60	Coal Tar Pitch							Electrode Binder Pitch	
			Barrett 63 - 68	Barrett 126 - 132	Barrett 98 - 103	Koppers 98 - 103	Koppers 105 - 115	Koppers 3 138 - 156	Type 4 128 - 138	Reilly 84	Reilly 100
Al	4	10.5	16.0	16	18	> 20	20	20	10	15	20
B	< 0.01	0.01	0.02	0.03	0.03	0.03	0.04	0.03	0.06	0.04	0.04
Ba	0.03	0.4	0.2	0.2	0.2	0.4	0.3	0.15	0.08	0.6	0.08
Ca	0.2	4.9	6.4	6.4	5.4	8	5	7	5	2.5	0.6
Cr	8	0.4	1.6	4.8	0.14	0.06	0.05	0.07	1.0	0.3	0.02
Cu	Matrix	1.8	0.08	1.2	0.4	0.06	3	0.12	0.04	0.3	0.15
Fe	20	14	16	16	18	> 20	> 20	> 20	Matrix	Matrix	18
K	0.05	1.8	0.8	0.6	0.8	0.4	0.35	0.2	0.2	0.3	0.3
Mg	0.2	14.0	0.6	1.6	1.3	0.6	0.3	0.6	0.35	0.3	1.2
Mn	0.6	0.04	0.2	0.16	0.11	0.12	0.12	0.18	0.25	0.15	0.08
Mo	0.08	0.01	0.008	0.02	0.009	0.008	0.015	0.008	0.01	0.02	0.01
Na	0.015	1.8	0.28	4.0	2.2	0.6	0.10	0.45	0.4	1.2	0.08
Ni	2.5	2.8	0.24	0.24	0.18	0.10	0.10	0.10	0.06	0.2	< .01
P	< 1	< 7	< 0.8	< .8	< .9	< 1	< 1	< 1	< 1	< 1	< 1
Si	0.9	14.0	16.0	14.4	18	8	4.5	3.5	4	7	Matrix
Sn	1.8	0.06	1.4	0.2	0.2	0.14	0.2	0.2	0.12	0.3	0.3
Ti	0.05	0.03	0.7	0.6	0.32	0.5	0.4	0.3	0.15	2.5	2.5
V	0.015	> 3.5	0.04	0.024	0.04	0.015	0.015	0.015	0.01	0.01	0.01
Zn	0.10	1.0	4.8	5.6	6.3	4	6	7	2	5	7

(1) Pitches identified by vendor name and softening point in ° C.

horizontal quartz tube and heated for one hour at 950° C. Flowing helium was used throughout the pyrolysis treatment. The coking yield, expressed as percent, is the carbonaceous residue obtained after baking the pitch in a nonoxidizing atmosphere. Each pyrolysis was characterized by the liberation of volatile gases and multicolored smokes over the range from 200 to 950° C, and the pitches foamed considerably at intermediate temperatures. A slow heating cycle was required, using increments not exceeding 50° C per half hour, to prevent plugging of the outlet lines by too rapid evolution of smokes and the condensation of resinous decomposition products. A summary of the coke yields and mercury displacement densities of the cokes obtained by pyrolysis at 950° C is given in Table 3.

Table 3
PYROLYSIS OF PITCH AT 950° C IN FLOWING HELIUM

Pitch Type	Softening Point (° C)	Coke Yield (%)	Coke Density (1) (gms/cc)
Vegetable	50	30.6	1.49
Petroleum	60	24.0	1.57
Coal Tar	126 - 132	50.0	1.62
Coal Tar	63 - 68	38.0	1.63
Coal Tar	138 - 156	50.7	1.69
Coal Tar	98 - 103	51.3	1.76
Coal Tar	105 - 115	41.3	1.78

(1) Determined by the mercury displacement method on porous fragments of coke.

Thermogravimetric analyses were made by heating the pitch to 1,000° C over a three-hour cycle in a flowing argon atmosphere. Large differences were found in the coking yields among the various types of pitch. A summary of the coking yields obtained under the conditions just described is given in Table 4. These data are in general agreement with the partial coking yields reported in Table 3. Typical thermogravimetric results for five pitch samples representing five different vendors are shown by the graph in Figure 1.

Spectrochemical analyses of seven coke residues obtained from pyrolyzing various pitch samples at 950° C in flowing helium are summarized in Table 5. The major metallic impurities present were chromium, copper, iron, and silicon which correspond to the same major impurities shown in Table 2 on oxidized or ashed samples of these various pitches.

The evolution of volatile gases during the pitch coking process in a nonoxidizing atmosphere causes considerable foaming and the formation of voids and pores

Table 4
THERMOGRAVIMETRIC COKING YIELD OF VARIOUS PITCHES
PYROLYZED IN FLOWING ARGON AT 1,000° C

Type of Pitch	Vendor(1)	Softening Point (° C)	Coke Yield (%)
Coal Tar	Koppers	138 - 156	47.2
Coal Tar	Barrett	126 - 132	45.7
Coal Tar	Koppers	128 - 138	42.7
Coal Tar	Barrett	98 - 103	41.3
Electrode Binder	Reilly	100	40.8
Coal Tar	Koppers	98 - 103	39.6
Electrode Binder	Reilly	84	37.6
Coal Tar	Koppers	105 - 115	37.5
Vegetable	Crowley	50	30.4
Petroleum	Trotter	60	20.5

(1) See Table 1 for more complete identification.

Figure 1. THERMOGRAVIMETRIC ANALYSES RESULTS FOR VARIOUS PITCHES AS A FUNCTION OF TIME AND TEMPERATURE.

Table 5
SPECTROGRAPHIC ANALYSIS OF COKE RESIDUES FROM VARIOUS PITCH SAMPLES
(All Values in Percent)

Element	Vegetable Coke ⁽¹⁾ Crowley, 50	Petroleum Coke Trotter, 60	Coal-Tar Cokes				
			Barrett 63 - 68	Barrett 126 - 132	Koppers 98 - 103	Koppers 105 - 115	Koppers 138 - 150
Al	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Ca	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Cr	0.02	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
Cu	0.25	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Fe	0.04	0.06	0.02	0.03	0.04	0.07	0.08
Li	< 0.002	< 0.005	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
Mg	< 0.01	0.04	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Na	0.015	< 0.01	0.01	< 0.01	< 0.01	< 0.01	< 0.01
Si	< 0.01	0.06	0.01	0.02	0.03	0.022	0.015
Zn	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08	< 0.08

(1) Pitch was coked in flowing helium at 950° C. Pitches identified by their softening point in ° C.

in the raw coke as it forms. Figure 2 gives a view of a five-gram sample of coal-tar pitch (mp, 126 - 132° C) coked in an Alundum crucible under flowing helium at 950° C, and depicts the porous nature of the coke residue after foaming and expanding upon pyrolysis. Photographs showing structural differences in some raw coke fragments obtained from pyrolysis of vegetable, petroleum, and coal-tar pitches are seen in Figure 3. These differences in the size and shape of the pores and voids may be attributed to differences in their foaming characteristics and pitch rheology during thermal decomposition.

In the course of current pitch carbonizing studies in flowing helium or argon, it was observed that a mirror-like coating of pyrolytic carbon usually formed on the interior surface of the quartz or porcelain vessels used. A typical pyrolytic carbon coating deposited on a glazed porcelain crucible from pitch pyrolyzed in argon at 1,000° C is shown in Figure 4. Since pyrolytic carbon is of interest because of its potential importance in high-temperature applications, the crucible was fractured to provide information on the structure and thickness of the pyrolytic deposit. A cross section of the fracture surface is seen in Figure 5. It was estimated that the carbon coating had a thickness of approximately 0.06 millimeter.

Infrared analyses were completed on samples of vegetable pitch and its pyrolyzed coke, and on coal-tar pitch and its pyrolyzed coke, to determine whether significant chemical structural differences could be detected. Infrared scans of the pitch and coke of vegetable origin showed the presence of alcohol and carbonyl groups in a mixed, aliphatic, monosubstituted aromatic structure. (The aromatic

106550

Figure 2. TYPICAL POROUS COKE RESIDUE AFTER PITCH PYROLYSIS AT 950° C.

constituents comprised the greater portion of the sample.) Infrared scans of the pitch and coke of coal-tar origin showed the presence of alcohol and carbonyl groups in a mixed, aliphatic, monosubstituted aromatic structure. (Here, the aliphatic groupings appeared to be predominant.)

Gel permeation chromatographic studies were made to characterize the molecular size distribution of five commercial pitch samples representing vegetable, aromatic, and coal-tar pitch types. The technique involved pumping a dilute solution of the pitch in tetrahydrofuran through a series of five columns, each four feet in length and containing crosslinked polystyrene gels of different pore sizes. The pore diameter for each column was 20,000, 1,000, 1,000, 750, and 250 Å. The smaller-sized polymer molecules are able to diffuse more completely into the gel matrix and thus have longer retention times than the larger polymer molecules and require different elution volumes. Gel permeation scans of the five commercial pitches are given in Figure 6. The average molecular weight and size distribution of these five pitches are summarized in Table 6.

(a) Crowley Vegetable Pitch

15357

(b) Trotter Petroleum Pitch

15358

(c) Barrett Coal-Tar Pitch

15359

Figure 3. COKE SAMPLES FROM THE PYROLYSIS OF VARIOUS PITCHES. (11X)

106161

Figure 4. TYPICAL CARBON DEPOSIT ON A PORCELAIN CRUCIBLE.

14608

Figure 5. CROSS SECTION OF THE FRACTURE SURFACE OF A GLAZED PORCELAIN CRUCIBLE AND ITS PYROLYTIC CARBON DEPOSIT. (100X)

Figure 6. GEL PERMEATION CHROMATOGRAMS OF VARIOUS PITCH BINDERS.

To obtain the larger quantities of carbonized pitch that would be required for subsequent carbon formulations involving carbon powder and pitch binders, a vertical pitch pyrolysis assembly was fabricated. The assembly (Figure 7) consisted of an inner 1 1/2-inch-diameter by 20-inch-long quartz tube mounted within a Hevi-Duty electric resistance furnace. Flowing helium gas was passed downward over a 100-gram charge of pitch loaded in the inner quartz tube.

Table 6
MOLECULAR SIZE DISTRIBUTION AND MOLECULAR WEIGHT OF VARIOUS TYPES OF PITCH

Elution Count(2)	Maximum Molecular Size (angstroms) ⁽¹⁾				
	Vegetable Pitch Crowley, 50	Aromatic Pitch Crowley, 77	Coal-Tar Pitch		
			Barrett 98 - 103	Koppers 138 - 156	Koppers 208 - 217
28 - 29	-	470	-	-	-
29 - 30	-	240	-	-	-
30 - 31	-	160	-	-	-
31 - 32	120	114	-	-	-
32 - 33	83	83	66	-	-
33 - 34	63	63	44	63	-
34 - 35	48	48	37.5	48	48
35 - 36	37.5	37.5	29.7	37.5	37.5
36 - 37	29.7	29.7	24	29.7	29.7
37 - 38	24	24	19.3	24	24
38 - 39	19.3	19.3	15.8	19.3	19.3
39 - 40	15.8	15.8	13	15.8	15.8
40 - 41	13	13	10.7	13	13
41 - 42	-	-	8.9	10.7	10.7
42 - 43	-	9.0	< 7.8	8.9	-
43 - 44	-	< 7.8	< 7.8	< 7.8	8.8
44 - 45	-	< 7.8	< 7.8	< 7.8	< 7.8
45 - 46	-	-	-	< 7.8	< 7.8
Average Molecular Weight ⁽³⁾	277	404	363	403	373

(1) By the gel permeation chromatographic method.

(2) Number of 5-ml volumes required for elution.

(3) By the osmometry method.

The exit gases were bubbled through water in a four-liter filter flask, then vented to the atmosphere.

Using the vertical quartz tube assembly for pitch pyrolysis, vegetable pitch, weighing approximately three pounds, was carbonized under flowing helium at 950° C in a series of pyrolysis runs employing 100-gram quantities of pitch. The collected coke residues were ground in an agate mortar and pestle and screened through 50, 100, 170, and 325-mesh sieves for subsequent carbon compact formulation studies.

CARBON COMPACT FORMULATION AND DENSITY STUDIES USING POLY-FURFURYL ALCOHOL RESIN

To develop suitable techniques for mixing, handling, and baking various binder formulations involving this coke powder, preliminary investigations were

Figure 7. VERTICAL PITCH PYROLYSIS ASSEMBLY.

conducted with various types of commercial graphite powder, Thermax^(b) carbon filler powder, and polyfurfuryl alcohol resin binder, using the method of Jones, et al⁽⁴⁾ for preparing the graphite for test purposes. Several 1 1/4-inch-diameter taper and perforated graphite molds were fabricated for preparing baked carbon cylindrical bodies so that their compressive strength and other physical properties could be evaluated. Details of a typical graphite baking mold are outlined in Figure 8. The inside of the mold was lined with a heavy wrapping-paper insert to contain the experimental formulation. The molds proved to be entirely satisfactory for preparing experimental carbon bodies that were baked at 950° C under flowing helium in the vertical quartz pyrolysis assembly. After baking, the experimental carbon cylinders were easily removed from the molds, and it was found that the molds could be reused many times.

Small compacts (~ 0.5" D x 0.7" L) for density studies were also prepared from the various graphite-Thermax formulations by pressing isostatically at

(b) A product of the R. T. Vanderbilt Company.

Figure 8. TAPERED GRAPHITE MOLD USED FOR BAKING POLYFURFURYL ALCOHOL RESIN-BONDED CARBON FORMULATIONS.

30,000 psi and baking at 950° C under a flowing helium atmosphere. It was found that these compacts did not become distorted by pyrolysis treatment, and identification marks inscribed on their external surfaces remained visible.

Density determinations of pressed compacts and 1 1/4-inch-diameter hand-tamped compacts made with perforated graphite molds were made on five experimental graphite-polyfurfuryl alcohol resin-Thermax formulations after blending for one hour in a Z-blade laboratory mixer and baking for one hour at 950° C under flowing helium. A six-hour heating period was employed for the baking cycle. The compacts were then high fired at 1,500° C for three hours in flowing helium in a graphite induction furnace. Results of these runs are summarized in Table 7.

In general, the larger (1 1/4" D) cylindrical bodies made by hand tamping the various graphite formulations into the perforated graphite molds showed lower densities than the smaller isostatically pressed compacts. This observation prompted a study of the effect of forming pressure on the density. The effect of an isostatic forming pressure on the green, baked, and high-fired densities of polyfurfuryl alcohol resin-bonded graphite compacts prepared from Formulation B (Table 7) is indicated in Figure 9. These results show that forming pressures greater than 15,000 psi produce a negligible increase in density. Although a large decrease in density occurred at any particular forming pressure

Table 7
COMPOSITION AND DENSITIES OF POLYFURFURYL ALCOHOL RESIN-BONDED GRAPHITE COMPACTS

Formulation Designation	Composition (wt %)	Density (gms/cc) ⁽¹⁾		
		Pressed at 30,000 psi	Baked at 950° C	High Fired at 1,500° C
A	77.0 Graphite-Thermax Powder Blend ⁽²⁾ 23.0 Resin	1.64	-	1.46
AA ⁽³⁾	77.0 Graphite-Thermax Powder Blend ⁽²⁾ 23.0 Resin	-	1.65	1.65
B	62.5 Graphite-Thermax Powder Blend ⁽²⁾ 37.5 Resin	1.65 1.64	1.50 1.49	1.49 1.48
C	53.9 Graphite-Thermax Powder Blend ⁽²⁾ 46.1 Resin	Mix was too Syrupy, Pellets would not Hold Shape		
D	62.5 Coarse Graphite Powder ⁽⁴⁾ 37.5 Resin	Mix was too Syrupy, Pellets would not Hold Shape		
E	66.7 Coarse Graphite Powder ⁽⁴⁾ 33.3 Resin ⁽⁵⁾	-	1.63	-

(1) By the mercury displacement method.

(2) Graphite-Thermax powderblend: coarse graphite (< 120 μ), 77.5 %; Thermax ($\sim 1. \mu$), 15.0 %; fine graphite ($\sim 10 \mu$), 7.5 %.

(3) Formulation AA was identical to A except compacts were aged for six weeks in the green state.

(4) Coarse graphite was - 50 + 100 mesh.

(5) Four grams of maleic anhydride added per 100 cc of polyfurfuryl alcohol resin.

after baking the compact at 950° C, a further decrease in density became negligible by firing at 1,500° C. The density of a hand-tamped, 1 1/4-inch-diameter cylinder prepared from Formulation B after baking at 950° C was 1.30 gms/cc.

Figure 9. EFFECT OF THE FORMING PRESSURE ON THE DENSITY OF POLYFURFURYL ALCOHOL RESIN-BONDED CARBON COMPACTS.

Table 7 also notes that the use of 37.5 weight percent polyfurfuryl alcohol resin in conjunction with a blend of graphite and Thermax powder (Formulation B) permitted compacts to be pressed isostatically at 30,000 psi. But this same proportion of polyfurfuryl alcohol resin, when mixed with a coarse graphite powder (Formulation D), did not have a good consistency for pressing compacts isostatically.

It is also shown in Table 7 that a significant increase in the density of fired compacts made from Formulation AA resulted by merely allowing the polyfurfuryl alcohol resin-bonded compacts to age in their green state for six weeks.

The vertical quartz pyrolysis tube used for carbonizing the polyfurfuryl alcohol resin-bonded graphite was satisfactory for these preliminary formulation studies; however, it was observed that some of the polyfurfuryl alcohol resin-bonded compacts exhibited cracks and internal fissures. Accordingly, a slower heating rate with improved temperature measurement and control would be required during the baking cycle to insure that the volatile constituents are not dispelled too rapidly. The need for employing a longer heating period during carbonization was also indicated by the large density differences obtained on the same polyfurfuryl alcohol resin-bonded compacts (Formulations A and AA, Table 7) simply by aging the compacts in the green state for six weeks. It is suspected that some of the resin binder probably evaporated slowly during this period and was accompanied by further polyfurfuryl alcohol polymerization to account for this increase in density.

STYRENE-DIVINYLBENZENE COPOLYMERS

Polymerization Studies

The preparation of various styrene-divinylbenzene copolymer mixtures was accomplished by heating a mixture of the monomers of styrene and divinylbenzene (DVB) in corked test tubes suspended in a mineral oil bath at a controlled temperature. It was found that the monomer mixtures polymerized readily at elevated temperatures without requiring the addition of any catalyst. The effect of temperature on the polymerization of caustic-washed 85 volume percent styrene-15 volume percent divinylbenzene monomer was studied by periodically withdrawing a sample from the reaction vessel, cooling the sample to terminate the polymerization, and measuring the viscosity in a Cannon-Fenske-Ostwald viscometer immersed in a 100° F constant-temperature water bath. The results of these tests, plotted on the graph of Figure 10, show that polymerization began within one hour at 100° C with the caustic-washed monomers, whereas more than ten hours were required at 70° C.

Figure 10. EFFECT OF TEMPERATURE ON THE POLYMERIZATION OF CAUSTIC-WASHED 85 VOLUME PERCENT STYRENE-15 VOLUME PERCENT DIVINYLBENZENE MIXTURES.

Caustic Treatment for Inhibitor Removal

Polymerization studies at 100° C on 85 volume percent styrene-15 volume percent divinylbenzene mixtures of monomers as received from the vendor showed an induction period of approximately seven hours before incipient polymerization began, as indicated by a change in viscosity. The induction period results from the presence of an inhibitor, para-tertiary-butylcatechol, which is added to the styrene and divinylbenzene monomers by the manufacturers to prevent polymerization during shipment and storage. The inhibitor was removed by washing the monomer four times with a ten weight percent sodium hydroxide solution using a 4:1 monomer-to-caustic volume ratio. The monomer was then washed with distilled water, dried by contacting with white Drierite granules, and filtered through Whatman 40 filter paper.

Analytical data showing the amount of inhibitor present in various batches of styrene and divinylbenzene monomers before and after caustic treatment are summarized in Table 8. After removal of the inhibitor, mixtures of liquid styrene-DVB monomers polymerized readily to solids in less than one hour at 95° C. The effect of the inhibitor in prolonging the time required for the polymerization of styrene and divinylbenzene monomers is given in Table 9.

Table 8
INHIBITOR CONTENT OF STYRENE AND DIVINYLBENZENE MONOMERS

Monomer	Vendor	Treatment	Inhibitor ⁽¹⁾ Concentration ($\mu\text{g}/\text{ml}$)
Styrene	Dow	None	5.8
Styrene	Shell, Lot 1	None	12.0
Styrene	Shell, Lot 2	None	15.3
Styrene	Shell, Lot 2	Caustic Washed	0.5
Divinylbenzene	Dow, Lot A	None	974
Divinylbenzene	Dow, Lot B	None	700
Divinylbenzene	Dow, Lot B	Caustic Washed	2.8

(1) Para-tertiary-butylcatechol.

When a mixture of styrene and divinylbenzene is subjected to polymerization, the viscosity of the mixture increases. The Cannon-Fenske-Ostwald viscosity tube is well suited for studying the polymerization at various temperatures since it requires relatively small volumes of sample (8 mls) which could be cooled quickly to terminate the polymerization reaction. The tubes were calibrated by comparing the efflux times of various mineral oils having known viscosities at 100° F.

Since chemically pure divinylbenzene is not readily available, the divinylbenzene used in preparing the copolymers with the styrene was a commercial product

Table 9
POLYMERIZATION INDUCTION PERIODS OF STYRENE AND
DIVINYLBENZENE MONOMERS

Monomer	Incipient Polymerization Time at 90 - 100° C ⁽¹⁾ (hrs)	Inhibitor ⁽²⁾ Concentration (ppm)	Water Content ⁽³⁾ (%)
Styrene (as received)	4	12	0.03
Styrene (caustic washed)	2 3/4		0.03
Divinylbenzene (as received)	13 3/4	974	0.03
Divinylbenzene (caustic washed)	1 1/2		0.03

(1) Time required for the monomer to form a visible gel.

(2) Para-tertiary-butylcatechol.

(3) By Karl Fischer titration.

consisting of a mixture of the divinylbenzene isomers (~ 55%) and ethylstyrene isomers (~ 45%).

Knoop Hardness Studies

The degree of polymerization is an important variable affecting the yield of coke obtained upon pyrolysis. An attempt was made to determine the degree of polymerization of two styrene-DVB copolymers by measuring the Knoop hardness at 100-gram indentation loads. Results are reported in Table 10. Assuming essentially complete polymerization for a sample of hard and brittle commercial polystyrene, it is indicated that although the Knoop hardness of one preparation of 75 volume percent styrene-25 volume percent DVB copolymer was considerably below that of the commercial polystyrene, its hardness could be increased to a comparable value by aging in a vacuum oven at 110° C.

Table 10
KNOOP HARDNESS VALUES OF STYRENE-DIVINYLBENZENE COPOLYMERS

Styrene Content (vol %)	DVB Content (vol %)	Vacuum Oven Aging Treatment	Color	Knoop Hardness Value ⁽¹⁾
75	25	None	Colorless	10
75	25	3 Days at 110° C	Yellow	21
75	25	6 Days at 110° C	Brown	20
100(2)	0	None	Colorless	19
85	15	None	Colorless	19
85	15	1 Day at 110° C	Yellow	47
85	15	2 Days at 110° C	Brown	38

(1) Average of 3 or 5 individual determinations at a 100-gram indenting load.

(2) Commercial polystyrene vial, Lerner Co, Garwood, N. J.

Uranium Dicarbide Oxidation Studies

The extent of oxidation of uranium dicarbide during the pyrolysis of a styrene-divinylbenzene copolymer, anion exchange resin, and solidified polyfurfuryl alcohol resin mixture was evaluated in a series of pyrolysis runs made at 950° C under flowing argon. Pyrolysis was conducted on samples of resin contained in shallow quartz boats located inside of a horizontal 1 1/2-inch-diameter quartz tube, and uranium dicarbide granules (-8 +20 mesh) were located both upstream and downstream from the resin sample to compare differences in the final oxygen content. A schematic diagram of the pyrolysis assembly unit is presented in Figure 11. Results, as summarized in Table 11, show that severe oxidation of uranium dicarbide resulted from the oxygen-containing anion exchange resin and polyfurfuryl alcohol resin pyrolysis

Figure 11. APPARATUS FOR DETERMINING THE EXTENT OF OXIDATION OF URANIUM DICARBIDE DURING RESIN PYROLYSIS.

products, whereas negligible oxidation occurred with the oxygen-free styrene-divinylbenzene copolymers.

Coking Yield Studies

A desirable property of any fuel element binder is its high yield of coke residue since the higher the coking yield the less the amount of volatile hydrocarbons that would be evolved to cause any undesirable porosity during heat treatment. A summary of the coking yields obtained by the pyrolysis of a styrene-divinylbenzene copolymer, anion exchange resin, and polymerized polyfurfuryl alcohol resin mixture under flowing argon at 950° C is given in Table 12. These data show that the coking yield of polyfurfuryl alcohol resin is considerably higher than either the laboratory-prepared styrene-divinylbenzene copolymers or the commercial anion exchange resin. An attempt was made to increase the coking yield of the 85 volume percent styrene-divinylbenzene copolymer by the addition of an oxygen-free third component to the monomer mixture. As the data in Table 12 show, some slight improvement in the coking yield was obtained with triethylamine and acrylonitrile. Spectrographic analyses comparing the purity of coke residues obtained from 85 volume percent styrene-15 volume percent divinylbenzene copolymer and polymerized polyfurfuryl alcohol resin are reported in Table 13.

According to Boundy and Boyer,⁽⁵⁾ pure styrene polymerizes into a long polymer chain which is completely soluble in a number of organic solvents and shows no evidence of crosslinkage. The copolymerization of styrene with divinylbenzene

Table 11
EFFECT OF RESIN PYROLYSIS PRODUCTS ON URANIUM DICARBIDE

Run Number	Resin	UC ₂ (upstream boat) ⁽¹⁾		UC ₂ (downstream boat) ⁽¹⁾	
		Oxygen ⁽²⁾ (%)	Free Carbon ⁽²⁾ (%)	Oxygen (%)	Free Carbon (%)
1(3)	Styrene-Divinylbenzene (85% - 15%)	0.28	1.0	0.17	0.65
2	Styrene-Divinylbenzene (85% - 15%)	0.15	-	0.20	0.93
3	Styrene-Divinylbenzene (85% - 15%)	0.23 ⁽⁴⁾	-	0.38 ⁽⁴⁾	-
		0.26	-	0.39 ⁽⁴⁾	-
4	Dowex 1X4 ⁽⁵⁾	0.27	1.0	1.5	2.2
5	Polyfurfuryl Alcohol Resin + 0.5% Maleic Anhydride	0.47	0.73	2.9	2.2
				12.2 ⁽⁶⁾	> 4

(1) Refer to Figure 11.

(2) Samples of unexposed UC₂, analyzed at the beginning and end of a two-month storage period in a vacuum desiccator, contained 0.16 and 0.18% oxygen, and 0.65 and 0.83% free carbon, respectively.

(3) Used Molecular Sieve trap to purify the inlet argon gas.

(4) UC₂ sample split to show the reliability of the oxygen analyses.

(5) Dry, nitrate form of resin used, 50-100 mesh.

(6) This sample, approximately 20% of the initial UC₂ charge, had degraded to a fine, black powder.

provides a crosslinked polymer structure which is insoluble in all solvents and infusible even at high temperatures. The polymerization of styrene is extremely sensitive to trace quantities of such substances as catalysts, inhibitors, solvents, and comonomers.⁽⁵⁾ Additions of triethylamine and acrylonitrile were, therefore, made to the styrene-divinylbenzene mixtures to study their effects.

Although some improvement in the coke yield was shown on the addition of triethylamine and acrylonitrile, it is not known whether these increases are due to these additions or to a higher degree of polymerization caused by the longer curing periods at 110° C. It is generally known that the degree of polymerization is an important variable affecting the coke yield. This relationship is indicated by the fact that the Dowex 1X4 and 1X10 anion exchange resins, which are also styrene-divinylbenzene copolymers containing four percent and ten percent divinylbenzene as crosslinking agents, respectively, showed considerably higher coking yields than did any of the laboratory-prepared copolymers.

According to Helfferich,⁽⁶⁾ the nominal divinylbenzene content of an ion exchange resin is used to indicate the degree of crosslinking. DVB content is expressed in terms of the mole percent of pure divinylbenzene (not of the commercial product) in the polymerization mixture. Thus, one reason why low yields were

Table 12
COKING DATA FROM THE PYROLYSIS OF RESIN UNDER ARGON AT 950° C

Resin	Curing Time at 110° C (hrs)	Coke Residue (%)	Coke Analyses	
			Carbon (%)	Oxygen (%)
85 vol % Styrene-15 vol % Divinylbenzene	2	3.0	92.5	-
85 vol % Styrene-15 vol % Divinylbenzene	2	2.8	-	-
85 vol % Styrene-15 vol % Divinylbenzene	64	2.1	-	-
85 vol % Styrene-15 vol % Divinylbenzene	-	2.9	-	-
70 vol % Styrene-30 vol % Divinylbenzene	20	6.6	93.0	-
70 vol % Styrene-30 vol % Divinylbenzene	20	6.0	-	-
99 vol % Styrene-Divinylbenzene(1) 1 vol % Triethylamine	88	3.9	95.3	0.43
95 vol % Styrene-Divinylbenzene(1) 5 vol % Triethylamine	88	4.0	94.5	-
90 vol % Styrene-Divinylbenzene(1) 10 vol % Triethylamine	88	4.4	-	-
99 vol % Styrene-Divinylbenzene(1) 1 vol % Acrylonitrile	88	4.9	96.2	0.43
Dowex 1X4	-	14.0	87.9	10.07(2)
Dowex 1X10	-	15.4	88.3	9.67(2)
Polyfurfuryl Alcohol Resin + 0.5% Maleic Anhydride	120	40.5	95.2	5.38
Polyfurfuryl Alcohol Resin + 0.5% Maleic Anhydride	120	41.8	95.7	2.94

(1) 85% styrene-15% divinylbenzene.

(2) Dowex 1X4 and 1X10 cokes analyzed 1.3 and 1.4 percent nitrogen, respectively.

shown by the laboratory-prepared copolymers was because a commercial-product divinylbenzene was used which provided a lower nominal divinylbenzene content than indicated in Table 12. Also, in the polymerization of commercial ion exchange resin spheres, benzoyl peroxide is added as a catalyst. Since no catalyst was used in the laboratory-prepared copolymers, the degree of polymerization and crosslinkage was probably not as complete. An attempt was made to determine the degree of polymerization of 85 volume percent styrene-15 volume percent divinylbenzene copolymers after various periods of oven curing at 110° C up to 88 hours by measuring the average crystallite size by X-ray diffraction techniques, but no differences were discernible. Another variable that could influence the coking yield is the rate of heating employed during pyrolysis. For this reason, all pyrolysis runs were conducted using a standard heating cycle of three hours to obtain the 950° C pyrolysis temperature which was then held for 0.5 hour. For those pyrolysis runs made in the presence of uranium dicarbide, the argon flow rate and total time of argon flow during the heating and cooling cycles were important variables since a small amount of oxygen or moisture impurities in the argon would be expected to have a cumulative

Table 13
SPECTROGRAPHIC ANALYSES OF COKE RESIDUES OBTAINED
FROM THE PYROLYSIS OF STYRENE-DIVINYLBENZENE-POLYFURFURYL
ALCOHOL RESIN AT 950° C
(All Values in ppm)

Impurity	Styrene-Divinylbenzene Residue	Polyfurfuryl Alcohol Resin Residue
Ag	< 50	10
Al	200	170
Au	< 200	< 20 ⁽¹⁾
B	300	< 10
Ba	< 20	9
Be	< 10	< 10
Bi	< 100	400
Ca	50	30
Cd	< 400	< 40
Co	< 50	< 5
Cr	< 20	50
Cu	2,000	< 5
Fe	1,200	600
K	< 400	250
Li	70	130
Mg	< 100	17
Mn	50	5
Mo	50	40
Na	< 100	< 10 ⁽¹⁾
Nb	< 200	20
Ni	< 100	250
P	< 1,000	< 1,000
Pb	< 100	10 ⁽¹⁾
Pt	50	400
Sb	< 40	< 40
Si	250	120
Sn	< 50	10
Ti	< 50	< 5 ⁽¹⁾
U	< 3,000	< 300 ⁽¹⁾
V	< 20	5
W	< 800	< 80 ⁽¹⁾
Zn	< 800	< 80 ⁽¹⁾
Zr	< 20	< 2 ⁽¹⁾

(1). Greater sensitivity shown for these elements was achieved because a larger sample was used.

degradation effect on the dicarbide. This combination of flow rate and time of flow was standardized by using an argon flow rate of 300 cc/min and a total argon flow time of nine hours and twenty minutes for the heating and cooling cycles.

Effect of Curing on the Coking Yield

It was shown that the degree of aging or curing in the vacuum oven after polymerization also affects the coking yield. As shown in Figure 12, thermogravimetric analysis of the styrene-DVB copolymer (75% - 25%) as polymerized and after oven curing for six days at 110° C showed a slightly higher coke residue after oven curing using equivalent pyrolysis conditions. Thermogravimetric analyses were made by heating the copolymers at 850° C at a rate of 3° C per minute in a flowing helium atmosphere.

Figure 12. THERMOGRAVIMETRIC ANALYSES OF A STYRENE-DIVINYLBENZENE (75%-25%) COPOLYMER.

Effect of the Divinylbenzene Content

Using the vertical pyrolysis assembly unit described previously, additional studies were made on various batches of styrene-DVB copolymer under flowing

argon in an attempt to increase the yield of coke. A typical heating cycle of less than three hours, as Figure 13 points out, was used to attain the temperature of 900° C, which was then held for 0.5 hour. Results, as summarized in Table 14, show that a considerable increase in the yield of coke (as high as approximately 15 percent) was realized by increasing the divinylbenzene content of the copolymer.

Table 14
COKING DATA FROM THE PYROLYSIS OF STYRENE-DVB
COPOLYMERS UNDER ARGON AT 900° C
(Arranged According to Increasing DVB Content)

Monomer Content (%)			Aging Temperature (° C)	Coke Yield (%)
Styrene	DVB	Other		
60	20	20 ⁽¹⁾	95	5.8
75	25	-	-	5.8
60	40	-	110	7.3
60	40	-	170	7.4
50	50	-	250	12.7
50	50	-	250	12.9
33	67	-	250	13.0
33	67	-	250	14.1
20	80	-	110	13.5
20	80	-	170	14.7

(1) Toluene. Monomer mixture on toluene-free basis corresponds to 75 vol % styrene-25 vol % DVB.

Also note in Table 14 that the yield of coke obtained from a copolymer made from a 60 volume percent styrene-20 volume percent DVB-20 volume percent toluene monomer mixture was essentially the same as that obtained from a monomer mixture of 75 volume percent styrene-25 volume percent DVB. After polymerization at 95° C it was observed that the toluene-containing copolymer was relatively soft and rubbery when compared to its toluene-free counterpart. Several weighings at room temperature showed that it would not attain constant weight, presumably because of volatilization of the toluene. After heating an eight-gram portion of the copolymer at 95° C until a constant weight was attained, a 1.6-gram loss in weight was found, corresponding to 20 percent of its polymerized weight. This 20 percent weight loss is in close agreement with the 20 percent toluene present in the monomer mixture. It appears that toluene merely acted as a diluent for the styrene-DVB copolymers and did not enter into the crosslinked molecular network of the copolymer.

Crosslinking is the process whereby two polymer chains become linked together by primary valence bonds, and usually results in an increase in the high-temperature

stability of the polymer. The amount of carbonaceous residue obtained upon thermal decomposition of a crosslinked polymer "depends greatly on the degree of crosslinking, the rate of polymer degradation, and the presence of foreign substances. Crosslinking immobilizes the carbon atoms and unites the crystallites in a randomly oriented mass, resulting in a high char yield. Increasing the rate of polymer degradation results in an undesirable higher fraction of vaporized products. A slow carbonization reaction is, therefore, recommended for maximum carbon yields."⁽⁶⁾

As shown by the thermogravimetric analyses of styrene-DVB copolymers in Figure 12, thermal decomposition proceeds very rapidly between 400 and 500° C. Since a high fraction of the vaporized decomposition products is evolved within this narrow temperature range, it is believed that the use of a considerably slower carbonization cycle within this range would cause a substantial increase in the carbon yield. For the typical argon pyrolysis cycle shown in Figure 13, a relatively short hold time of only 55 minutes was employed over the temperature range from 400 to 500° C.

Figure 13. TYPICAL TIME-TEMPERATURE CYCLE USED FOR THE PYROLYSIS OF STYRENE-DIVINYLBENZENE COPOLYMERS IN FLOWING ARGON.

META-DIVINYLBENZENE AND PARA-DIVINYLBENZENE ISOMERS

Samples of meta-divinylbenzene and para-divinylbenzene monomers were obtained^(c) to study the effects of isomer type and purity of DVB on the coking yield after pyrolysis. A comparison of the divinylbenzene monomers from the Cosden Company with those from Dow that had been used for all previous polymerization and pyrolysis studies is given in Table 15. The para-DVB obtained from Cosden was of particular interest since it showed a para-isomer content of approximately 92 percent compared to only 55 percent for the Dow monomer material that had been used.

Table 15
ANALYSES OF COMMERCIAL PARA-DIVINYLBENZENE AND META-DIVINYLBENZENE MONOMERS
USED IN POLYMERIZATION AND PYROLYSIS STUDIES
(All Values in Percent Except where Shown)

Constituent	DVB-55(1)	<u>Para</u> -DVB(2)	<u>Meta</u> -DVB(2)
<u>Para</u> -divinylbenzene	55.0	91.9	6.4
<u>Meta</u> -divinylbenzene	-	4.6	39.2
<u>Para</u> -ethylvinylbenzene	35.4	1.6	12.8
Saturates	9.6	-	-
Diethylbenzene	-	0.1	3.0
<u>Meta</u> -ethylvinylbenzene	-	1.5	29.2
Toluene	-	-	6.0
Unidentified	-	0.3	3.4
Inhibitor (<u>para</u> -tertiary-butylcatechol)	1,000 ppm	1,500 ppm	1,500 ppm

(1) Obtained from the Dow Chemical Company, Midland, Michigan.

(2) Obtained from the Cosden Oil & Chemical Company, Chicago, Illinois.

Polymers of Cosden para-DVB, meta-DVB, and copolymer mixtures of Cosden para-DVB and meta-DVB were prepared by heating both as-received and inhibitor-free monomers in corked test tubes suspended in a mineral oil bath maintained at approximately 80° C. The polymers were then cured by heating to 250° C over 48 hours and pyrolyzed under flowing argon by heating to 900° C over 48 hours. Results are presented in Table 16.

These data show that the para-DVB isomer gives a higher coking yield than the meta-DVB isomer and also show that a slight improvement in the coking yield is realized when pyrolysis is conducted with a lidded ceramic crucible.

(c) From the Cosden Oil & Chemical Company.

Table 16
COKING YIELDS OF VARIOUS POLYMERS AND COPOLYMERS AFTER
PYROLYZING AT 900° C IN FLOWING ARGON

Polymer Number ⁽¹⁾	Description	Initial Weight (gms)	Net Weight After 250° C Cure (gms)	Net Weight After 900° C Pyrolysis (gms)	Coking Yield ⁽²⁾ (%)
1	<u>para</u> -DVB, with Inhibitor	1.1597	1.1022	0.3215	29.2
2	<u>para</u> -DVB, without Inhibitor	0.8634	0.8591	0.2497	29.1
3	<u>meta</u> -DVB, with Inhibitor	1.7316	1.3016	0.2734	21.0
4	<u>meta</u> -DVB, without Inhibitor	1.1261	0.9472	0.1773	18.7
5	25 vol % <u>meta</u> - 75 vol % <u>para</u> , without Inhibitor	0.7017	0.6899	0.1823	26.4
6	50 vol % <u>meta</u> - 50 vol % <u>para</u> , without Inhibitor	0.8757	0.8637	0.2114	24.5
7	75 vol % <u>meta</u> - 25 vol % <u>para</u> , without Inhibitor	0.5724	0.5225	0.1157	22.2
8	Isoprene (BF ₃ catalyzed) ⁽³⁾	0.8787	0.8028	0.0531	6.6
9	Divinyltoluene	0.8939	0.8181	0.0230	28.2
10	<u>para</u> -DVB, with Inhibitor, Lidded Crucible	1.6803	1.6198	0.5117	31.6
11	<u>para</u> -DVB, without Inhibitor, Lidded Crucible	0.9827	0.9743	0.2944	30.3
12	Polybutadiene	-	3.0143	0.0543	1.8

(1) Polymers 1 - 7 and 10 - 11 were from Cosden monomer material.

(2) Based on weights after 250° C curing.

(3) Preheated at 285° C prior to pyrolysis.

Also listed in Table 16 are the coking yields obtained on divinyltoluene, isoprene, and a commercial polybutadiene polymer. The effect of the para-DVB content (92% isomer) in the meta-DVB and para-DVB copolymer system on the coking yield is indicated in Figure 14.

Figure 14. EFFECT OF PARA-DIVINYLBENZENE CONTENT ON THE 900° C COKING YIELD OF PARA AND META-DIVINYLBENZENE COPOLYMERS.

Removal of the para-tertiary-butylcatechol (TBC) inhibitor from the meta-DVB and para-DVB monomers was accomplished by treating the mixture with a ten percent sodium hydroxide solution. After washing with distilled water, the DVB was dried with Molecular Sieves (Type 5A) prior to polymerization. As indicated in Table 17, the yield of coke obtained from DVB polymers in which the TBC inhibitor had not been removed prior to polymerization was slightly higher than for those polymers prepared after the inhibitor removal treatment. Even after drying, there may have been some residual moisture in the inhibitor-free monomer which may have had an adverse effect on polymerization.

Table 17
EFFECT OF PROLONGED POLYMER CURING AND GRAPHITE POWDER ADDITIONS
ON THE COKING YIELD OF PARA-DIVINYLBENZENE

Polymerization Conditions	Polymer Weight After 150° C Cure (gms)	Residue Weight After 900° C Pyrolysis (gms)	Weight Ratio of Graphite to Polymer	Coking Yield ⁽¹⁾ (%)
With Inhibitor	1.1466	0.4085	-	35.6
Without Inhibitor	1.0479	0.3655	-	34.9
With Inhibitor, Graphite Added ⁽²⁾	1.3674	0.5026 ⁽³⁾	1.14	36.8
With Inhibitor, Graphite Added ⁽⁴⁾	1.1987	0.4419 ⁽³⁾	1.66	36.9
With Inhibitor, Crucible Lid Used	0.8824	0.3185	-	36.1
Without Inhibitor, Crucible Lid Used	0.4406	0.1521	-	34.5

(1) Based on weights after curing at 150° C for eighteen days.

(2) Graphite powder poured over polymer sample prior to coking.

(3) Graphite-free basis.

(4) Graphite powder blended in with polymer sample prior to coking.

A distinct difference was observed between the structures of the carbonaceous coke residues obtained from the Cosden meta-DVB and para-DVB isomers. The coke structure from the meta-DVB was considerably more porous and fluffy, showing large voids from the evolution of gaseous products. In contrast, coke from the para-DVB was much more dense and compact. A comparison of typical coke residues obtained after pyrolysis of meta-DVB and para-DVB is given in Figure 15.

Other samples of Cosden para-DVB polymers were oven cured for 18 days at 130 - 150° C prior to pyrolysis to study the effects of adding graphite powder (-325 mesh) and the use of a lidded crucible on the coking yield. Results are reported in Table 17. These data indicate that a prolonged polymer curing period at 150° C and additions of graphite powder to the polymer prior to pyrolysis had beneficial effects on the coking yield.

A173

Figure 15. CARBONACEOUS COKE RESIDUES AFTER PYROLYZING THE META AND PARA ISOMERS OF DIVINYLBENZENE IN FLOWING ARGON. (Full Size)

The coking yields listed in Table 17 for polymerized para-DVB (92% isomer) that has been cured for 18 days at 150° C represent the highest results that have been obtained to date with divinylbenzene as an oxygen-free binder. Previously, the highest coking yield had been attained with the polymer prepared from Dow para-DVB (55% isomer) and pyrolyzed in the presence of a graphite powder additive under equivalent conditions of temperature cycling. The increase in coking yield, shown in Table 17, for the two tests (in which graphite powder had been added to the polymer prior to pyrolysis) again confirms that the incorporation of already formed carbon graphite as a filler has a pronounced effect on the mechanisms of the carbonization process.⁽⁷⁾

The effect of adding graphite powder (-325 mesh) to polymers of divinylbenzene and divinyltoluene was also studied. Results, reported in Table 18, indicate that the highest yield of the coke from divinylbenzene was obtained when graphite powder was added to the divinylbenzene monomer before polymerization. Because of the large number of variables associated with the polymerization, curing, and pyrolysis steps, however, further tests will be required to substantiate this conclusion.

VARIOUS DIVINYLBENZENE COPOLYMERS

Various oxygen-free copolymers of divinylbenzene were made by heating inhibitor-free monomer mixtures in corked test tubes suspended in a mineral oil bath maintained at a controlled temperature. Polymers of divinylbenzene and copolymers of divinylbenzene and styrene, divinylbenzene and divinyltoluene, and divinylbenzene and alpha-methylstyrene were prepared. Their coking yields, obtained after pyrolysis at 900° C, were then compared.

Table 18
EFFECT OF GRAPHITE ADDITIONS ON THE COKING YIELD

Polymer	Polymer Weight After Curing (gms)	Weight of Graphite Added (gms)	Weight Ratio of Graphite to Polymer	Coking Yield ⁽¹⁾ (%)
Divinylbenzene	3.3975	1.3573 ⁽²⁾	0.40	25.4
Divinylbenzene	4.1084	0.6053 ⁽³⁾	0.15	27.7
Divinytoluene	1.3080	None	-	4.1
Divinytoluene	1.6340	0.8884 ⁽²⁾	0.54	3.4

(1) Based on graphite-free polymer after a 250° C cure.

(2) Graphite poured over polymer sample prior to coking.

(3) Graphite blended in with monomer sample during polymerization.

The polymers were cured by heating to 250° C over 50 hours and pyrolyzed under flowing argon by heating to 900° C over 50 hours using the heating cycles shown in Figure 16. Results are presented in Table 19.

The graph of Figure 17 shows the effect of the divinylbenzene content in the styrene-divinylbenzene copolymer system on the coking yield.

Figure 16. HEATING CYCLES USED FOR THE CURE AND PYROLYSIS OF CO-POLYMERS IN FLOWING ARGON.

Table 19
COKING YIELDS OF VARIOUS OXYGEN-FREE POLYMERS

Monomer Composition (vol %)	Polymerization Time (hours)	Polymerization Temperature (° C)	Weight Loss on Curing ⁽¹⁾ (wt %)	Coking Yield ⁽²⁾ (wt %)
Divinylbenzene (100)	70	70 - 73	18	22.4
Divinylbenzene (100)	19	70 - 72	42	22.4
Divinylbenzene (67)-Divinyltoluene (33)	19	80 - 82	6.5	14.4
Divinylbenzene (50)-Divinyltoluene (50)	19	80 - 82	3.6	11.8
Divinylbenzene (50)-Alpha-Methylstyrene (50)	65	75 - 77	28.2	12.0
Divinylbenzene (67)-Alpha-Methylstyrene (33)	65	75 - 77	18.9	13.4
Divinylbenzene (17)-Styrene (83)	64	70 - 75	1.4	7.6
Divinylbenzene (29)-Styrene (71)	64	70 - 75	3.4	9.4
Divinylbenzene (50)-Styrene (50)	64	70 - 75	6.4	14.9
Divinylbenzene (71)-Styrene (29)	64	70 - 75	9.9	19.3
Divinylbenzene (83)-Styrene (17)	64	70 - 75	11.3	22.1
Divinylbenzene (100)	64	70 - 75	10.2	23.3

(1) Cured by heating to 250° C over 50 hours in flowing argon.

(2) Based on the cured weight after pyrolysis by heating to 900° C over 50 hours in flowing argon.

The effect of various catalysts on the coking yield was evaluated by adding certain catalysts to monomer mixtures containing 20 volume percent styrene

Figure 17. EFFECT OF THE DIVINYLBENZENE CONTENT ON THE COKING YIELD OF STYRENE-DIVINYLBENZENE COPOLYMERS.

and 80 volume percent divinylbenzene. After polymerization, the copolymers were coked simultaneously under flowing argon at 900° C. Results, listed in Table 20, show that the coking yield obtained with one weight percent p-toluene-sulfonic acid as a catalyst was significantly higher than that obtained in the absence of a catalyst under equivalent conditions. The carbon residue obtained after pyrolysis of the p-toluene-sulfonic acid-treated copolymer also appeared to be denser than any other copolymer residue.

Table 20
EFFECT OF CATALYSTS ON THE COKING YIELD
OF STYRENE-DIVINYLBENZENE COPOLYMER

Catalysts ⁽¹⁾	Coking Yield (%)
None	16.87
None	17.23
Benzoyl Peroxide	15.66
Benzoyl Peroxide	15.36
Citric Acid	17.25
Citric Acid	16.37
<u>p</u> -toluene-sulfonic Acid	19.15
<u>p</u> -toluene-sulfonic Acid	19.32

(1) Added to monomer mixture in 1% concentration.

ISOPRENE POLYMERIZATION

Studies on the preparation of other oxygen-free polymers were also made. An attempt to prepare polyphenylene by heating para-dibromobenzene with sodium was unsuccessful. Attempts to thermally polymerize the isoprene monomer (2-methyl-1, 3-butadiene) after removing the inhibitor by washing the monomer with ten weight percent sodium hydroxide, were likewise unsuccessful. In one test, no visible polymer formed after heating the monomer in a flask equipped with a reflux condenser for one week at 120° C. Additions of benzoyl peroxide to catalytically initiate polymerization were also made, but no polymer resulted.

Polymerization of isoprene resulted upon adding boron trifluoride in ether as a catalyst. A violent exothermic reaction occurred and a brown polymer product formed which was solid at room temperature, but which melted upon heating to 100 - 200° C. Upon curing two portions of this isoprene polymer at 250° C and pyrolyzing at 900° C under flowing argon, coking yields of only 1.0 and 1.2 percent were obtained.

Copolymers are polymers which contain recurring units of the same monomer (such as styrene), but which are interrupted in their recurrence by the insertion of a second monomer (such as divinylbenzene). In the styrene-divinylbenzene copolymer, the linear polystyrene molecular systems are bound to each other through bridges which consist of the benzene nuclei of the divinylbenzene. The structural arrangement of the three-dimensional crosslinking between polymer chains is an important consideration affecting the thermosetting characteristics of the polymer.

According to Clark,⁽⁹⁾ in order to obtain a polymerization, the initial reacting monomers must be polyfunctional in that there must be more than one reacting group or position in each molecule. The double bond between carbon atoms represents a difunctional grouping because of the possibility of an electronic shifting of the chemical unsaturation to the end carbon atoms of the molecule. Reacting molecules possessing difunctional properties produce linear, chain-like polymer molecules, generally spiral in form. Reacting molecules possessing more than two centers of reactivity (functionality) present the possibility of a crosslink formation in the polymer molecule between basic chain formations. The results are the development of spatial polymers. Since divinylbenzene contains two double bonds, it would have a functionality of four. The higher coking yields associated with the high divinylbenzene contents of the styrene-divinylbenzene copolymers, shown in Figure 17, would thus be expected because of the greater spatial complexity of the copolymer.

Spatial copolymers of styrene using divinylbenzene as the crosslinking agent were also studied by Veselovskii and Vorobeva⁽¹⁰⁾ using peroxide initiators in an inert gas medium. They found that the thermal stability of the copolymers increased linearly with the increasing amount of divinylbenzene used, which is in general agreement with the coking yield data presented in Figure 17. Although these styrene-DVB copolymers, as prepared in this study, gave a coking yield of less than 50 percent, the coke residue obtained showed high purity. Schmidt and Jones⁽⁷⁾ have reported that a considerable increase in the yield of coke was realized by increasing the divinylbenzene content of the copolymer and by using slower temperature cycling during pyrolysis.

Polymers are usually formed by the application of heat, light, or the use of catalysts. Although polymerization of styrene, divinylbenzene, divinyltoluene, alpha-methylstyrene was readily accomplished by heat, it was found that isoprene did not readily polymerize by this method, possibly because of its greater sensitivity to the inhibitive effects of air on moisture contaminants. The low coking yields obtained with the catalyzed polymer $[\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2]$ may be attributed to the formation of a low-molecular-weight polymer as evidenced by the low melting point ($< 200^\circ \text{C}$) that was observed on heating.

REFERENCES

- (1) Hooker, J. R.; Pitch Binders for Graphite: A Review of the Literature, Report GA-3985, General Dynamics Corporation, San Diego, California; March 7, 1963.
- (2) Industrial Carbon and Graphite, pp 152-176; Society of Chemical Industry (1958).
- (3) Mantell, C. L.; Industrial Carbon, pp 127-229; D. Van Nostrand Company, Inc (1946).
- (4) Jones, H. L., Jr; Simon, A. W., and Wilt, M. H.; Journal of Chemical and Engineering Data, 5, pp 84-86; January 1960.
- (5) Boundy, R. H. and Boyer, R. F., Editors; Styrene, Its Polymers, Copolymers and Derivatives, Reinhold Publishing Corporation (1952).
- (6) Helfferich, R.; Ion Exchange, p 35; McGraw-Hill Company (1962).
- (7) Schmidt, D. L. and Jones, W. C.; Chemical Engineering Progress, 58, pp 42-45; October 1962.
- (8) Coffman, J. A., et al; Carbonization of Plastics and Materials Research, Technical Report WADD-TR-60-646, Part II, p 13; January 1963.
- (9) Clark, F. M.; Insulating Materials for Design and Engineering Practice, p 403; J. Wiley and Sons (1962).
- (10) Veselovskii, P. F. and Vorobeva, E. P.; "The Dielectric Properties of Spatial Copolymers of Styrene", International Chemical Engineering, 3, p 383; July 1963.

ACKNOWLEDGEMENTS

Assistance of the following is gratefully acknowledged: L. E. Peters, for laboratory assistance in preparing some of the divinylbenzene copolymers; S. S. Cristy, for assistance in the determination of some of the coking yields; Anna G. Dobbins, of the Y-12 Development Metallurgy Laboratory, for the Knoop hardness measurements and coke particle photography; and N. J. Williams for the gel permeation chromatography studies.

Thanks are also extended to the following vendors who supplied the samples of pitch, styrene, divinylbenzene, and isoprene used in this study: Crawley Tar Products Co, E. T. Trotter Co, Allied Chemical Co, Koppers Co, Reilly Tar and Chemical Co, Cosden Oil and Chemical Co, Dow Chemical Co, and Shell Chemical Co.