ARF 6039-4

INVESTIGATION OF GRAPHITE BODIES

Wright Air Development Center
Wright-Patterson Air Force Base, Ohio
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Project ARF 6039

INVESTIGATION OF GRAPHITE BODIES

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ABSTRACT

Preliminary data are presented illustrating the properties of molded multicrystalline graphite made using calcined petroleum coke (in some instances mixed with a thermal carbon) bonded with coal tar pitch, furfuryl alcohol, or limited mixtures of the two.

No conclusions have yet been drawn regarding the relation between these properties, since a large number of specimens remain to be measured. Most obvious is the difficulty of achieving a sound structure from bodies of maximum green density, particularly when the binder is not thermoplastic.

Graphitized specimens made with furfuryl alcohol reflect the high density of the binder coke. X-ray data show that this coke is poorly graphitizable as compared to pitch; modulus and electrical resistance data show it to be more dense.

A full description of the use of differential thermal analysis and dilatometry in investigating the behavior of thermosetting resins is appended.

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INVESTIGATION OF GRAPHITE BODIES

I. INTRODUCTION

The objective of this project is to gain an understanding of multi-crystalline graphite adequate for its use as an engineering material. This objective tacitly includes an ultimate improvement in the strength of molded, fine-grained bodies in a reproducible way.

Experimental specimens have now been made from calcined petroleum coke (sometimes mixed with a thermal carbon) bonded with coal tar pitch and with the most promising of the synthetic resins for this purpose, furfuryl alcohol (FA).

The specimens have now been graphitized to 2875°C in a single pack at the National Carbon Company's Fostoria, Ohio laboratory. It is the purpose of this report to describe preliminary data obtained from some of these specimens. These data should, since they represent a small proportion of the total statistical family, be applied with caution.

II. EXPERIMENTAL WORK AND DISCUSSION

A. Graphitization of Binders

The experimental procedures employed were described in Appendix I of Report No. 3. Additional details of the graphite-tube resistance furnace are presented in Figures 1-4. The graphite resistance tube element and its dimensions are shown in Figure 1. During graphitization, the inner working space is kept under a positive pressure of helium. An outer annulus surrounding the tube is also maintained under helium pressure to protect the inner resistance tube at elevated temperature. Observation of the process and temperature measurements is possible through a window upstream from the helium gas inlet.

Figure 2 is a side view of the graphite-tube resistance furnace and indicates various operational features. Figure 3 is an end view which shows the method of connecting the bus bar to the graphite tube. Figure 4 is a wiring diagram of the electrical components used in operating the furnace.

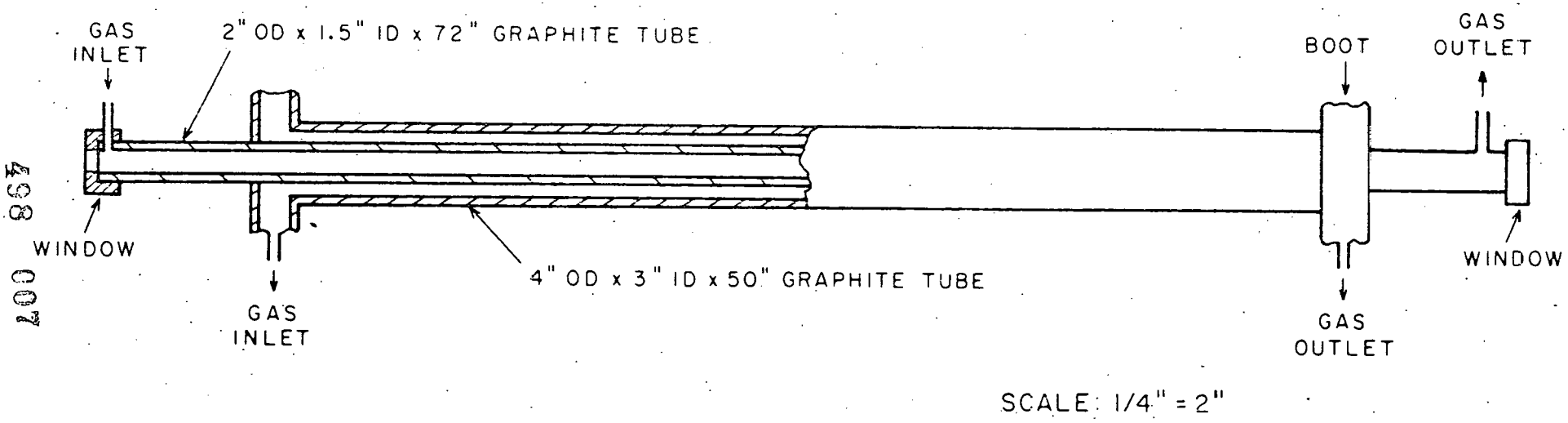

Fig. 1. GRAPHITE RESISTANCE TUBE ASSEMBLY

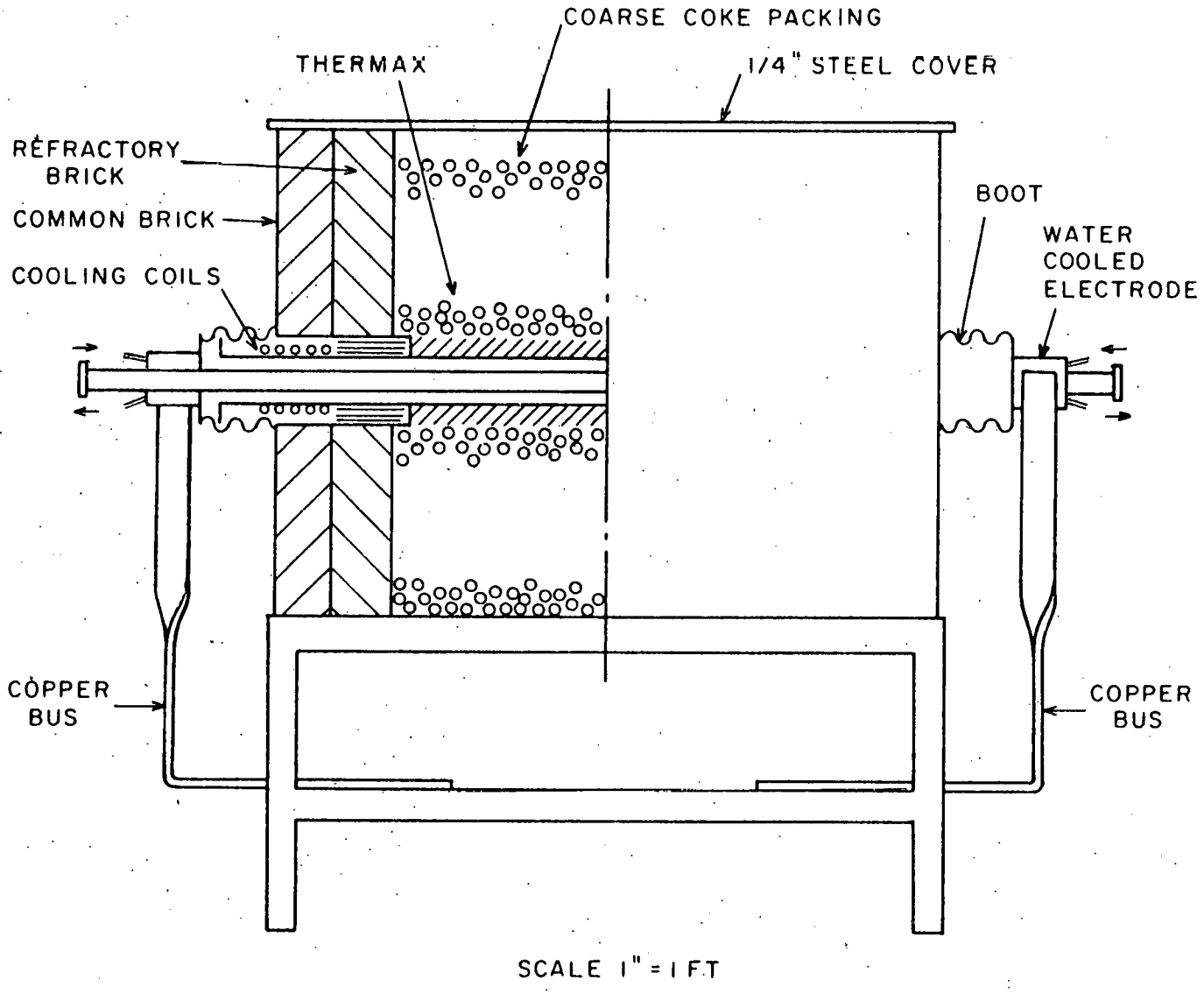

Fig. 2. GRAPHITE-TUBE RESISTANCE FURNACE

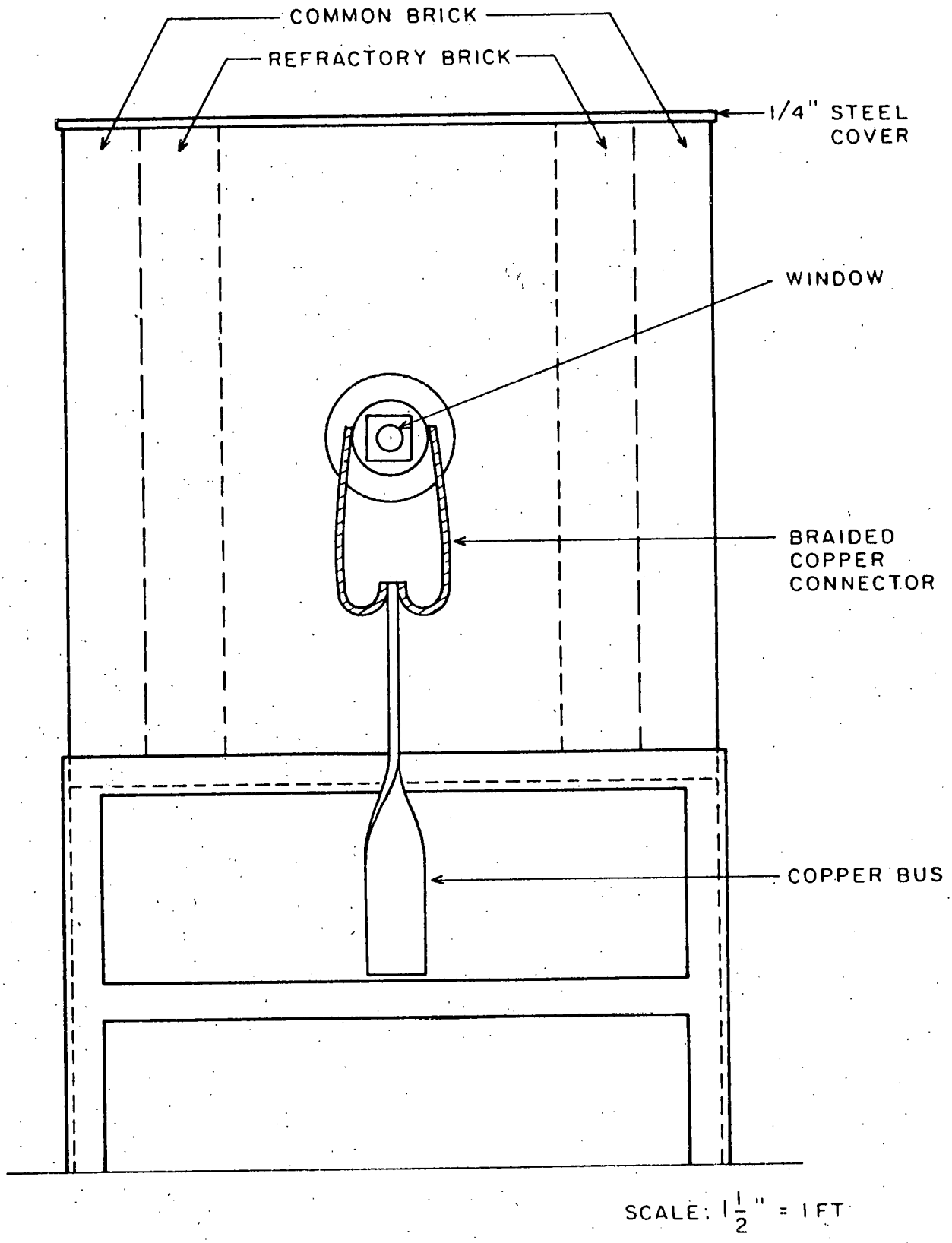

Fig. 3. GRAPHITE-TUBE RESISTANCE FURNACE, END VIEW SHOWING TERMINAL CONNECTION

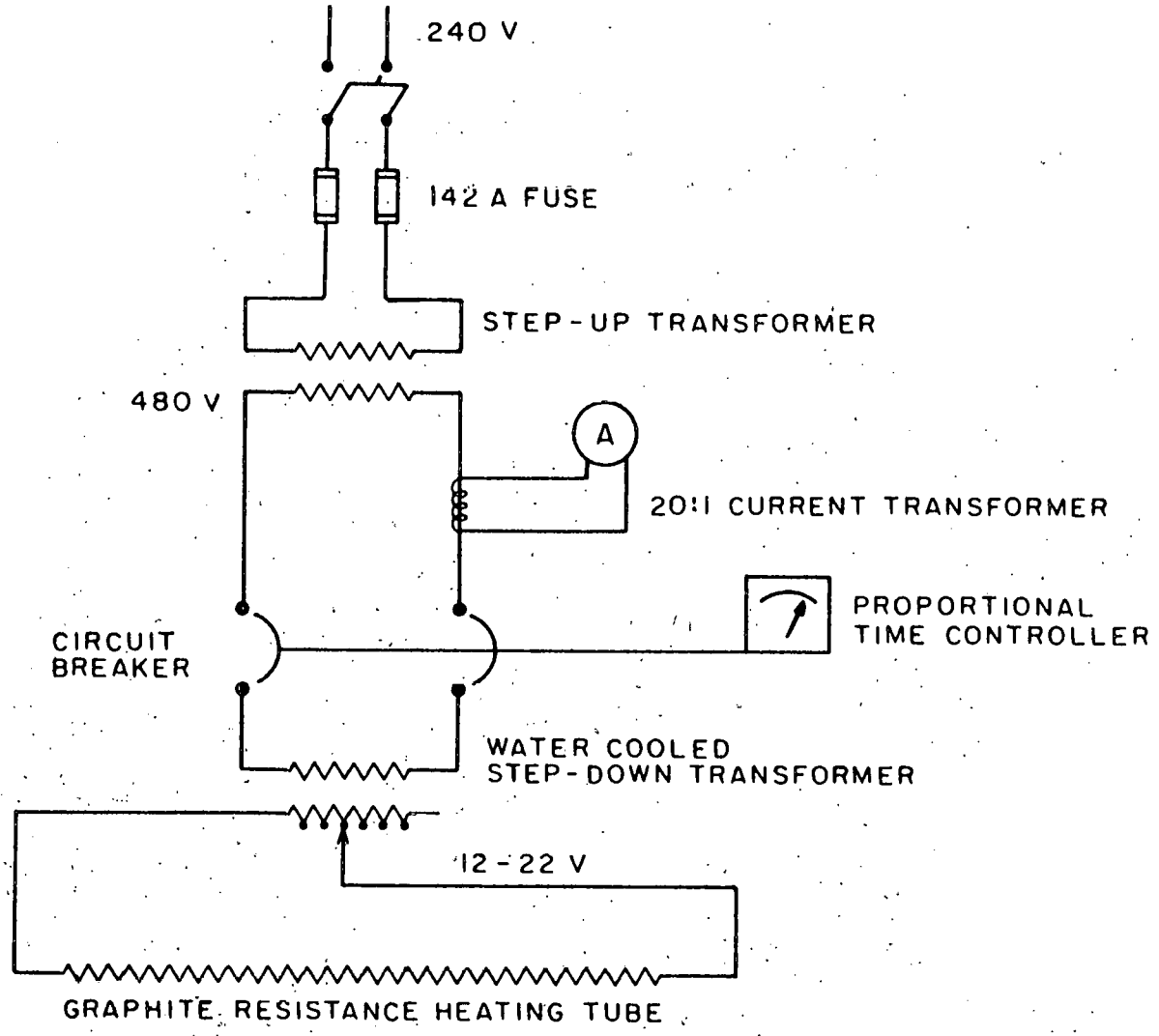

Fig. 4. WIRING DIAGRAM FOR GRAPHITE-TUBE FURNACE

1. X-Ray Examination of Synthetic Formulations

Four formulations of binder and petroleum coke have been subjected to a peak temperature of approximately 2870°C for about two hours. The four formulations presented in Table 1 were comprised as follows:

Sample	Formulation (resin/coke
X-119	phenol formaldehyde (60 p/100 p)
XVIII-200	furfuryl alcohol (20 p/100 p)
XVI-190	coal tar pitch (38 p/100 p)
XX-237	phenol benzaldehyde (50 p/100 p)

It is evident that the x-ray diffraction results provide little information on the performance of the binder since the structure of the Texas Lockport No. 90 petroleum coke dominates the pattern. Perhaps the most useful information is the value of L_c, which is the dimension of the parallel layer group normal to the layer plane. It is presumed that the parallel layer groups result from the packing of disk-shaped graphite layers and that the larger the disk diameter, the larger the number of layers in the group. It may be seen that the value of L_c for the phenol formaldehyde product (208 a.u.) is slightly lower than for the other samples (220-223 a.u.). Since an inhibition of graphitization by formaldehyde additives will be described in the next section, it appears possible that this small difference might be significant.

The value of d varies from 3.35 to 3.37 a.u. Since ideal graphite has a layer spacing of 3.35, it is apparent that a significant degree of graphitization has occurred. Because the spacing is an average property, the binder will have minor influence on this value.

2. X-Ray Examination of Furfuryl Alcohol Polymers

As indicated in the previous section, the contribution of the binder to the x-ray diffraction pattern is difficult to interpret because of the predominating amounts and influence of the petroleum coke component of the formulations. Three furfuryl alcohol products were separately polymerized, baked and graphitized. The individual samples were prepared by polymerizing FA (furfuryl alcohol, 99% purity), FA Pol. (furfuryl alcohol dimer, prepared by polymerization, viscosity of 262 centiposes) and FA-CH_2O Pol (furfuryl alcohol polymerized with 0.6 mol of formaldehyde per mol of FA). The above materials (100 g) were polymerized with 0.5% of p-toluene sulfonic

Table 1

X-RAY DIFFRACTION DATA ON SYNTHETIC FORMULATIONS

Sample	hkl	I	Peak d (A°)	Width at 1/2 Max. (°2θ)	L_c (A°)	Remarks
X-119	002	896	3.35	~0.45	208	Peak very sharp and intense
XVIII-200	002	968	3.37	0.42	223	
XVI-190	002	992	3.36	0.44	220	
XX-237	002	944	3.36	0.42	223	
X-119	004	47	1.68	~0.68		Peak fairly sharp
XVIII-200	004	50	1.68	0.56		
XVI-190	004	52	1.68	0.56		
XX-237	004	43	1.68	0.56		
X-119	100	32	2.12	~0.53		Peak fairly sharp
XVIII-200	100	26	2.13	0.41		
XVI-190	100	26	2.13	0.42		
XX-237	100	27	2.13	0.40		
X-119	101	52	2.03	1.34		Peak somewhat broad
XVIII-200	101	42	2.04	0.30		
XVI-190	101	41	2.04	1.35		
XX-237	101	40	2.04	1.28		
X-119	110*	99.5	1.23	~0.62		Peak fairly sharp
XVIII-200	110	101	1.23	0.58		
XVI-190	110	80	1.23	0.60		
XX-237	110	27**	1.23	0.50		
X-119	112*	65	1.16	1.35		Peak somewhat broadened
XVIII-200	112	67	1.16	1.22		
XVI-190	112	60	1.16	1.30		
XX-237	112	14**	1.16	1.10		

* 4° slit used to increase intensity.

** 1° slit used in error.

acid, and were then baked with a controlled temperature cycle at 1000°C. The materials were baked under helium with a uniform temperature rate increase of 11.3°C/hr up to 1000°C, were held at 1000°C for 12 hours and then were cooled at a rate of 19.8°C/hr down to 50°C. The samples were then graphitized in the same furnace loading as the previous samples (peak temperature of approximately 2870°C for about two hours). The x-ray diffraction results are shown in Table 2.

The development of the crystalline reflections (002) and (004) and the two-dimensional reflections (10) and (11) can be used for following the graphitization process. The (hk) two-dimensional reflections sharpen considerably but retain their characteristic two-dimensional shape indicating that the layer diameter increases in size but that the orientation of the layer about the normal remains random. When neighboring layers begin to align with the graphite mode of structure, modulations appear in the (10) and (11) two-dimensional reflections. These begin to split into (100) (101) and (110) (112) reflections, respectively. Further, the layer spacing, d, should approach the graphite value, 3.35 a.u., as ordering occurs.

The data of Table 2 indicate that the furfuryl alcohol-formaldehyde polymer is quite resistant to polymerization. Presumably, the formaldehyde acts to form a polymer with a high degree of cross-linking which fixes the carbon skeleton in a highly random fashion that, in turn, requires more heat to assume the highly ordered graphite lattice. This is shown not only by the symmetrical shape of the (002) peak but also the lack of modulation of the (10) and (11) reflections. Additionally, calculation of the L_c value, the dimension of the parallel graphite layer normal to the layer, is lowest for this copolymer. It is known that furfuryl alcohol polymer in its formation released formaldehyde molecules and, therefore, the finding that the monomer material is somewhat difficult to graphitize is not unexpected. The furfuryl alcohol polymer under mild reaction conditions is converted substantially to dimer. If this procedure produces less formaldehyde, this polymer structure would graphitize somewhat more readily than the other two products, as demonstrated in Table 2.

The low values of L_c (28-38 a.u.) compared to previously observed values from the petroleum coke formulation (208-223 a.u.) is an indication of the inherent resistance of furfuryl alcohol to graphitization. An estimate

Table 2

GRAPHITIZATION OF SEVERAL FURFURYL ALCOHOL POLYMERS

Sample	hkl	I	Peak d (A°)	Width at 1/2 Max. (°2θ)	L_c (A°)	Remarks
FA	002	156	3.38	∿24	29	Asym. peak. Somewhat sharper on high angle side than on low angle side.
FA Pol.	002	220	3.34	∿17.5	38	Asym. peak. Sharp on high angle side and tailing on low angle side.
FA-CH_2O	002	120	3.43	∿28	28	Almost sym. peak. Only a slight sharpening on high angle side.
FA	004	8	∿1.69	very broad		Broad asym. peak.
FA Pol.	004	10	∿1.68	∿17		Broad asym. peak.
FA-CH_2O	004	4	∿1.71	very broad		Broad asym. peak.
FA	10*	30	2.10	∿26		Asym. peak tailing on high angle side. Modulations barely discernible.
FA Pol.	10*	35 24	2.10 2.03	∿30		Asym. peak tailing on high angle side. Some modulation in the higher angle side indicating a splitting of the (10) reflection into (100) and (101).
FA-CH_2O	10	22	2.10	∿24		Broad asym. peak tailing on high angle side. Almost no indication of modulations.
FA	11**	30	1.22	∿28		Asym. peak tailing on high angle side. Modulations just beginning.

* (10) reflection beginning to split into (100) and (101).

** (11) reflection beginning to split into (110) and (11$\bar{2}$).

Table 2 (cont.)

Sample	hkl	I	Peak d (A°)	Width at 1/2 Max. (°2θ)	L_c (A°)	Remarks
FA Pol.	11**	35 18	1.22 1.15	~26		Very broad asym. peak tailing on high angle side. Modulation of the 2-dimensional (11) reflection into (110) and (112).
FA-CH_2O	11	17	1.22	~29		Broad asym. peak tailing off on high angle side. Modulations not observed.

was made as to the degree of graphitization after the method of B.E. Warren, who determines P_1, the probability of nearest neighbor ordering. Essentially, our relative peak heights were compared with those of Warren. The following estimates were made:

Polymer	Estimate of Graphitization, %
FA	3
FA-Pol.	25-33
Fa-CH_2O	3

While these estimates are relatively crude, it appears that furfuryl alcohol polymers resist graphitization and a highly cross-linked polymer structure formed by copolymerization of furfuryl alcohol and formaldehyde further increases resistance to graphitization.

In a further set of experiments, the furfuryl alcohol resin identified as FA Pol. was subjected to a peak graphitization temperature approximating 2870°C for periods of time which may be characterized as 1, 2, and 3 hours. Table 3 presents the x-ray diffraction data obtained. The most significant feature of the data are the L_c values. As graphitization progresses, the layer thickness increases from 37 to 38 a.u., respectively. Significantly, this value is far below that observed in Table 1 where the petroleum coke orientation predominates and an average value for L_c is over 200 a.u. The values for d may appear inconsistent, but this is attributed to the difficulty of determining the peak location for an asymmetric curve.

In summary, x-ray diffraction studies indicate that thermal degradation of furfuryl alcohol polymers produces carbons which resist graphitization. Incorporation of formaldehyde in furfuryl alcohol resins further increases resistance to ordering processes. Thus, with furfuryl alcohol binders, it should be possible to achieve a relatively high degree of structural isotropy within the binder bridges while the filler character will determine the bulk anisotropy. Appropriate combinations of furfuryl alcohol binder and filler should permit optimization of properties influenced by anisotropy.

Table 3

REPETITIVE GRAPHITIZATION OF A FURFURYL ALCOHOL POLYMER

Treatment	hkl	I	Peak d (A°)	Width at 1/2 Max. (°2θ)	L_c (A°)	Remarks
1 hr	002	178	3.34	~20	37	Asym. peak. Sharp on high angle side and failing on low angle side.
2 hr	002	220	3.34	~17.5	38	
3 hr	002	186	3.38	~15.5	44	
1hr	004	6	~1.69	very broad		
2hr	004	10	~1.68	~17		Broad asym. peak.
3hr	004	8	1.68	~16.5		
1 hr	10*	29	2.10	~29		Asym. peak tailing on high angle side. Some modulation in the higher angle side indicating a splitting of the 2-dimensional (10) reflection into (100) and (101).
		21	2.03			
2hr	10*	35	2.10	~30		
		24	2.03			
3 hr	10*	23	2.11	~28		
		16	2.05			
1 hr	11**	30	1.22	~28		Very broad asym. peak tailing on high angle side. Modulation of the higher angle side from the 2-dimensional (11) reflection into (110) and (112).
		14	1.15			
2 hr	11**	35	1.22	~26		
		18	1.15			
3 hr	11**	35	1.23	~23		
		16	1.15			

* (10) reflection beginning to split up into (100) and (101).

** (11) reflection beginning to split up into (110) and (112).

3. Summary

X-ray diffraction analysis affords an insight into the processes which occur when furfuryl alcohol polymers are heated to graphitization temperature. The rigid carbon structure produced at low temperatures persists up to high temperatures and resists the ordering required to form graphite. Increased cross-linking provides a further measure of resistance. In a carbon body formulation, changes of the binder structure are obscured by the highly ordered x-ray diffraction pattern developed by the filler which is present at high concentration, e.g., 80% by weight.

B. Physical Property Data

Evidence regarding the interrelated properties of experimental specimens is presently limited to the relatively small number of specimens which have been evaluated.

The evaluation of a given specimen has included the following:

1. With rigid control of formulating, mixing, and fabricating procedures, a series of specimens is produced using a single heated die. The thickness of the specimens is deliberately varied.

2. Each green specimen is weighed; its volume is measured by immersion in water for pitch-binder specimens, or in mercury for furfuryl alcohol.

3. The specimens are packed by series, in saggers, supported by a mixture of clean silica sand and Thermax (a fine-grained thermal carbon), in such a way that no specimen is closer to another nor to a wall than one-fourth inch.

4. After carbonizing, the specimens are reweighed and examined for changes in thickness, cracks or other special features. Certain specimens are immersed in mercury for volume measurement, and some specimens may be subjected to room-temperature measurement of flexural modulus and strength. A small proportion of these carbonized specimens may now also be ground on all four sides to precise (± .001-inch) dimensions to provide evidence regarding skin effects and warpage during graphitization.

5. After single-pack graphitization (see p. 31-32, WADC Technical Report 58-503), the specimens are reweighed, measured, and ground to final dimensions. Room-temperature data are shown in Table 4; these

Table 4

ROOM TEMPERATURE PROPERTIES* OF MOLDED SPECIMENS AFTER GRAPHITIZATION

Series	Composition as Molded			Density g/cc	Dynamic Modulus of Elasticity (psi x 10^6)	Volume Resistivity (oh-cm x 10^{-4})
	Binder[1] (parts)	Thermal[2] Carbon (parts)	Coke[3] (parts)			
2-11	35 pitch	10	90	1.628	1.100	14.75
2-12	35 pitch	12.5	87.5	1.641	1.091	15.69
2-6	35 pitch	15	85	1.702	1.209	15.72
2-13	35 pitch	20	80	1.674	1.137	18.59
2-7	37 pitch	0	100	1.558	0.926	13.76
2-8	37 pitch	10	90	1.621	1.069	14.78
2-9	37 pitch	12.5	87.5	1.625	1.045	15.56
2-5	37 pitch	15	85	1.701	1.329	14.63
2-10	37 pitch	20	80	1.686	1.214	16.55
2-17	39 pitch	10	90	1.640	1.127	15.10
2-18	39 pitch	12.5	87.5	1.626	1.099	16.17
2-19	39 pitch	15	85	1.637	1.090	15.90
2-16	39 pitch	20	80	1.731	1.316	16.20

* Average of 20-30 specimens
1 Barrett 30 Medium Pitch
2 Thermax
3 Texas-Lockport No. 90, Calcined

include density, dynamic flexural modulus, volume d.c. resistance, and, of course, the original composition of the body.

6. Measurements which involve destruction of the specimen are the last to be made. A few specimens are first broken in flexure at room temperature using electric strain gages to obtain a comparison between dynamic and static moduli. Similar specimens are broken at arbitrarily chosen elevated temperatures (usually 1500°, 2000°, and 2250°C), their moduli being computed by microscopic observation or dilatometer measurement of specimen deflection at rising stress levels. A number of specimens are measured by dynamic flexural modulus while being heated to the creep threshold and cooled again to room temperature. Table 5 shows flexural strength values obtained at room and elevated temperatures for a limited number of specimen compositions. Where possible, the linear thermal expansion and contraction of the specimen is also measured. One or more specimens are subjected to several heating cycles to observe whether a change in the temperature-sensitive properties is occurring.

7. Ultimately, the remaining specimens are broken in flexure or are machined into ring specimens for the brittle ring test. Mean property values and deviations from them are calculated to determine the coefficient of error for a given series and the reproducibility of each property.

8. Table 6 lists the flexural and tensile strength of Speer graphite from room temperature up to 2250°C. Attempts were made to obtain data at 2500°C but the material exhibited considerable plastic flow at this temperature and no data were recorded.

Examination of the table shows that, with the exception of the orientation of A, the tensile strength of graphite continues to increase up to 2250°C. The flexural strength reaches a peak around 2000°C and begins to fall off at higher temperatures. Behavior of the flexural samples at 2250°C gives doubt for the validity of the tensile strength at this temperature; however, inspection of the ring samples reveals continued brittle failure. This indicates elastic behavior of the samples at the time of rupture.

The Young's modulus of elasticity values, obtained from stress-deflection data, follow the same trend as the flexural strength. The values obtained from a secant drawn through the origin and 50% of the ultimate load

Table 5

FLEXURAL STRENGTH OF MOLDED SPECIMENS AFTER GRAPHITIZATION

Series	Composition as Molded			Flexural Strength - psi[4]			
	Binder[1] (parts)	Thermal[2] Carbon (parts)	Coke[3] (parts)	Room Temp.	1500 °C	2000 °C	2250 °C
2-11	35 pitch	10	90	3544 (2236)*	4052 (2472)*	5527 (3341)*	6634 (3446) *
2-13	35 pitch	20	80	3049 (1781) *	3654 (2191) *	4778 (2848)*	4683 (2791) *
2-7	37 pitch	0	100	2574 (1664)*	3527 (2707)*	3522 (2319) *	3864 (2537) *
2-8	37 pitch	10	90	2780 (1712) *	3429 (2127)*	3800 (2367)*	4778 (2949) *
2-10	37 pitch	20	80	3524 (2082) *	4363 (2675)*	5145 (3068) *	5356 (3125) *
2-17	39 pitch	10	90	2477 (1510)*	3774 (2291)*	3818 (2566)*	4184 (2554)*
2-16	39 pitch	20	80	2736 (1567)*	3398 (1988)*	5012 (2902)*	5185 (3011)*

* strength/density ratio

1. Barrett No. 30 medium pitch
2. Thermax
3. Texas-Lockport No. 90, calcined
4. Average of three specimens

Table 6

MECHANICAL PROPERTIES OF SPEER GRAPHITE 3499

Sample Orientation		Room Temperature	1500°C	2000°C	2250°C
A. Tensile Strength, psi					
(1)	A	3726	6024	5913	7686
(2)	W_1	3917	5317	5940	7896
(3)	W_2	4175	4964	5573	7283
B. Flexural Strength, psi					
	A	3498	5591	7414	5862
	W_1	3817	5860	7564	6380
	W_2	3777	5082	7474	4441
C. Young's Modulus of Elasticity, psi					
	A secant	.772	.802	1.382	1.07
	tangent	.799	.802	1.382	1.51
	W_1 secant	.870	.915	1.382	1.15
	tangent	.925	.915	1.382	1.39
	W_2 secant	.870	0.909	1.16	0.93
	tangent	.994	0.909	1.16	1.057

D. Coefficient of Thermal Expansion, in/in/°C

	0-1500°C	0-2500°C	1500-2500°C
A	4.92	-	9.67
W_1	4.05	-	6.05
W_2	4.12	-	7.7

(1) Stressed across the grain
(2) Stressed along the grain, platelets flat
(3) Stressed along the grain, platelets on edge

show a peak at 2000°C while values from a tangent, except for the W_2 orientation, through the origin show increasing elastic moduli through 2250°C.

The coefficient of thermal expansion is higher for the A orientation than for the W orientations. The expansion from 1500° to 2500°C was 50% to 100% greater than from room temperature to 1500°C.

III. CONCLUSIONS

Rigorous conclusions cannot be drawn regarding the attainment of better properties in these experiments, although cautious optimism is suggested by the strength/density ratios of some specimens and the apparent increase in creep threshold for mixes containing thermal carbon.

IV. RECOMMENDATIONS

It is recommended that future work include research in development in the following areas in order to help define more closely the influence of raw materials, processing and production variables on the uniformity and reproducibility of graphite bodies.

1. Investigate, using differential thermal analysis and dilatometry, the following binder materials to improve the physical properties:
   a. Coal tar pitch
   b. Furfuryl alcohol
   c. Mixtures of coal tar pitch and furfuryl alcohol
2. Investigate the interrelation between physical and chemical binder properties and its setting and coking mechanisms considering such parameters as:
   a. Binder composition
   b. Composition and distribution of materials and fine aggregate
   c. Optimum forming and baking conditions, and
   d. Precise definition of physical properties obtained and deviations from them.
3. The following properties should be regarded as a means to evaluate graphite specimens, and will be maximized by experimental means.
   a. High strength-density ratio
   b. High resistance to thermal shock
   c. High thermal stability.

4. Conditions under which the properties will be measured will include:

a. Temperatures from room temperature to about 6000°F

b. Atmospheres of inert gases and hydrogen.

V. CONTRIBUTING PERSONNEL

The following personnel contributed to the work described herein: C. W. Boquist, S. A. Bortz, W. A. Loseke, H. H. Lund, H. H. Nakamura, R. S. Olsen, C. H. Riesz, and S. Susman.

VI. LOGBOOK RECORDS

Detailed laboratory data are recorded in ARF Logbook Nos. C-8570, C-8573, C-8580, C-8633, C-8744, C-1053, D-1254, D-1255, D-1256, and D-1257.

Respectfully submitted,

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Appendix I

INVESTIGATION OF SYNTHETIC BINDERS BY DIFFERENTIAL THERMAL ANALYSIS AND DILATOMETRY

INVESTIGATION OF SYNTHETIC BINDERS BY DIFFERENTIAL THERMAL ANALYSIS AND DILATOMETRY

H. Henry Nakamura and Leon M. Atlas

ABSTRACT

The pyrolysis of acid catalyzed furfuryl alcohol, phenol formaldehyde, and coal tar pitch binders has been studied by differential thermal analysis and dilatometry. Reactions such as the evolution of volatiles, polymerization, and condensation appear as reproducible endothermic and exothermic peaks on the DTA records. Size and location of these peaks not only reflect differences between the binder resins, but also detect changes caused by partial pre-polymerization or by the use of different catalysts. DTA curves are also sensitive to changes in the atmospheric gas, and even to a pressure variation of one atmosphere.

Dilatometric curves obtained at the same rate of temperature rise as used in the DTA studies, show that maximum shrinkage rates appear to coincide approximately with regions of greatest endothermic or exothermic activity.

I. INTRODUCTION

Because of its ability to record complex patterns of endothermic and exothermic reactions, differential thermal analysis has been successfully used to characterize such variable mixtures as soils and clays. Recently this technique was applied by Glass[1] and others to the study of coals; thermograms were related to the standard ranking system, and to the suitability for coking. Similarities between this process and the baking of carbon suggested that binders of possible interest in carbon production might also be amenable to characterization by their DTA curves. Ultimately, DTA might serve as a rapid means for screening new binder compositions, and for establishing optimum carbonizing schedules. Thermograms have shown that the peak rates of volatilization and structural condensation occur at somewhat different temperatures for the various binders studied in this program. Adjustment of baking cycles to the information provided by DTA curves might materially aid in the control of gas evolution and its consequences. In addition, further refinements of heating schedules, leading to increased densities, might be suggested by dilatometric curves.

The objectives of this program were:

1. the development of special apparatus and techniques for examining carbonaceous materials by DTA, and

2. the DTA and dilatometric investigation of a few promising synthetic binders. This work has progressed to the point where thermograms and dilatometric curves have been obtained for several groups of binders. It has been found that the DTA records are not only characteristic for each binder, but that changes in catalyst, atmospheric gas and pressure also produce significant variations.

II. APPARATUS AND PROCEDURES

A. DTA Apparatus

Differential thermal analysis is the process of accurately recording the difference in temperature between a thermocouple surrounded by the sample being studied and an opposed thermocouple embedded in a standard

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[1] H. D. Glass, "Differential Thermal Analysis of Coking Coals," Fuel, 34, 253-268, (1955).

substance, while both are being heated at the same rate. The theoretical basis and manifold ramifications of this procedure have been extensively described by Mackenzie[2] and by Smothers and Chiang[3]. The temperature differences in question are created by phase transformations or chemical reactions in the unknown which either absorb or evolve heat. Apparatus used in this program to detect and record these small temperature differences (about one or two degrees is common) consists of three basic units:

1. a DTA furnace and control system,
2. an atmosphere control system, and
3. electrical apparatus for amplifying and recording the temperature difference between the sample and standard, and for recording the actual temperature of the standard.

1. Furnace and Heating Controls

Construction details of the furnace and pedestal are shown in Figure 1. The furnace consists of a non-inductively wound zircon tube having an I.D. of 1-1/2" (however, the wire shown in Figure 1 has recently been replaced by a 3/16" x 0.010" Kanthal strip). Within the furnace stands a pedestal consisting of a nickel tube filled with insulating brick. The leads to three Pt-Pt 10% Rh thermocouples, encased in porcelain protection tubes, pass through the pedestal and are positioned by ceramic disc spacers. The bare thermocouple junctions are embedded in wells in three nickel specimen cups which are held in a recessed ceramic disc. With this arrangement, the platinum of the thermocouples is protected from direct contact with carbon, and the specimen cups are thermally isolated from each other (in contrast to the more common metal specimen block). Thus, the loss of sensitivity caused by the use of thermocouple wells is to some extent offset

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2 R. C. Mackenzie (Ed.), "The Differential Thermal Investigation of Clays" Mineralogical Soc. (London) (1957).

3 W. J. Smothers and Yao Chiang, "Differential Thermal Analysis: Theory and Practice" Chemical Publishing Co. (1958).

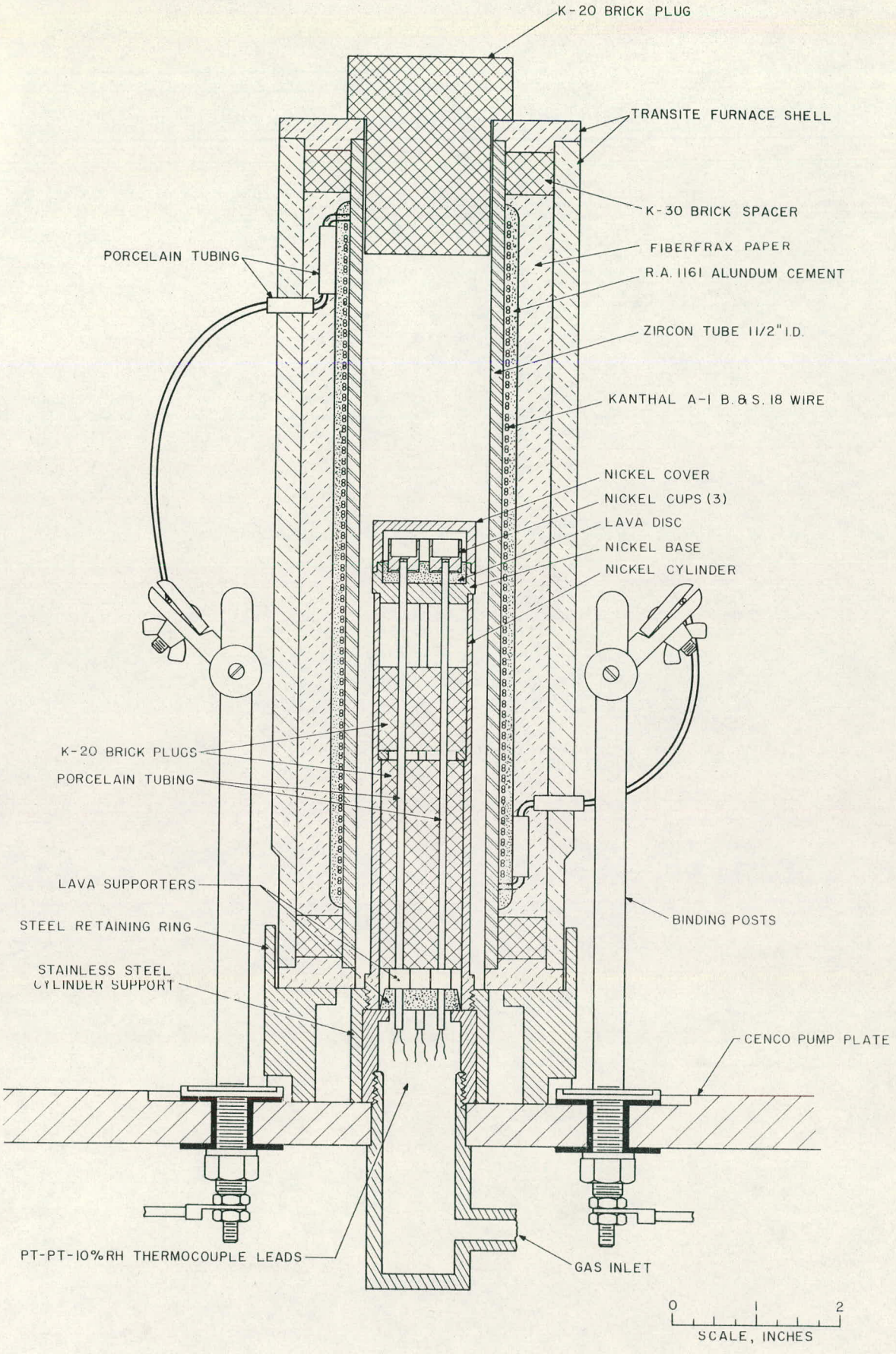

FIG. 1 — DIFFERENTIAL THERMAL ANALYZER

by the increased sensitivity produced by thermal isolation of the sample. Decreasing the heat capacity of the specimen holder raises the sensitivity; consequently, the bottoms of the cups shown in Figure 1 have been recessed so that all wall thicknesses are 0.012". This serves the additional purpose of surrounding the thermocouple wells with sample instead of limiting the effective area of contact to the top of the well. The volume surrounding the sample cups has been enclosed by a nickel cover which, while not gas tight, builds up sufficient gas pressure around the samples to keep them in contact with their emitted volatiles.

Use of a nickel cover with a grounded nickel pedestal results in the thermocouples being well shielded from extraneous electrical fields. Combination of the shielding features with a non-inductive heater winding effectively minimized electrical drift.

The rate of heating of the DTA furnace was determined by the initial setting on a variable power transformer, and on the rate at which the transformer setting was changed by a variable speed motor drive. This system incorporated a universal series wound motor coupled through fixed ratio reductions to the shaft of the variable transformer. Changes in drive rate were made by varying the voltage to the drive motor with a potentiometer which in turn derived its power from a constant voltage source (Figure 2). By means of this system, heating rates could be varied from about 5°C to 25°C per minute.

2. Atmosphere Control System

The furnace and pedestal described above were mounted on a steel vacuum plate which permitted the entire assembly to be covered by either a Pyrex glass dome(for work at one atmosphere pressure) or a steel cover (for experiments up to two atmospheres).

Gases were introduced to the furnace chamber through a purification train in which oxygen and water were removed by heated copper turnings and a Linde Type 5A molecular sieve. Pressure control up to two atmospheres was effected by a mercury bubbler whose column height determined the maximum pressure in the system.

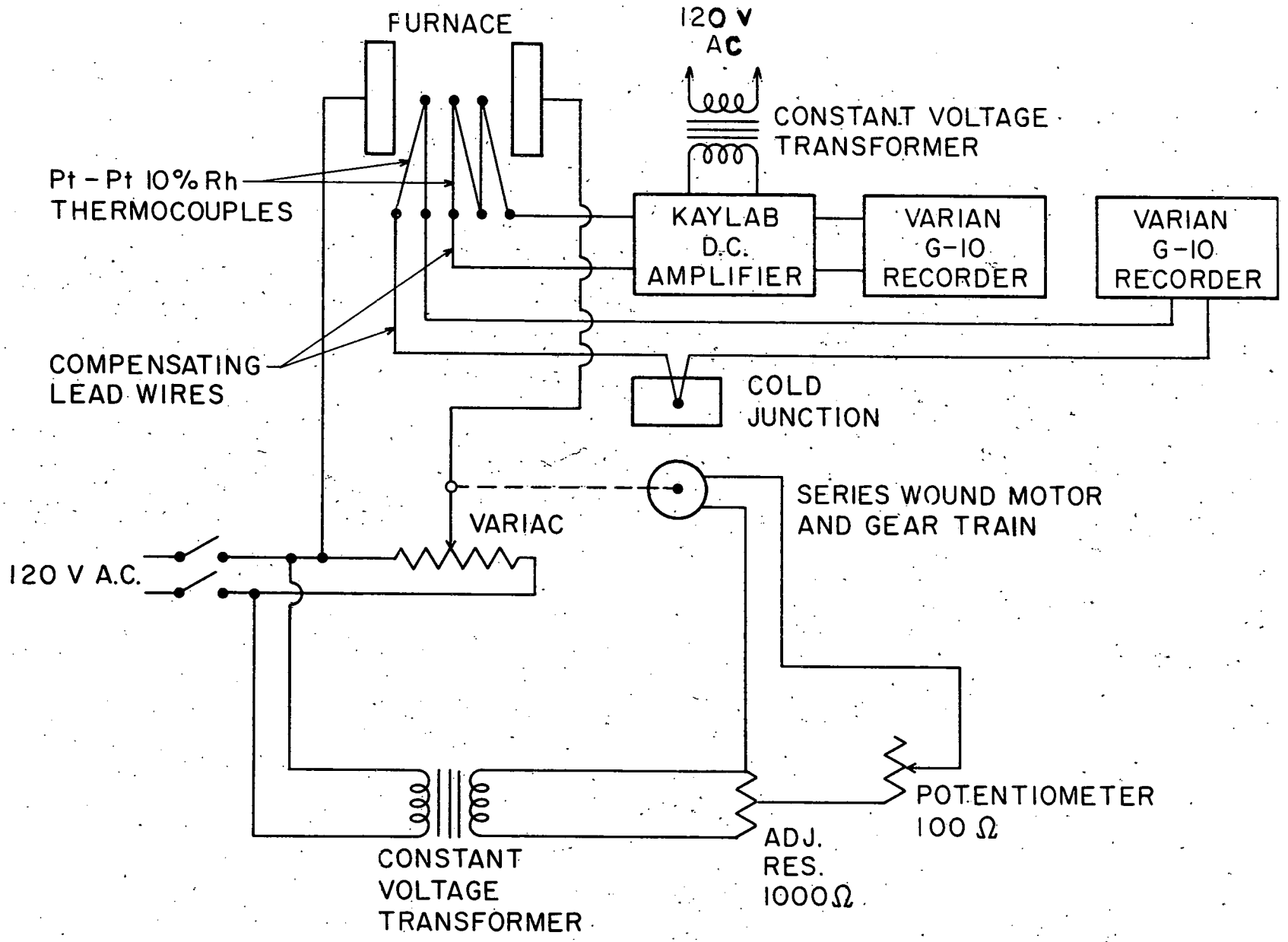

FIG.2 - CIRCUIT FOR DIFFERENTIAL THERMAL ANALYZER

3. Electrical System

A schematic diagram of the electrical circuitry is presented in Figure 2. The signal voltage from the differential thermocouple was first amplified 100 times by a Kay Lab Model 110A d.c. amplifier which obtained its power from a constant voltage transformer. The resulting signal was further amplified and recorded by a Varian G10 recording millivoltmeter. With this arrangement of components, a one inch deflection on the differential temperature record is equivalent to approximately 0.02 millivolts (from a Pt-Pt 10% Rh thermocouple) or 2° at 500°C. The much larger voltage generated by the temperature measuring thermocouple was directly recorded by a second Varian instrument. Since the chart speeds of both recorders were the same, the furnace temperature trace could be superimposed on the differential temperature record for direct comparison.

B. Materials

Pyrolysis reactions were followed by DTA for representatives of several groups of binders which have high coke residue values. These groups included the following:

1. coal tar pitch (Barrett No. 30)
2. a Novolak type phenol formaldehyde resin (Bakelite BPR 5095 bonding powder)
3. a phenol benzaldehyde resin prepared at Armour Research Foundation.
4. three furfuryl alcohol resins including: (a) Quaker Oats Company monomer, (b) Quaker Oats Company 268-184 (a partly polymerized material averaging the dimer in molecular weight) and (c) a furfuryl alcohol (provided by Dr. E. Nielsen of ARF) which had been partly polymerized with an alumina catalyst. Either maleic acid or p-toluene sulfonic acid were used as subsequent catalysts to complete the polymerization of these furfuryl alcohols.

To prevent excessive volatilization from the sample cup (which would cause permanent displacement of the DTA base line) all of the binder resins were diluted with Texas Lockport No. 90 calcined petroluem coke flour. This material was also used as the reference standard and as the filling for the third cup surrounding the furnace temperature thermocouple.

C. DTA Procedures

Batches were prepared by mixing 25% of the binder to be studied with 75% of coke flour. In the case of the furfuryl alcohols, the maleic acid catalyst was blended directly with the alcohol before the binder was added to the coke. However, with p-toluene sulfonic acid as catalyst, polymerization was so rapid that the acid was mixed with the coke flour rather than directly with the furfuryl alcohol. The BPR 5095 bonding powder was dissolved in acetone before being blended with the coke. After mixing was completed, the solvent was allowed to evaporate.

One gram samples of each composition were cold pressed in a special die that formed a well in one end of the pellets. In this way, a close fit in the nickel specimen cup was achieved for maximum sensitivity. The remaining two cups were filled and tamped with calcined coke flour: one of these served as the reference standard and the other was the target for the furnace temperature thermocouple.

Samples were heated at a rate of 9 to 13°C per minute under helium, nitrogen, or argon, at one or two atmospheres pressure. After cooling, the samples were weighed (to permit calculation of approximate coke residue values for the binder), and their densities were measured by mercury immersion.

Systematic drift of the DTA apparatus was in large part corrected by exchanging the positions of the standard and sample cups, and repeating each thermogram with a new sample of the same composition. Each pair of curves was then oriented so that their thermal directions coincided, and an average curve was drawn.

D. Dilatometric Apparatus and Procedures

The dilatometer shown in Figure 3 is essentially a sensitive device for measuring the changes in height of a cylindrical specimen while it is being heated in a furnace. Two sensors were used: a direct reading 0.001" dial gage, and a linear variable differential transformer. The changing a.c. signal of the latter was demodulated and recorded on one of the DTA recording millivoltmeters. Both of the sensors were connected with an aluminum yoke which was fastened to a graphite follower rod passing through a graphite bushing. This rod contacted the specimen through a permeable ceramic

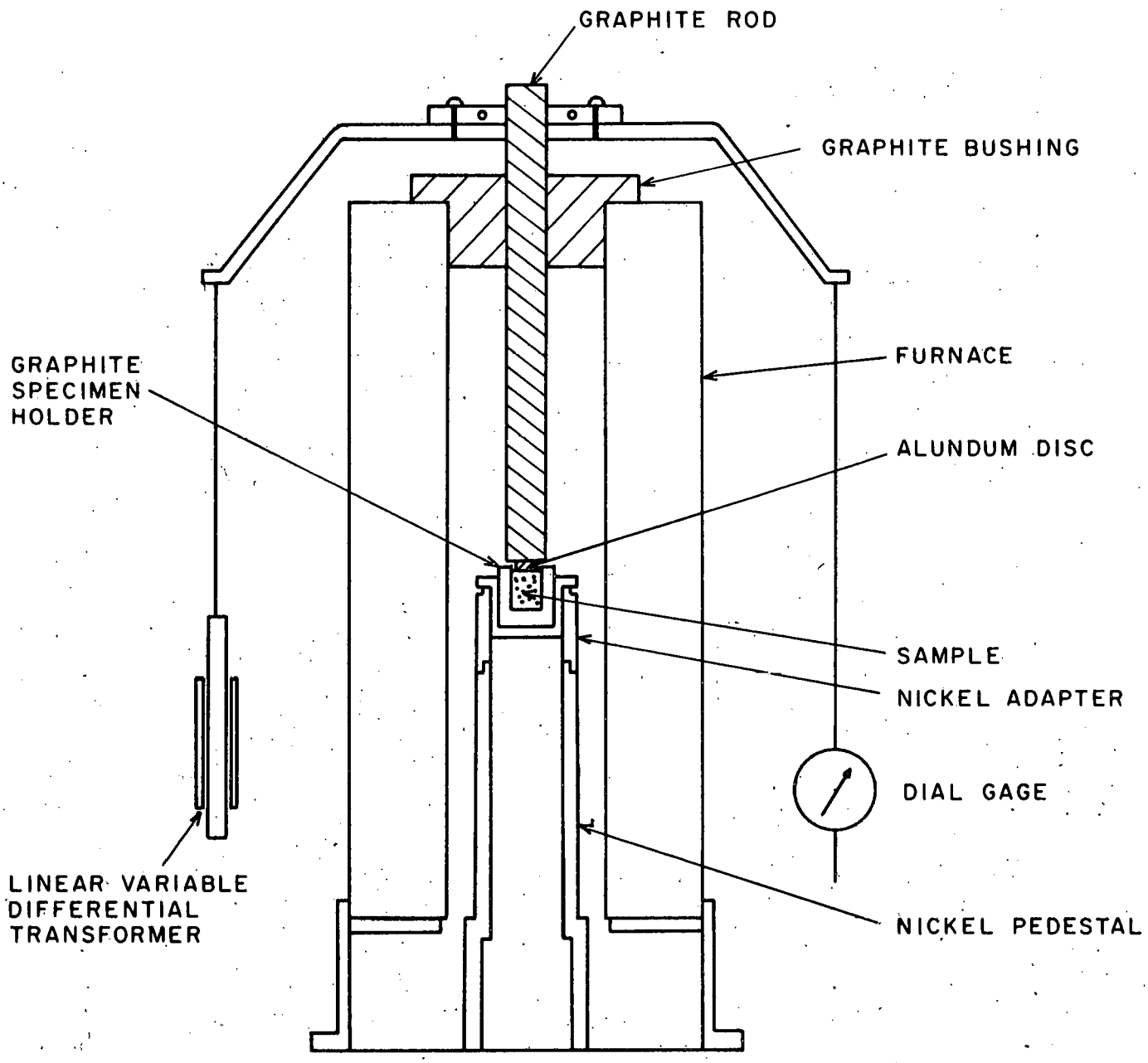

FIG. 3 - SCHEMATIC ASSEMBLY FOR DILATOMETER.

spacer (for thermal insulation), and both were held in a graphite cup at the top of the DTA pedestal.

In practice, a specimen was cold pressed into a cylinder measuring about 0.5" in diameter and 0.6" in length. This cylinder was heated in an argon atmosphere at about 9 to 13°C per minute (after the first 150°C), and the change in length was recorded. The resulting curve included both the length variation of the specimen and the thermal expansion of the apparatus. A correction for the latter reaction was obtained by recording a calibration curve with the follower rod and ceramic spacer resting on the rim of the empty specimen cup.

III. EXPERIMENTAL RESULTS

A. DTA Curves

DTA examinations may be grouped into three series: Figures 4 and 5 compare curves for various binder mixtures heated in one atmosphere of argon; Figure 6 shows the effect of changing the atmospheric pressure of nitrogen on the pyrolysis of two furfuryl alcohol binders; and Figure 7 contrasts the thermograms obtained for a furfuryl alcohol binder in helium, nitrogen, and argon. Pertinent data associated with these figures, including heating rates, coke residue values, and baked densities are summarized in Table I.

The surprisingly clear endothermic and exothermic peaks shown by the DTA curves of Figures 4 to 7 undoubtedly reflect volatilization, polymerization and structural condensation reactions. Unfortunately, the precise nature of the reactions related to each peak are not at all known. However, they may be described in a general way as follows:

1. Figure 4. The curves of Figure 4 all describe reactions of furfuryl alcohol resins. Although the patterns are basically alike, dissimilarities relating to differences in catalyst or degree of pre-polymerization are apparent.

In curve A, (furfuryl alcohol monomer catalyzed by 3% of maleic acid) the original endothermic trend to about 80°C probably reflects differences in thermal diffusivity ($\lambda / \rho c$; where λ = thermal conductivity, ρ = bulk density, and c = specific heat) between the sample and reference standard. The endothermic direction is reversed with the formation of a

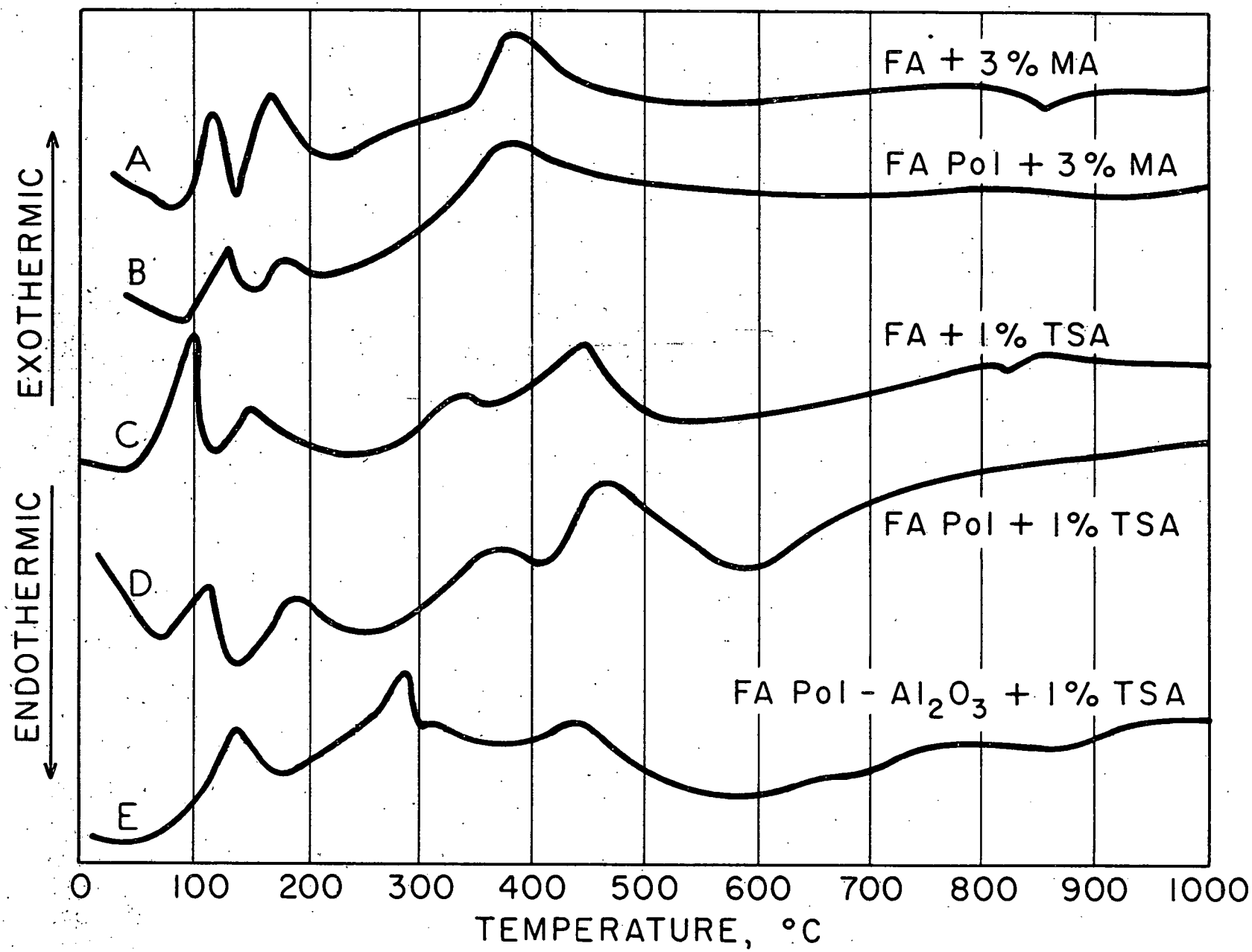

FIG. 4 THERMOGRAMS OF FURFURYL ALCOHOL AND FURFURYL ALCOHOL POLYMER BINDER AND COKE MIXES IN ONE ATMOSPHERE ARGON.

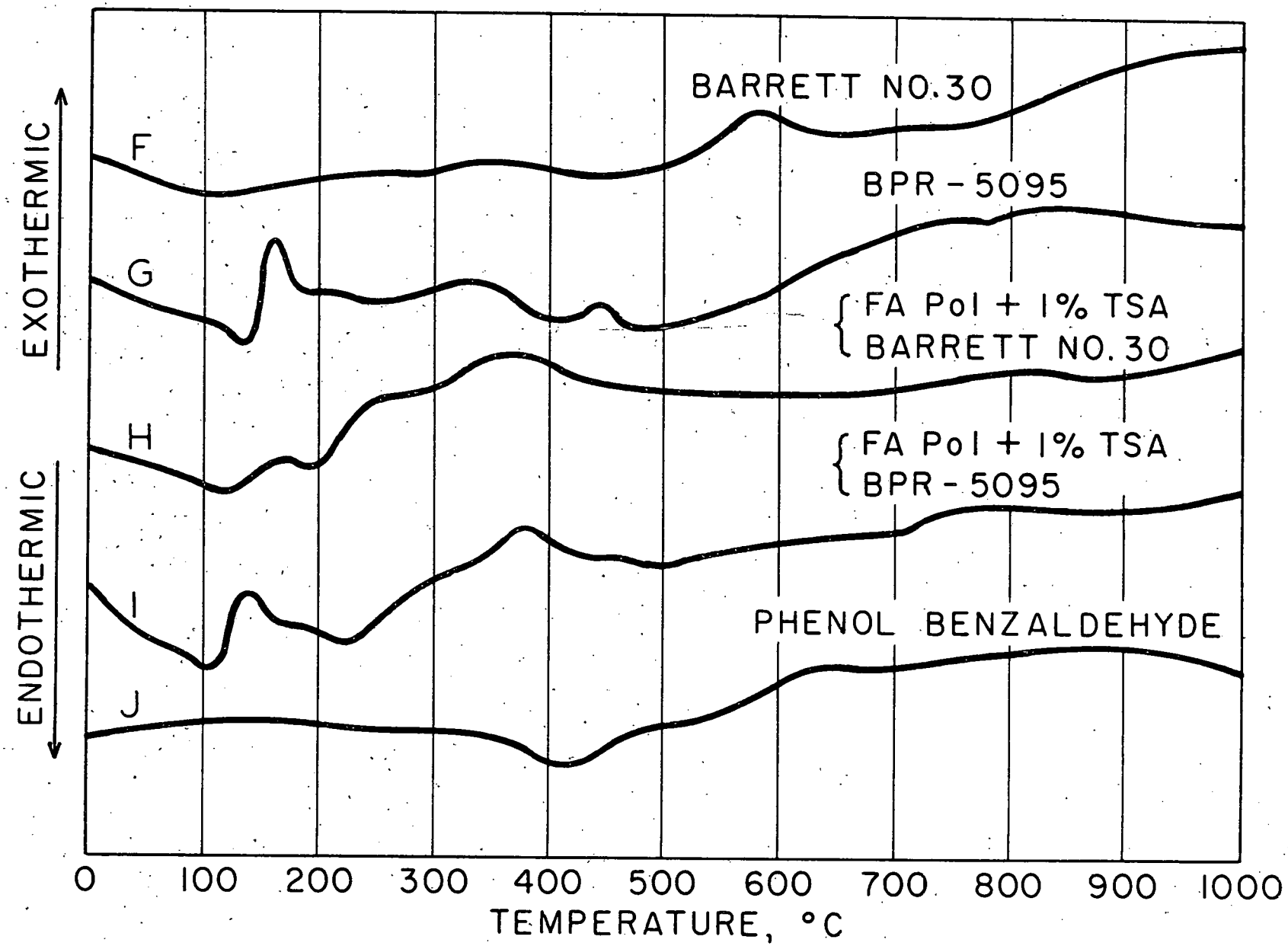

FIG. 5 THERMOGRAMS OF VARIOUS BINDER AND COKE MIXES IN ONE ATMOSPHERE ARGON.

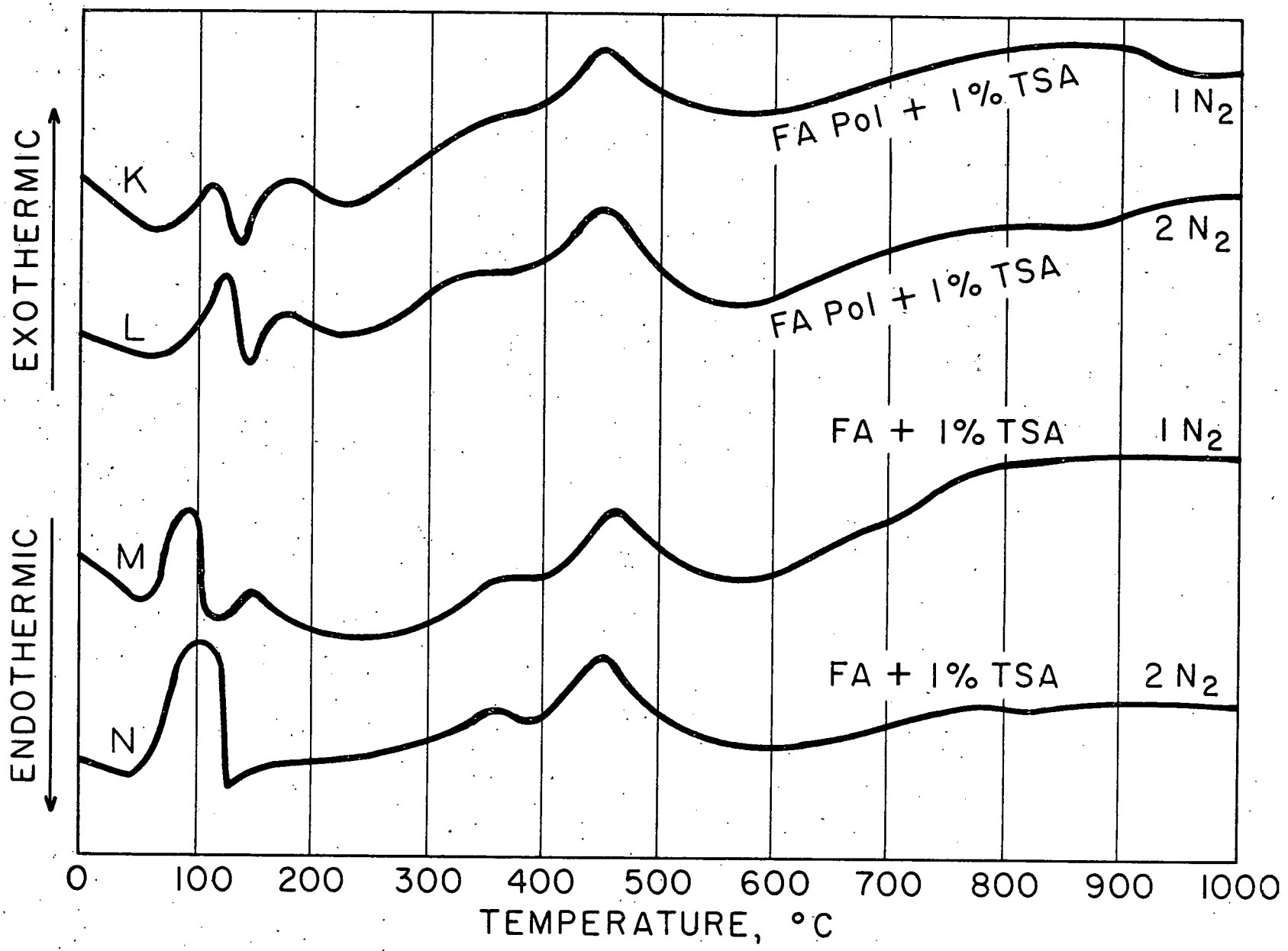

FIG. 6 COMPARISON OF ONE AND TWO ATMOSPHERES NITROGEN PRESSURE ON FURFURYL ALCHOL AND FURFURYL ALCOHOL POLYMER AND COKE MIXES.

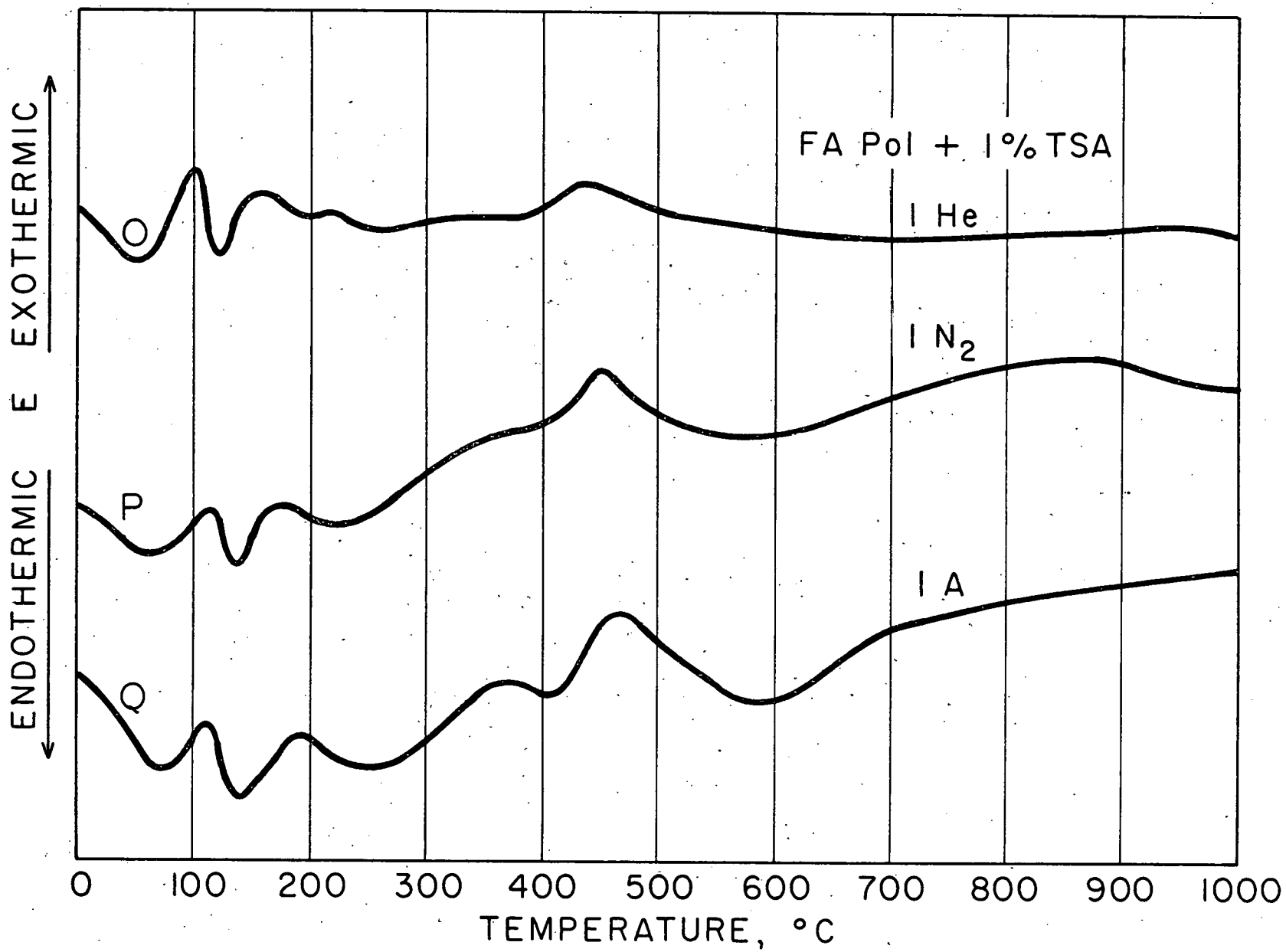

FIG. 7 THERMOGRAMS OF FURFURYL ALCOHOL POLYMER AND COKE IN HELIUM, NITROGEN, AND ARGON.

Table I

CONDITIONS OF DTA EXPERIMENTS

AND SOME PROPERTIES OF THE BAKED SAMPLES

Binder	Catalyst (conc. in wt%)	Gaseous Atmos. (pressure in atmos.)	Heating Rate (°C/minute)	Curve in Figs. 4-7	Density (g/cm^3)	Coke Residue (wt%)
FA monomer[1]	3 maleic acid	1 argon	10-12.5	A	-	40.4
FA pol[2]	3 maleic acid	1 argon	9-12.5	B	1.53	43.4
FA monomer	1 p-tol. sulf. acid	1 argon	10-12	C	-	52.7
FA pol	1 p-tol. sulf. acid	1 argon	10-13	D	1.57	49.4
FA pol-Al_2O_3[3]	1 p-tol. sulf. acid	1 argon	9-11	E	1.64	54.3
coal tar pitch	-	1 argon	9-12.5	F	-	63.1
phenol formald.	-	1 argon	-	G	-	42.0
FA pol + coal tar pitch[4]	1 p-tol. sulf. acid	1 argon	10-12.5	H	-	54.8
FA pol + phenol formaldehyde[5]	1 p-tol. sulf. acid	1 argon	10-12.5	I	-	42.6
phenol benzald.	-	1 argon	9-11.5	J	-	43.1
FA pol	1 p-tol. sulf. acid	1 nitrogen	9-12.5	K	1.58	50.9
FA pol	1 p-tol. sulf. acid	2 nitrogen	9-13.5	L	1.58	51.3
FA monomer	1 p-tol. sulf. acid	1 nitrogen	10-13.5	M	1.50	52.3
FA monomer	1 p-tol. sulf. acid	2 nitrogen	10-14	N	1.51	55.1
FA pol	1 p-tol. sulf. acid	1 helium	10-12.5	O	1.54	46.1
FA pol	1 p-tol. sulf. acid	1 nitrogen	9-12.5	P	1.58	50.9
FA pol	1 p-tol. sulf. acid	2 argon	10-13	Q	1.57	49.4

1 Quaker Oats Co. furfuryl alcohol monomer
2 Quaker Oats Co. partially polymerized furfuryl alcohol (268-184)
3 Furfuryl alcohol partially polymerized with Al_2O_3 (E. Nielsen)
4 50% Quaker Oats Co. 268-184 and 50% Barrett No. 30 coal tar pitch
5 50% Quaker Oats Co. 268-184 and 50% Bakelite BPR 5095 bonding powder

polymerization exotherm at about 110°. This peak is probably caused by: (a) chain formation involving reaction of the alcohol group from one furfuryl alcohol molecule with an active hydrogen from the ring of an adjacent molecule (forming difurfuryl alcohol and so on); and (b) the reaction of two adjacent alcohol groups to form difurfuryl ether. On splitting off formaldehyde, difurfuryl ether is converted to difurfuryl methane. The resulting formaldehyde can be reabsorbed, forming methylene and ether bridges between furan nuclei in adjacent chains. These cross linking reactions may also be contributing to the 110° exotherm. Chains and cross linking mechanisms described briefly above have been summarized in detail by Dunlop and Peters[4].

Endothermic activity culminating at 130° may correspond to a sudden evolution of water or formaldehyde, or, more likely, merely represents the end of the first exothermic reaction. This second hypothesis is favored by the fact that this endotherm never reaches below, and generally coincides with, the general trend of the DTA base line.

The second exotherm at 170° may reflect a new cross linking mechanism involving polymerization through the double bonds of the furan nuclei (see Alexander[5]). This exotherm is followed by an interval of relative quiescence, in which CH_2 and ether bridges may be broken, and some of these groups as well as CO may be eliminated.

At 390° a third exotherm appears which may represent a rearrangement of the furan nuclei and the methylene bridges into six membered rings, and initial coalescence of these rings into layer structures.

No other rapid reactions occur until 850°C, when a small endotherm probably marks the loss of hydrogen from the ring carbons.

Curve B is quite similar to A except for a slight reduction and broadening of the polymerization exotherms at 120° and 180° - a reasonable consequence of partial polymerization before the DTA experiment.

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4 A. P. Dunlop and F. N. Peters, "The Furans" ACS Monograph No. 119, 220-224, Reinhold Publishing Co. (1953).

5 J. Alexander (Ed.), "Colloid Chemistry" Vol. VI, Chap. 57 "Furan Resins" A. P. Dunlop and F. N. Peters, 1048-1062, Reinhold Publishing Co. (1946).

Another difference is the lack of an endotherm at 850° in curve B. This variation in the dehydrogenation reaction may be related to the extent of layer growth: an assemblage of very small layers of varying size might be expected to lose hydrogen over a relatively wide range of temperatures - which is not conducive to forming a well defined endothermic peak. Groups of larger and more uniform layers should release their hydrogen over a smaller temperature interval and an endotherm may then appear on the DTA curve. Variations in layer growth in these experiments are probably related to differences in the structure of the polymer (i.e., chain length and extent and type of cross linking) after the early exothermic activity.

Curves C and D show reaction differences caused by changing the catalyst to a stronger acid (p-toluene sulfonic acid). In curve C, the second exotherm is much smaller than in A (possibly indicating less additional polymerization of the furan nuclei) and it has been shifted down to about 150°C. In addition, the third exotherm of curve A has been divided into a double peak with maxima at 340° and 450°. This may reflect a separation between the processes of structural condensation following CH_2 bridge elimination, and rearrangement of five membered rings to six membered graphite nuclei. Alternatively, the minimum between the peaks may represent a period of strong gas evolution which momentarily predominates over the condensation reactions.

In most respects, curve D is very similar to C; the differences between the two are like the dissimilarities between A and B. The lowering and broadening of the first exotherm in D is to be expected in the light of the partial pre-polymerization of the starting material. This phenomenon is carried still further in curve E, where the first exotherm is displaced to a higher temperature (130°). In this case, the furfuryl alcohol has been extensively pre-polymerized with alumina - to a much greater degree than the Quaker Oats material.

According to Nielsen[6], alumina catalysis of furfuryl alcohol polymerization tends to favor increased formation of difurfuryl ether which converts to difurfuryl methane with the splitting off of formaldehyde.

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6 E. Nielsen, Armour Research Foundation, personal communication.

Absorption of this additional formaldehyde should lead to increased cross linking by methylene or ether bridges between adjacent chains. As a result, polymerization through the nuclear double bonds may be reduced - which is in accord with the absence of the second exotherm just below 200°. This may also explain differences in the exothermic activity of the alumina catalyzed material above 200°. Degradation of a CH_2 or ether linked structure should occur in a different manner than one containing appreciable numbers of directly joined furan nuclei. Finally, a broad dehydrogenation endotherm peaking at 875° suggests somewhat better layer development than occurs in curves B and D.

2. Figure 5. The curves of Figure 5 compare the pyrolysis reactions of coal tar pitch, phenol formaldehyde, mixtures of furfuryl alcohol with pitch and phenol formaldehyde, and phenol benzaldehyde. Unlike thermograms of furfuryl alcohol binders, the DTA curve of a pitch bonded coke (F) is relatively featureless. A broad endotherm peaking at 100° is probably caused primarily by loss of water. A second broad devolatilization at about 450° followed by an exotherm at 580° appear to coincide with corresponding peaks noted by Glass[1] in coals. According to Diamond[7], disordered material including OH and CH_2 groups is lost from coal up to about 500°; this volatilization is probably the cause of the 450° endotherm. Removal of the volatiles permits better packing of the layers, and between 500° and 600° layer growth (corresponding to the 580° exotherm) becomes important. A broad endotherm after the layer growth reaction probably reflects gradual loss of aromatic hydrogen from the pitch.

Curve G represents the polymerization and pyrolysis of a Novolak type phenolic bonding powder containing hexamethylene tetramine or a similar additive. The first endotherm culminating at 130° probably reflects the loss of water and ammonia. This is followed immediately by a strong exotherm at 160° representing polymerization of the Novolak to an infusible mass. This Resite material evidently has a different thermal diffusivity

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7 R. Diamond, "A Study of Some Carbonized Coals Using New X-Ray Techniques," Proc. of the Third Conference on Carbon, 367-375, (Univ. of Buffalo 1957, published by the Pergeman Press, 1959).

than the original Novolak because the DTA trace does not return to its original base line after the polymerization. The curve continues with minor irregularities to about 330°, when a broad endotherm - related to elimination of CH_2, and other bridging groups - occurs. This endotherm is interrupted by a small exothermic peak at 440°, which corresponds to a condensation of the aromatic rings after removal of the bridges. An interesting feature here is the small size of the condensation exotherm as compared to those shown by the furfuryl alcohol resins. This may be related to the fact that the furan nuclei and the cross links must rearrange to form six membered graphite rings, whereas the carbon atoms in the aromatic rings of the phenolic resin require relatively little reorientation. Finally, curve G shows a very small endotherm at 780° corresponding to dehydrogenation of the aromatic ring structures.

Curves H and I for the furfuryl alcohol - pitch, and furfuryl alcohol - phenolic mixtures both have patterns which are not simply composites of the thermograms for the individual components. In H, a trace of furfuryl alcohol polymerization is reflected by a small exotherm at 170°. The subsequent rearrangement and condensation reactions of curve D also appear in the pattern of the mixture, but they, like the polymerization peak, are displaced in temperature. It is difficult to say whether the peaks at 170° and 250° in H correspond to those at 110° and 190°, or those at 190° and 375° in curve D. In any case, the 580° pitch exotherm and the dehydrogenation endotherm do not occur in the thermogram of the mixture.

Curve I also has unique characteristics: between 100 and 200°, the pattern resembles that of the pure phenolic in curve G, but subsequent condensation reactions more closely follow those of furfuryl alcohol displaced about 80° to lower temperatures. Again, the dehydrogenation endotherm does not occur for the mixture.

Examination of the phenol benzaldehyde curve (J) immediately shows that this material did not polymerize during the DTA experiment. Subsequent investigation of preparation methods used for this resin revealed that it was probably already polymerized before it was blended with the coke flour and pressed into a specimen cylinder. The main features of curve J are an endotherm at 410° which is probably caused by elimination of bridge groups and a possible condensation exotherm at about 630° -

slightly higher than for pitch.

3. Figure 6. In this figure the effect of changing the ambient pressure is shown for two furfuryl alcohol resins. Curves K and L for the pre-polymerized material are very similar. However, the high pressure record shows a slight enlargement and temperature shift of the first polymerization exothern as well as a small dehydrogenation endotherm (at 875°). As indicated by curves M and N similar changes occur for furfuryl alcohol monomer.

Since the thermal conductivity of a gas is relatively independent of pressure in this range, the observed effects are probably not due to a variation of the thermal diffusivity of a specimen whose porosity is changing. On the other hand, a pressure change can influence the chemical reactions by affecting the loss of volatiles from the sample. This action can be of considerable significance in polymerization - where increased retention of formaldehyde derived from the decomposition of difurfuryl ether will produce greater cross linking by methylene and ether bridges. This is in accord with the enlargement of the first polymerization exotherm under the higher pressure conditions. Similarly, higher ambient pressures might also affect the dehydrogenation of the aromatic rings. It is possible that this can take the form of retarding gradual volatilization of hydrogen at lower temperatures, and concentrating it in a higher and narrower temperature interval - thus producing an endothermic peak.

4. Figure 7. Curves O, P, and Q were obtained by heating furfuryl alcohol in helium, nitrogen, and argon. Increasing the molecular weight of the surrounding gas produces three effects: (a) a progressive shift to higher temperatures of the various peaks; (b) an increasing deviation of the curve as a whole from the original base line; and (c) an enlargement of the exotherms and the endotherms between 300 and 500°. All of these phenomena can be explained in terms of the decreasing thermal conductivity of the gases proceeding from helium to argon. This factor produces a similar change in the thermal diffusivities of porous specimens and reference standards, and also influences the rate of heat absorption and loss from the specimen cup to the surroundings. In a gas of high thermal conductivity such as helium, heat from the furnace is quickly transferred to the materials in the

various cups and to the thermocouples by conduction from the surrounding atmosphere as well as from the metal cups. Consequently, both the materials and the thermocouples are heated at nearly the same rate, and there is relatively little temperature lag between them. Conversely, if the surrounding gas is a good insulator, the thermocouples which have good thermal contact with the metal cups, are heated at a faster rate than the materials within the cups. The resulting temperature lag displaces all of the reaction peaks to slightly higher temperatures. Moreover, filling the pores of the sample and the reference standard with a low conductivity gas emphasizes differences in their thermal diffusivities caused by different porosities. Therefore, as the sample carbonizes, the resulting change in its porosity and diffusivity (while the characteristics of the standard material remain more stable) causes a drift from the original base line. This effect is much reduced in a gas whose thermal conductivity more closely approaches that of the carbonaceous sample. Under these conditions, the effect of porosity variations is minimized, and base line drift is diminished.

Finally, the use of a thermally insulating gas like argon reduces the rate of heat transfer to or from the specimen. Consequently, temperature differences between it and the standard (caused by reactions) are maximized and the resulting endotherms and exotherms on the DTA curve are enlarged.

B. Dilatometric Curves

In addition to measuring the relative shrinkage of mixtures containing various binders, it was an objective of the dilatometric experiments to relate temperature variations in shrinkage to features on the DTA curves. The three curves of Figure 8 show the carbonization shrinkage of coke specimens bonded with (a) coal tar pitch, (b) pre-polymerized furfuryl alcohol, and (c) a phenolic bonding powder. Because of the rather specialized conditions of the dilatometric experiments, the absolute height changes of the specimens are not as useful as comparisons of the three curves, and analyses of their shapes.

A cursory glance at Figure 8 shows that maximum shrinkage was obtained with the phenolic binder, somewhat less with the furfuryl alcohol, and least with the pitch. Interestingly enough, a comparison of Figure 8

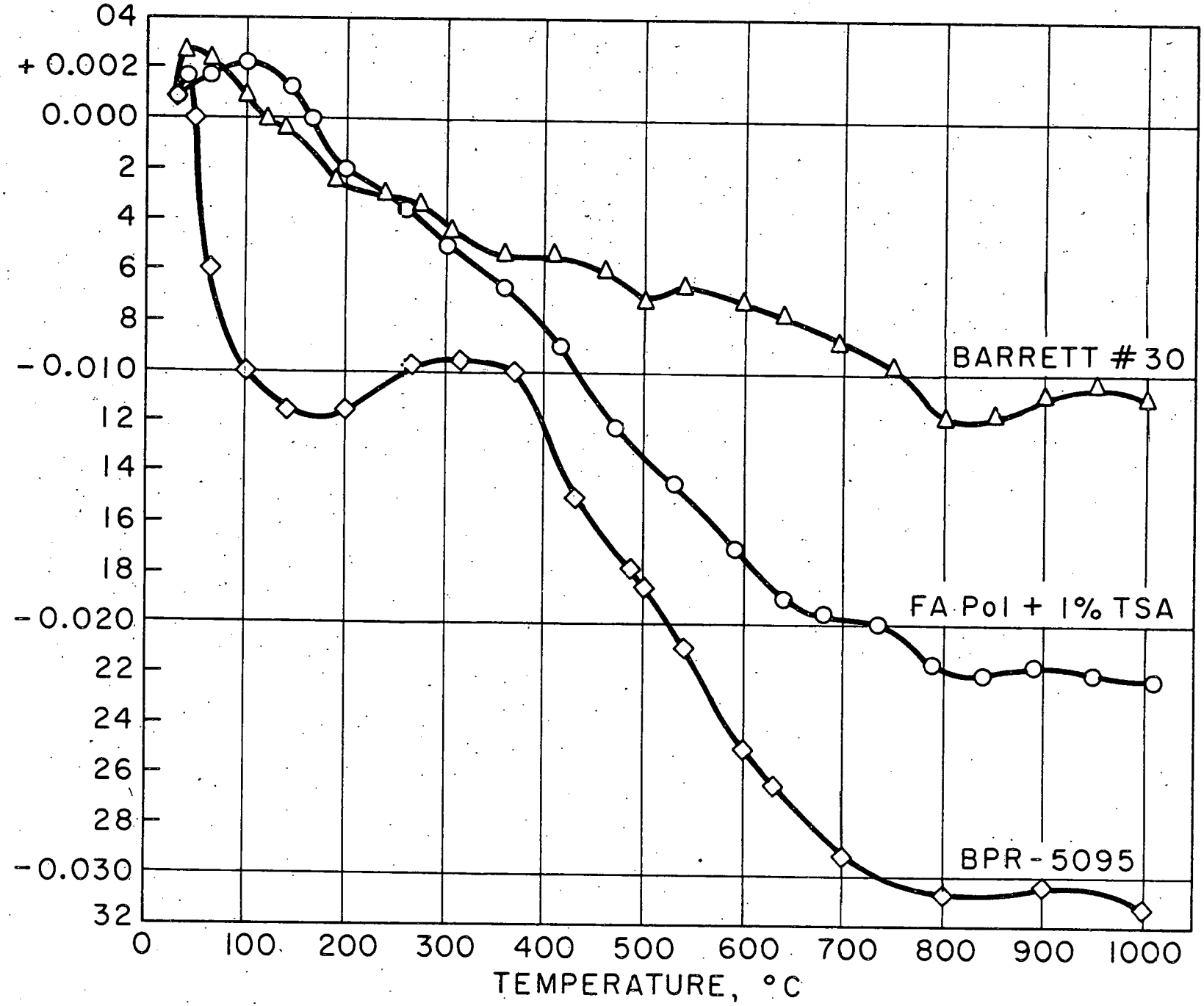

FIG. 8 LINEAR SHRINKAGE OF BINDER-COKE MIXES.

and Table II shows no relationship between shrinkage data and unbaked densities; instead, the former follows an inverse relationship to coke residue values listed for these binders in Table I. Note that the pitch bonded specimens had the lowest unbaked density (because it was cold pressed), but the highest coke residue value and consequently, the least shrinkage.

Table II

PROPERTIES OF DILATOMETRIC SPECIMENS

Binder	Cold Pressed Density (g/cm^3)	Coke Residue of Binder After Baking*	Total Linear Shrinkage (%)
coal tar pitch	1.28	63.1	1.83
pre-polymerized furfuryl alcohol (1% p-toluene sulfonic acid)	1.60	49.4	3.68
phenolic bonding powder	1.38	42.0	5.22

* From Table I

From these considerations it is tempting to deduce that maximum shrinkage should occur during periods of greatest devolatilization; i.e., during endothermic peaks on the DTA curves. A comparison of the DTA and dilatometric curves shows that this simple relationship is apparently true for pitch. The height of pitch bonded cylinders diminishes most rapidly in the following intervals: between 50 and 200°, 275 and 350°, 425 and 500°, and 750 and 800°. Except for the 275 to 350° range, each roughly corresponds to a broad endotherm on curve F (Figure 5).

Correlations with furfuryl alcohol bonded specimens are complicated by the occurrence of strongly exothermic polymerization or condensation reactions which may be superimposed on the endothermic activity. These specimens show maximum contraction between 150 and 200°, and again between 400 and 475°. A sudden rise also occurs between 750 and 800°.

The first of these intervals corresponds to the latter part of the polymerization activity shown in curve D. The second period coincides with the structural rearrangement or condensation exotherm, and the last shrinkage occurs during dehydrogenation (although this does not occur as a well defined peak in curve D).

Cylinders bonded with phenolic resin shrink very rapidly during the initial period of gas evolution before polymerization. After an interval of little change extending to about 375°, contraction is resumed at a nearly linear rate until about 700°, when it gradually tapers off. This second period of rapid shrinkage corresponds roughly with the broad endotherm extending from 350 to about 700° in curve G.

IV. EXTENSIONS OF THE DTA TECHNIQUE

The particular advantage of differential thermal analysis is that it gives a rapid and continuous record of reactions occurring in a sample - although it does not tell directly what these reactions are. Moreover, variations in slope and peak area can provide much relative information on the heats and rates of the reactions in progress. In this report, DTA data alone have led to interesting speculations on the connection between the dehydrogenation endotherm and graphite layer development, and on the correlation of multiple exothermic peaks with polymerization and condensation mechanisms in furfuryl alcohol. Support of the DTA curves with thermogravimetric data and with X-ray analyses of the type described by Diamond[7] would raise these speculations to a much more respectable level. Questions on whether the furfuryl alcohol condensation exotherms correspond to a single peak interrupted by devolatilization, or two separate reaction peaks might be quickly resolved by noting the weight loss curve in this region. Furthermore, a correlation of X-ray data on layer stacking and growth with various key points on the DTA curve would show how these structural transformations develop with temperature.

An even further refinement of the DTA apparatus would be incorporation of a system for sampling the gases escaping from a carbonizing sample. A combination of gas analyses and X-ray data with DTA and thermogravimetric curves would provide a fairly rapid, yet quite detailed characterization of the chemical and structural changes occurring during

the baking of a coke-binder mixture. Much of the resulting data might even be placed on a semiquantitative basis - including the heats and rates of specific reactions. A system such as the one outlined above need not be limited to the field of carbon and graphite. Extension of these techniques to the general problem of the degradation of plastics may well yield fruitful results.