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Abstract

Graphite Binder Studies

The proprietary furfuryl alcohol resin used by the Astrofuel Facility as a graphite bond in the manufacture of extruded fuel elements was studied from the quality control viewpoint to determine what characteristics of the resin must be controlled in order to assure uniform trouble-free performance during processing of fuel elements and a final product of acceptable quality. Acceptance criteria for the resin based on measurement of solids content, viscosity, gel time, pH, and boron content were established and test methods for these determinations were specified.

Modification of the furfuryl alcohol resin system to expedite production of fuel elements and to improve quality of the product was undertaken. Primary goals were to accelerate present very slow and tedious resin curing schedules and to reduce porosity in fuel elements resulting from escape of volatiles during cure of the resin. Although cure of any condensation resin system to produce a relatively void free body of appreciable cross-section must necessarily be slow in order to allow for elimination of volatile condensation products by diffusion processes, elimination or reduction of severe exotherms in the furfuryl alcohol resin curing process should make some acceleration of cure schedule without loss of quality possible. In particular, elimination or reduction of amount of furfuryl alcohol monomer in the system lowers volatility of the resin. Furfuryl alcohol prepolymers containing less furfuryl alcohol

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monomer than the presently used graphite bond and in some cases none at all were prepared by water-modified liquid phase polymerizations and also by vapor phase dehydration over catalysts. Monomer content of these products was adjusted to bring viscosity of the material into the required range and low molecular weight of the prepolymers prepared by these methods made the reduced monomer content possible. In some cases the vapor phase dehydration prepolymers were of acceptable viscosity in the complete absence of monomer. Reactivity of the resin as indicated by gel time measurements decreased with decreasing monomer content and coking values tended to increase.

In a limited amount of work with modification of the catalyst system, it was found that use of pyromellitic dianhydride resulted in delay of curing exotherm until a higher temperature was reached. Use of small amounts of this curing agent in conjunction with small amounts of a low temperature exotherm catalyst like maleic anhydride may well have the effect of spreading the curing exotherm over a wider temperature range and further study of this effect is needed.

The characteristics of extruded graphite bodies bonded with selected examples of the compositions reported here must be studied before any evaluation of the processing improvements made possible by these modifications can be attempted. The most promising long range approach to improvement of fuel element quality and simplification of production procedures is the search for an addition resin system having properties adaptable to fuel element production. Only by this means can the basic problem of elimination of volatiles such as water be overcome.

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I Introduction

The three basic raw materials incorporated in present nuclear rocket engine fuel elements are graphite flour, fuel particles, and organic binder. The organic binder specified is a commercial grade of partially polymerized furfuryl alcohol, a medium viscosity liquid at room temperature. This material was selected as a binder for the graphite flour and fuel particles after extensive tests had been conducted on a variety of thermosetting resins, thermoplastic resins, and coal-tar pitches. Results of these tests indicated that furfuryl alcohol possessed superior properties to other candidate materials. The coking values were the highest and the volume contractions the lowest with the thermosetting furfuryl alcohol. Absence of binder softening throughout the cure, bake and firing cycles contributed to excellent dimensional stability during heat treatment. The coal-tar pitches exhibited a wide softening range during carbonization heat treatment and were eliminated from consideration.

Having chosen a commercially available furfuryl alcohol resin for use in manufacture of fuel elements, two problem areas were immediately presented. The first problem involved the development of suitable quality control test methods to assure that the furfuryl alcohol resin received from vendors was of a consistent, acceptable quality before being certified suitable for use. The other area concerned the necessity of further improving the existing binder material by modification of its composition, with the objective of shortening the thermal treatment process cycle used for fuel element production. Allied to the reduction of process cycle time would be a corresponding improvement

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in the quality of elements produced as determined by physical and mechanical property measurements.

Therefore, an experimental program was initiated in the laboratory to study these two aspects of binder development. Attention was devoted initially to development of specifications for quality control tests to be used on the standard resin. Following successful completion of this work, emphasis was then placed on modification of binder composition to achieve improved performance characteristics. Sufficient experimental work was conducted to bring forth several possible alternate modifications. At the present time, evaluation tests are being planned in which small batches of reference fuel material containing modified binders will be prepared, fabricated, and heat treated according to present process schedules. The properties of these materials will be determined during and after the processing and compared with the characteristics of standard binder batches.

II Chemistry of Furfuryl Alcohol Resinification

The early stages of polymerization of furfuryl alcohol (I) to low molecular weight linear polymers are rather well understood and there is little disagreement among investigators as to the mechanisms of the process. Polymerization of furfuryl alcohol is normally carried out with acidic catalysts at elevated temperatures, but the uncatalyzed alcohol will polymerize slowly at its boiling point. Kinetic studies performed at the Quaker Oats Company¹ showed the reaction rate at a fixed temperature to be a simple function of pH. Furfuryl alcohol heated in the presence of an acidic catalyst is subject to three competing reactions¹ as outlined in

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Fig. 1. Condensation with the reactive nuclear alpha-hydrogen in the 5-position of a second molecule of furfuryl alcohol results in the formation of 5-furfurylfurfuryl alcohol (III). Elimination of a molecule of water between the methylol (CH_2OH) groups of two furfuryl alcohol molecules produces furfuryl ether (II). Water formed by either of the preceding reactions can react under acidic conditions with furfuryl alcohol to form levulinic acid (VI) by hydrolytic ring cleavage.

Reactions Occurring During the Early Phases of Furfuryl Alcohol Polymerization

If the polymerization temperatures are sufficiently high, either furfuryl ether or 5-furfurylfurfuryl alcohol can degrade by the loss of formaldehyde to form di-2-furylmethane (IV). Both formaldehyde and

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di-2-furylmethane have been isolated in small amounts from polymerization reaction mixtures. Continued reaction of the growing polymer chain as represented by 5-furfurylfurfuryl alcohol with furfuryl alcohol produces a "trimer", assigned structure (V), which has been isolated and characterized. The formation of levulinic acid is an undesirable side reaction not only because it is a small molecule which is not part of the resin structure, but also because its acidity tends to accelerate the polymerization reaction. Yield of this product can be minimized by polymerization techniques which remove water of dehydration as it is formed.

Conley and Metil² report that resin from thermal polymerization of furfuryl alcohol or from polymerization over gamma alumina by the method of Nielsen³ contains a low molecular weight substance not present in acid catalyzed resins. This product was isolated and found to be spectrally identical to 5-hydroxy-3-pentenoic lactone (VII). No mechanism for formation of this product is suggested, but it should be noted that 4-hydroxy-3-pentenoic lactone (VIII) would result from internal esterification of the enolization product of levulinic acid and spectra of (VII) and (VIII) might well be very similar.

Fig. 2

Lactone Structures

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Conley and Metil found that a carbonyl absorption band was present in all furfuryl alcohol polymers, and that this band remained after alkaline extraction of the resin, indicating that it was not associated with levulinic acid. The absence of aldehydic carbon-hydrogen absorption indicated that the carbonyl present must be ketonic in nature and the reaction outlined in Fig. 3 was postulated to occur in a certain proportion of the furan rings present in the polymer chains.

Fig. 3

Hydrolytic Ring Cleavage of Furfuryl Alcohol Resin

As the polymerization of furfuryl alcohol advances, cross linking of the polymer occurs as evidenced by its outstanding resistance to solvents and chemical reagents. The nature of this cross linking is not known. A possible process is polymerization through the double bonds of the furan nucleus, although peroxide type catalysts do not appear to be effective at accelerating polymerization. Evidence in support of the double bond cross linking system was provided by Norris and Terry⁴ who observed that the iodine number* (representing degree of unsaturation) of fatty esters of furfuryl alcohol decreased during resinification. It had been observed that formaldehyde evolved during furfuryl alcohol polymerization and was not present after cure was completed, even when polymerization was carried out in a sealed tube. It is possible that

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the formaldehyde methylolates either the beta positions of furan rings in polymer chains or methylene bridges. It is also quite possible that this attack occurs on the methylene groups in cleaved rings of the type shown in Fig. 3. Actually, the third possibility may be most likely since hydrogen atoms located alpha to a carbonyl would be more reactive. In any event, such methylation would result in methylene or oxydimethylene cross links. Fig. 4 illustrates possible cross linking mechanisms. It is of interest to note that Nordlander⁵ has observed that driers of the type used in paints accelerate curing of furfuryl alcohol resin in thin films.

Fig. 4

Hypothetical Cross Linking Mechanisms for Furfuryl Alcohol Resins

III Objectives of Binder Program

Study of the furfuryl alcohol resin system used as a binder for graphite matrix fuel elements divides itself logically into two sections, quality control of the proprietary resin used for fuel element production, and modification of the furfuryl alcohol resin system to better adapt it to the fuel element application.

Trouble free production of fuel elements of uniform quality is dependent upon uniformity of the resin binder. To insure this uniformity it is necessary

to determine what properties of the resin must be controlled and to establish test procedures and acceptance criteria.

Fuel element quality would be improved by any changes in the resin system which would result in lower porosity in the cured composition. Minimizing of resin cure shrinkage which can result in distortion of fuel element geometry is necessary. If this shrinkage cannot be eliminated, at least resin cure must be controlled so as to avoid local exotherms and make curing shrinkage uniform.

Production of fuel elements would be considerably facilitated if the present tedious and time-consuming cure schedule could be accelerated. Although the cure must necessarily be slow in order to permit diffusion of water of reaction from the polymerizing resin without formation of voids, it is possible that reduction of severity of curing exotherms by reducing reactivity of the resin or by spreading them over a wider temperature range would permit faster curing schedules.

Presumably any modification of the furfuryl alcohol resin system which results in higher coking values will benefit fuel element quality if for no other reason than that higher coking values must be associated with smaller quantities of volatiles to be dissipated.

IV Quality Control of Furfuryl Alcohol Resin

The Varcum 8251 resin used by the Astrofuel facility as a binder for extruded graphite matrix fuel elements is a solution of a linear prepolymer of furfuryl alcohol in furfuryl alcohol monomer. Its uniformity as a production graphite bond is dependent primarily upon its viscosity and reactivity.

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From the standpoint of quality control of fuel elements it is necessary that boron content of the resin be controlled. It was necessary to establish not only acceptance criteria for Varcum 8251, but also test methods.

A. Viscosity

Viscosity is dependent upon both solids content (amount of prepolymer dissolved in monomer) and degree of polymerization of prepolymer. Obviously it is possible to meet a particular viscosity specification with prepolymers of widely varying viscosities simply by adjusting the amount of furfuryl alcohol monomer used to cut back the resin after the polymerization has been carried out. Since a considerable variation in resin reactivity at a particular viscosity could result from use of such an expedient, it is evident that solids content and viscosity must be controlled independently.

Measurement of viscosity of furfuryl alcohol prepolymer resins is complicated by the thixotropic behavior of such compositions. When a measurement is made on a solution which has been allowed to stand undisturbed for some time, a relatively high viscosity value will be observed due to the development of some type of "structure" or molecular orientation in the solution. If the solution is vigorously stirred and the viscosity measurement repeated immediately, a much lower reading will be obtained owing to the disruption of the orientation originally present.

1. Experimental Procedures

Solids content was determined initially by vacuum distillation of 100 g. samples of Varcum 8251. A good separation between furfuryl alcohol monomer and other low molecular weight species present should be possible

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because of the rather large differences in boiling points. Furfuryl alcohol (I), its "dimer" (III), its "trimer" (V), and furfuryl ether (II) have the boiling points reported in Table I.^{6,7,8}

In practice, the distilling flask containing 100 g. of sample resin was heated under vacuum until distillation began. Pot temperature tended to rise slowly and quality of vacuum to improve until distillation finally stopped at pot temperatures in the vicinity of 140°C and pressures of the order of 1 - 3 mm. At this point refractive index of the distillate agreed well with that of furfuryl alcohol. Although more material could be distilled by stronger heating of the residue, refractive index of the distillate began to rise sharply after this point. Results of a number of such distillations are reported in Table 2. Percent solids reported is simply the weight in grams of undistilled residue remaining in the distilling flask at the end of the determination.

The Varcum Chemical Division of Reichhold Chemicals, Inc. uses a solids content test in which a 1.5 g. sample of furfuryl alcohol resin is weighed into an open aluminum cup and heated in a convection oven for three hours at 135°C and then reweighed. This test was carried out on a sample of Batch #49 of Varcum 8251 and results for samples heated in both convection and blower ovens are tabulated in Table 3.

When early viscosity measurements on Varcum 8251 made with a Brookfield viscometer proved not to be reproducible, a standard stirring procedure was introduced to correct the situation. A 500 g. sample of resin

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(considerably smaller samples can be used, but stirring efficiency may be lessened with larger samples) is placed in a one quart glass jar having an inside diameter of 3.25 inches. A Cenco variable speed friction cone drive stirring motor (Cat. No. 18802) is used to operate a Kontes glass stirring shaft (Cat. No. K-78500) with a Kontes blade (Cat. No. K-78900, size A). This blade has a flat upper edge 2.5 inches long and a circular lower edge, the maximum height in stirring position being $5/8$ inches. The stirrer is mounted with about one-half inch clearance above the bottom of the jar. A voltage regulator supplies power to the motor in order to prevent speed variations due to fluctuations in line voltage. The motor is adjusted to operate the stirrer shaft at 650 rpm as checked with a stroboscope. It was found experimentally that no significant change in viscosity took place when stirring was extended beyond an initial four-minute period.

In some experiments carried out before standardization of the viscosity determination procedure, viscosities were measured on Varcum 8251 samples during and after oxygen gas was bubbled through them. The Brookfield viscometer was used without stirring. The purpose of these experiments was to determine whether the head space in a drum of resin should be flushed with inert gas following withdrawal of resin in order to improve storage stability. The rise in viscosity observed during and after oxygen treatment appeared to confirm the need for flushing with inert gas. After the extent of the thixotropic behavior of the resin was realized, these experiments were repeated and the rate of viscosity rise due to thixotropy was studied concurrently. Table 4

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outlines the behavior of some representative samples.

Table 5 presents viscosity changes in samples of Varcum 8251 stored under air at room temperature for longer times. Sample No. 1 is taken from a one gallon can of resin ordered directly from the Varcum Chemical Div. by the Westinghouse R & D Center and Sample No. 2 is taken from a drum of Batch #46 of Varcum 8251 at the Astrofuel facility. Neither sample had received any oxygen treatment. All measurements were made after preliminary stirring.

Variation of viscosity with temperature in the range of 25°C to 50°C was checked for four samples of Varcum 8251, two of which had received oxygen treatment. The resin samples were surrounded by a thermostatically controlled bath and the apparatus was set up so that stirring to eliminate thixotropic effects and actual viscosity measurements were carried out without removing the resin sample from the bath. Results of these measurements are reported in Table 6.

A few preliminary experiments were carried out to determine whether the thixotropic behavior of furfuryl alcohol prepolymer resin was dependent upon the nature of the solvent in which the resin is dissolved. Samples of the furfuryl alcohol monomer-free residue from the distillation of a sample of Varcum 8251 were cut back to 58% solids in each of three solvents, furfuryl alcohol, xylene, and diethyle carbitol (bis (2-ethoxyethyl ether)). Viscosity was checked by measuring the time required for the bubble to rise in a Gardner viscosity tube. If the solution is thixotropic, this time will decrease and finally level off with repeated determinations as agitation of the solution associated with repeated measurement destroys molecular orientation. The ratio of initial bubble rise time to

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final bubble rise time is a measure of the degree of thixotropy. Results of this experiment are reported in Table 7.

2. Experimental Results

Table 1

Boiling Points of Volatile Compounds Present in Furfuryl Alcohol Prepolymer

<u>Compound*</u>	<u>Boiling Point</u>	<u>Pressure</u>
I	170 - 171°C	750 mm
	73 - 74	15
	68 - 69	10
III	131 - 133	2.5
V	199 - 202	3
II	101 - 102	2
	88 - 89	1

* The compound designations are those used earlier in the discussion of furfuryl alcohol resin chemistry, i.e. I is furfuryl alcohol monomer, III is "dimer", V is "trimer", and II is furfuryl ether.

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Table 2

Percent Solids in Varcum 8251 by Vacuum Distillation

<u>Sample</u>	<u>Percent Solids</u>	<u>Refractive Index</u> (distillate)
1. Drum 4132 Varcum Run 43. Sample from top of drum	56.0	1.4862
2. Drum 7429 Sample from top of drum Varcum Run 44.	56.6	1.4862
3. Drum 7429 Drum rolled before sample taken	57.4	
4. Drum 4132 Drum rolled before sample taken	54.5	
5. Varcum Run 46	56.1	1.4870 1.4924 (last drops of distillate in Claisen head)
6. Varcum Run 49	57.7	1.4861

Table 3

Percent Solids in Varcum 8251 Run 49 by Oven Weight Loss Test

<u>Blower Oven</u>		<u>Convection Oven</u>	
1.	49.7%	1.	53.5%
2.	50.3	2.	53.4
3.	50.1	3.	53.7
Av.	50.0	Av.	53.5

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Table 4

Effects of Thixotropy and Oxygen Treatment on Viscosity of Varcum 8251

<u>Treatment</u>	<u>Elapsed Time</u>	<u>Temp. of Measurement</u>	<u>Viscosity (cps)</u>	<u>Treatment</u>	<u>Elapsed Time</u>	<u>Temp. of Measurement</u>	<u>Viscosity (cps)</u>
None	None	23.0°C	660 * 560	None	None	23.3°C	387* 331
Stirred 4 min.	None	23.0	302 303	Stirred 4 min.	None	23.3	182 180
Stand 10 min.	10 min.	23.0	300 * 302	Stand 10 min.	10 min.	23.3	182 * 182
Stand 35 min.	45 min.	23.0	321 * 320	Stand 35 min.	45 min.	23.3	191 * 186
Stand 1 hr.	105 min.	23.0°C	324 * 320	Stand 1 hr.	105 min	23.3°C	202 * 197
Stand 3 days	72 hrs.	24.0	846 * 684	Stand 22 hours	23 hrs., 45 min.	23.5	417 * 350
Stirred 4 min.	72 hrs.	24.0	276 268	Stirred 4 min.	23 hrs., 45 min.	23.5	178 171
	(1)				(1)		
O ₂ bubbled in 5.5 hrs.	5.5 hrs	24.2	298 * 297	O ₂ bubbled in 5.5 hrs.	5.5 hrs.	24.2	184 * 188
Stirred 4 min.	5.5 hrs.	24.2	265 266	Stirred 4 min.	5.5 hrs.	24.2	166 169
Stand 7 days	7 days	23.0	288 289	Stand 4 days	4 days	23.0	470 * 389
Stand 9 hrs.	7 days, 9 hrs.	24.7	485 * 424	Stirred 4 min.	4 days	23.0	182 180
Stand 19 hrs.	8 days, 4 hrs.	22.5	954 653	O ₂ bubbled in 6.25 hrs.	4 days, 6.25 hrs.	24.5	196 * 189
Stand 53 hrs.	10 days, 9 hrs.	22.0	1166 * 850	Stirred 4 min.	4 days, 6.25 hrs.	24.5	178 179

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Table 4 Con't.

Stirred 4 min.	10 days, 9 hrs.	23.0	286	Stand 13	17 days	24.5	194
			291	days			194
				Stand 7	24 days	23.0	204
				days			210
				Stand 11	35 days	24.0	200
				days			202

* Brookfield viscosity was measured at both 10 rpm, and 20 rpm. In each case the first value presented is the 10 rpm value. Determinations marked with * were carried out without preliminary stirring in order to observe thixotropic viscosity increases. All determinations not so marked were carried out after the standard 4 min. stirring period. Sample No. 1 is Varcum 8251 Batch #44 and sample No. 2 is Varcum 8251 Batch #43.

(1) The table presents results of studies on resin samples both with and without oxygen treatment. Both samples here were treated with oxygen and time after this point is reckoned from the start of the oxygen treatment even though this treatment in each case was carried out on the original resin sample.

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Table 5

Stability of Varcum 8251 Stored in Air at Room Temperature

Sample 1*			Sample 2*		
<u>Elapsed Time</u>	<u>Temp. of Measurement</u>	<u>Viscosity (cps)</u>	<u>Elapsed Time</u>	<u>Temp. of Measurement</u>	<u>Viscosity (cps)</u>
None	25.0°C	178 (10 rpm) 180 (20 rpm)	None	25.0°C	202 202
372 days	25.0	250 249	273 days	25.0	260 259

* Sample No. 1 is from a one gallon can of resin ordered directly from the Varcum Chemical Div. by the Westinghouse R & D Center and sample No. 2 is from a drum of Varcum 8251 Batch #46 at the Astrofuel Facility.

Table 6

Variation of Viscosity of Varcum 8251 with Temperature

<u>Temp. of Measurement</u>	<u>Viscosity of Sample* (in cps.)</u>			
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
25.0°C	178 (10 rpm) 180 (20 rpm)	182 179	276 271	260 260
30.0	122 131	122 122	200 197	169 170
35.0	88 92	84 83	134 131	119 113
40.0	64 80	62 67	90 100	76 80
45.0	45 52	52 55	68 73	62 63
50.0	38 41	39 44	56 57	48 58

* Samples 1 and 4 have received no oxygen treatment while both 2 and 3 have had

Table 6 con't

this treatment. Sample No. 1 is a sample of Varcum 8251 of unknown batch number from a shipment of Varcum 8251 direct from the Varcum Chemical Division to the Westinghouse R & D Center. No. 2 and 3, both obtained from the Astrofuel Facility, are Varcum 8251 from Batch Nos. 43 and 44 respectively. Sample No. 4 is identical to No. 3 save that it had no oxygen treatment.

Table 7
Thixotropy of Furfuryl Alcohol Prepolymer in Various Solvents*

<u>Condition for Measurement</u>	<u>Temp. of Measurement</u>	<u>Time for Bubble Rise in --</u>		
		<u>Furfuryl Alcohol</u>	<u>Xylene</u>	<u>Diethyl Carbitol</u>
After thorough shaking	24.6°C	2.6 sec.	1.4 sec.	1.2 sec.
First determination after standing 18 hrs. 45 min.	24.5	3.5	4.5	2.4
Thorough shaking after 18 hr. 45 min. stand	24.5	2.6	1.6	1.4

* All solutions were made from a sample of Varcum 8251 from which the monomer had been vacuum distilled, and each solution was 58% solids.

3. Discussion of Results

a. Solids Content

It is felt that the oven weight loss test is less reliable than vacuum distillation because of poorer control over the volatility of the products escaping. The latter test provides an opportunity for less volatile constituents to condense and return to the body of resin. The "dimers" and "trimers" have significant vapor pressures at 135°C as indicated by the data in Table 1 and escape to some extent in the oven test. The fact that weight losses are greater when a 135°C blower oven is substituted for the convection

oven indicates that escape of some of the lower molecular weight species present is still going on at the end of the standard convection oven test. On the other hand, furfuryl alcohol and its low molecular weight polymers are undoubtedly bonded to the prepolymer through hydrogen bonds and it is unlikely that furfuryl alcohol monomer is quantitatively removed in either test. The convection oven test agrees surprisingly well with the vacuum distillation test and is considered acceptable as a quality control test, particularly because far less time and effort are required to carry it out.

b. Thixotropy of Varcum 8251 and Effect of Exposure to Oxygen

Examination of Brookfield viscometer readings on the two samples of Table 4 shows a wide disparity between 10 rpm and 20 rpm values when considerable thixotropic false body is present, but rather good agreement when measurements are made after preliminary stirring. This, of course, indicates local disruption of orientation effects in the solution by the higher stirring speed of the Brookfield spindle.

Sample No. 1 does not show significant bodying 10 days after having received the oxygen treatment. Sample No. 2, which received more than double the oxygen exposure of No. 1, does show rather mild bodying after 17 days but no significant additional bodying after a total of 35 days. Since both samples received vastly more exposure to oxygen than would result from admission of air to the head space in a drum with only mild consequences, it is evident that exposure of the resin to air in shop practice is not a serious problem. This conclusion is confirmed by the data in Table 5 where only relatively small viscosity increases occurred in samples of Varcum 8251 stored

under air at room temperature for much longer periods of time.

c. Variation of Varcum 8251 Viscosity with Temperature

It is of interest to note that the shapes of the viscosity-temperature curves for the oxygen treated samples parallel very closely those for the samples without oxygen treatment. In the samples chosen for these measurements, there is an example of a resin with and without oxygen treatment in both the low and relatively high viscosity regions. The similarity of the viscosity curves for resin samples with and without oxygen exposure tends to confirm the belief that no significant structural change in the resin prepolymer is brought about by the oxygen treatment.

d. Effect of Solvent on Thixotropic Behavior of Varcum 8251

The three solvents used were selected with a view to their differences in hydrogen bonding characteristics. Xylene is inert in this respect and the prepolymer molecules in xylene solution can associate by hydrogen bonding between the furfuryl alcohol hydroxyls and the ether linkages in the furan rings. Diethyl carbitol is an oxygenated solvent having no hydrogen sufficiently labile to participate in hydrogen bonding. The furfuryl alcohol methylols ($-\text{CH}_2\text{OH}$ groups) in the prepolymer can associate solvent molecules by hydrogen bonding to the ether linkages in the diethyl carbitol. Furfuryl alcohol is an oxygenated solvent containing active hydrogen. It can associate with prepolymer molecules by hydrogen bonding of its own active hydrogen to the ether linkages in the furan rings of the prepolymer or by hydrogen bonding from the active hydrogen of the prepolymer methylols to the ether linkage in the solvent.

If the thixotropy of the furfuryl alcohol prepolymer is due at least in part to association of prepolymer molecules in solution through hydrogen bonding, then one might expect to observe the least thixotropy in the furfuryl alcohol solution since this solvent is the most effective of the three at forming hydrogen bonds between solvent and prepolymer and association of solvent with prepolymer by this means would largely prevent association of prepolymer molecules with each other. The solution in xylene on the other hand should exhibit the most thixotropy since the xylene has no tendency to associate with prepolymer molecules through hydrogen bonding. Examination of the data reveals that this is actually the case. If we divide the high viscosity value (in sec.) for each solution in Table 7 by the low value in order to obtain an "index of thixotropy", we find that the values are 1.3 for the furfuryl alcohol solution, 1.7 for the diethyl carbitol solution, and 2.8 for the xylene solution. Furfuryl alcohol prepolymer was found to be insoluble in butyl alcohol, 1,4-butanediol, diethylene glycol, and Solvesso 150 (a mixture of high-boiling aliphatic hydrocarbons).

B. Reactivity

Since the polymerization of furfuryl alcohol is an acid-catalyzed reaction, the reactivity of a particular formulation is dependent upon its pH. Reactivity is also dependent upon the size of the molecular species present and in particular upon the amount of furfuryl alcohol monomer, increasing with monomer content. The pH is adjusted by the Varcum Chemical Division by neutralization of the maleic anhydride polymerization catalyst

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with triethanolamine. A pH determination on the resin as received suffices to check the accuracy of this process and the convection oven weight loss test is adequate for determination of monomer content. An added hazard, however, is the fact that many resin formulations are prepared in the same reaction kettles at Varcum and, although the kettles are cleaned between runs, some contamination with alien substances is a definite possibility. Since the nature of such contamination is not predictable, possible inhibiting or accelerating effects on resin polymerization cannot be predicted. For this reason an additional test which measures resin reactivity directly is needed. A gel time measurement fills this need.

The test established to measure gel time involves use of a gel time meter (Cat. No. 22) manufactured by the Sunshine Scientific Instrument Co. A 10.0 g. sample of resin catalyzed by the addition of 0.33 g. of maleic anhydride is placed in a test tube of 19 mm O.D. and the test tube is immersed in a thermostatted bath maintained at 135.0°C. A 1/4 inch diameter glass rod is used as a probe for the gel time meter and is adjusted so that it reaches to about 1/4 inch from the bottom of the test tube. Results of gel time tests on two batches of Varcum 8251 resin are reported in Table 8. In general, reported gel time should be the average of at least three determinations.

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Table 8

135°C Gel Time of Varcum 8251 Resin

<u>Sample No.</u>	<u>Gel Time (min)</u>	
	<u>Batch #46</u>	<u>Batch #49</u>
1	5.3	5.7
2	5.3	5.7
3	5.6	6.2
4	6.1	5.6
5	5.9	5.4
Av.	5.6	5.7

C. Boron Content of Varcum 8251

Boron was determined spectrographically on samples of Varcum 8251 which had been coked before analysis. Results indicated boron to be present in quantities not greater than 2 ppm and usually less than 1 ppm. Since coking values are slightly less than 50%, this indicates a boron level of not more than 1 ppm in the initial resin if it is assumed that no boron is lost in the coking process. Boron is probably the only high neutron capture cross section element likely to be present as a contaminant in Varcum 8251. A catalyst containing boron is used in the manufacture of another resin formulation at the Varcum Chemical Division and it seems likely that this material is occasionally used in kettles in which Varcum 8251 is subsequently manufactured.

D. Recommendations for Purchase Specifications on Varcum 8251

As a result of the work reported in this section, the following acceptance standards are recommended for Varcum 8251 purchased by the Astro-fuel Facility.

1. Solids content. To be $54 \pm 1\%$ as determined by the 135°C convection oven test.

2. Viscosity. To be $250 \text{ cps} \pm 15\%$ at 25°C . Equilibrium value obtained after repeated inversion of Gardner bubble tube is acceptable.

3. Gel time. To be within range of 5.0 - 6.5 min. at 135°C as determined with Sunshine Gel Time Meter. Resin is to be catalyzed by the addition of 1.0 g. of maleic anhydride to 30.0 g. of resin and value reported is to be average of three determinations.

4. Acidity. pH is to fall within range of 5.0 - 6.0

5. Boron content. Boron as determined spectrographically on coked sample of resin shall not be more than 2 ppm in uncoked resin.

V Furfuryl Alcohol Resin Modification

As previously stated, principal objectives of this work were to minimize loss of volatile substances during cure of the resin and to reduce severity of curing exotherms. Elimination of furfuryl alcohol monomer from the resin appears as a desirable step since it is relatively volatile itself, has more water to lose than other molecular species present, and, as will be shown later, contributes to the severity of polymerization exotherms. If monomeric furfuryl alcohol is to be eliminated from the prepolymer, then the

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average molecular weight of remaining molecular species must be drastically reduced in order to retain an acceptable binder viscosity. A series of furfuryl alcohol prepolymers were prepared in the laboratory in attempts to increase the proportion of low molecular weight species formed. These experiments have, for the sake of convenience in presentation, been divided into liquid phase and vapor phase polymerizations.

Some work was done with catalysts other than maleic anhydride and combinations of catalysts were used in attempts to reduce severity of curing exotherms by spreading curing reactions over a wider temperature range. DTA, gel time measurements, and coking value determinations were used in evaluation of catalyst systems.

A. Liquid Phase Polymerization of Furfuryl Alcohol

This investigation for the most part involved use of water in the reaction mixtures to moderate the reaction and limit formation of higher molecular weight prepolymers. After a method for preparation of a relatively low molecular weight prepolymer had been developed, experiments directed toward scaling up the reaction were carried out. Larger batches tend to exotherm more severely during early phases of the polymerization and these exotherms may result in somewhat higher molecular weight polymers. Cooking schedules designed to minimize exotherms were devised.

1. Experimental Procedures

The liquid phase reactions were carried out in three-necked flasks fitted with thermometer, mechanical stirrer, and reflux condenser.

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At the conclusion of the reaction, the maleic anhydride catalyst used in most cases was neutralized by the addition of triethanolamine. The aqueous layer was then decanted from the mixture as completely as possible and the dark, heavy residue was vacuum distilled to remove water, furfuryl alcohol monomer, and in some cases, dioxane. Distillation was stopped when refractive index of the distillate began to rise above that of furfuryl alcohol. Resin yield and viscosity were observed. Table 9 summarizes liquid phase reaction conditions and results.

Runs GB-24 through GB-28 were concerned with attempts to resinify furfuryl alcohol by the procedure of Nielsen³ in which gamma-alumina is used as the dehydrating catalyst. Nielsen reports this dehydration to go smoothly using Alcoa F-10 alumina. Since this grade of gamma-alumina is no longer on the market, grade F-110, which has superseded it, was used. The latter grade is said to be identical in composition but to have a more uniform particle shape (approximately spherical). It is likely that the F-110 alumina has a lower surface area, since the particles appear to be quite smooth.

Furfuryl alcohol was heated and stirred while in contact with F-110 alumina which had been reactivated by periods of heating at 1,000°F ranging from 2 to 13 hours. Distillate was collected in attempts to separate water and returned to the flask when phase separation failed to occur. No resinification occurred until reaction mixtures containing water added to the furfuryl alcohol were used. Resinification then took place very slowly and yields of resin were small. When zirconium dioxide was used as a dehydrating

Table 9.

Summary of Liquid Phase Polymerizations of Furfuryl Alcohol

Run No.	Ingredient ¹	Charge		Cooking Schedule		Resin Yield ²	Viscosity ³	
		Wgt. in g.	Wgt. %	Time	Temp.		% sol. in FA	cps.
GB-3	FA	270.0 g.	90.0%	2 hrs. 45 min. Reflux		79.0%	55.0%	182
	Water	30.0	10.0					
	MAA	0.3						
	TEA	0.46						
GB-4	FA	150.0	50.0	2 hrs. 45 min. Reflux		72.0	70.0	400
	Water	150.0	50.0					
	MAA	0.3						
	TEA	0.46						
GB-5	FA	150.0	50.0	3 hrs.	Reflux	88.3	55.0	1400
	Dioxane	100.0	33.3					
	Water	50.0	16.7					
	MAA	0.3						
GB-6	FA	150.0	50.0	1 hr. 30 min. Reflux		70.7	70.0	290
	Water	150.0	50.0					
	MAA	0.3						
	TEA	0.46						
GB-7	FA	100.0	33.3	3 hrs.	Reflux	71.3	65.0	191
	Water	200.0	66.6					
	MAA	0.15						
	TEA	0.23						
GB-8	FA	300.0	100.0	3 hrs. 19 min. Reflux		40.0	80.0	490
	MAA	0.3						
	TEA	0.46						

(1) FA indicates furfuryl alcohol, MAA maleic anhydride, and TEA triethanolamine. The latter ingredient was added at the end of the polymerization to neutralize the catalyst.

(2) Resin yield figure is simply weight of prepolymers after vacuum distillation divided by weight of furfuryl alcohol in initial charge x 100.

(3) Material in residue was cut back with furfuryl alcohol monomer to approximately the viscosity of Varcum 8251 (about 250 cps.). Solids content at this viscosity is therefore an indication of prepolymer viscosity.

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Table 9. Cont'd.

Run No.	Ingredient	Charge		Cooking Schedule		Resin Yield	Viscosity	
		Wgt. in g.	Wgt. %	Time	Temp.		% sol. in FA	cps.
GB-9	FA MAA	300.0 g. 0.10	100.0 %	10 hrs. 15 min.	Reflux	Color indicated very little conversion to polymer. Not distilled.		
GB-10	FA Water ZnCl ₂	285.0 15.0 4.5	95.0 5.0 (1.5)	6 hrs. 30 min.	Reflux	Color indicated very little conversion to polymer. Not distilled.		
GB-11	FA Water ZnCl ₂	285.0 15.0 9.0	95.0 5.0 (3.0)	6 hrs. 30 min.	Reflux	66.1	47.5	150*
GB-12	FA Dioxane MAA	150.0 150.0 0.3	50.0 50.0	27 hrs. 15 min.	Reflux	Color indicated little conversion. Addition of 50 g. cellosolve did not make reaction go. Not distilled.		
GB-13	FA Dioxane ZnCl ₂	150.0 150.0 15.0	50.0 50.0 (5.0)	19 hrs. 30 min.	Reflux**	59.0	50.0	500
GB-14	FA Water MAA TEA	300.0 1200.0 0.75 2.25	20.0 80.0	3 hrs.	Reflux	69.7	60.0	235
GB-15	FA Water MAA TEA	150.0 1350.0 0.75 2.25	10.0 90.0	3 hrs.	Reflux	58.4	60.0	263

*One third of the reaction mixture of Run GB-11 was neutralized with enough NaOH to convert the zinc salts to hydroxide. Yield figure and viscosity are based on results from distillation and cut back of this portion. A second portion was neutralized with enough aqueous NaOH to convert Zn salts to the water soluble zincate and the aqueous layer was separated from the residue. Distillation of this portion resulted in polymerization of the resin. Viscosity figures reported are somewhat unreliable owing to presence of solids in the resin.

**The GB-13 reaction mixture was neutralized with enough NaOH to convert Zn salts to the hydroxide. The mixture was then cut back with dioxane to obtain a viscosity low enough for filtration and the residue was washed with excess dioxane. The dioxane solution was then vacuum distilled.

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Table 9. Cont'd.

Exp. No.	Ingredient	Charge		Cooking Schedule		Resin Yield	Viscosity		
		Wgt. in g.	Wgt. %	Time	Temp.		% sol. in FA	cps.	
GB-16	FA	600.0 g.	33.3 %	1 hr.	Reflux	70.8%			
	Water	1200.0	66.7	Exotherm caused spontaneous refluxing for 16 min.			65.0%	165	
	MAA	0.9					80.0	1400	
	TEA	1.38							
GB-17	FA	450.0	25.0	3 hrs.	Reflux	71.0			
	Water	1350.0	75.0	Exotherm caused spontaneous refluxing for 10 min.			65.0	455	
	MAA	0.9					60.0	241	
	TEA	1.38							
GB-18	FA	600.0	33.3	3 hrs.	Reflux	61.7			
	Water	1200.0	66.7	Exotherm caused spontaneous refluxing for 22 min.			70.0	1200	
	MAA	0.9					60.0	287	
	TEA	1.38							
GB-19 (Rpt. of GB-16)	FA	600.0	33.3	1 hr.	Reflux	71.0			
	Water	1200.0	66.7	Exotherm caused spontaneous refluxing for 16 min.			60.0	130	
	MAA	0.9					65.0	216	
	TEA	1.33							
GB-20	FA	600.0	33.3	1 hr.	80°C	77.1			
	Water	1200.0	66.7	3 hr.	Reflux		60.0	225	
	MAA	0.9	6 min. spontaneous reflux at 100°C.						
	TEA	1.38							
GB-21	FA	600.0	33.3	1.5 hrs.	70°C	72.8			
	Water	1200.0	66.7	3 hrs.	Reflux		65.0	250	
	MAA	0.9	Exotherm at 70°C, but very little at 100°C						
	TEA	1.38							
GB-22	FA	600.0	33.3	1.5 hrs.	60°C	74.7			
	Water	1200.0	66.7	3 hrs.	Reflux		65.0	370	
	MAA	0.9	No perceptible exotherming.						
	TEA	1.38							
GB-23	FA	1500.0	33.3	1.5 hrs.	60°C	Reaction mixture not distilled			
	Water	3000.0	66.7	3 hrs.	Reflux				
	MAA	2.25	No perceptible exotherming						
	TEA	3.45							

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agent in similar experiments, no resinification was observed either in the presence or absence of water.

2. Discussion of Results

Although the Varcum Chemical Division has not released the precise procedures used in the manufacture of Varcum 8251, they have indicated that the reaction is water moderated and catalyzed by the addition of 0.1% maleic anhydride. They expressed the opinion that lower molecular weight polymers than Varcum 8251 might be prepared through use of larger quantities of water.

Run GB-3 with 10% water produced a resin having a viscosity slightly lower than that of Varcum 8251. Increasing the amount of water to 66% produced the lowest viscosity resin in the series of smaller scale preparations (Run GB-7), but further increase of water content to 80% and 90% (Runs GB-14 and GB-15) resulted in lower yields and higher viscosity polymers.

Examination of the data indicates that shortening the reaction time decreases the resin yield only moderately and lowers the viscosity of the product at the same time. This point is illustrated by a comparison of Run GB-4 with GB-6 and of GB-16 with GB-18 although the resin yield in GB-18 was unexpectedly low. Run GB-20 had a still longer reaction time and shows both higher yield and higher viscosity than GB-16. This behavior apparently is due to initial rapid formation of a large number of short linear polymers in water moderated reactions and subsequent rather slow growth of these polymers by reaction with the limited amount of monomer still present.

The effect of water moderation in reducing molecular weights of the prepolymers formed, although evident, was less profound than had been hoped

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for. It is not altogether unexpected however, since the reaction mixture separates into an aqueous and an alcoholic phase early in the course of the polymerization, and it would seem that only an equilibrium amount of water could be present in the phase in which the polymerization is occurring. It was for this reason that dioxane was introduced as a component of the reaction mixture. This compound is an excellent solvent for both furfuryl alcohol prepolymers and water and was expected to make the water more effective as a polymerization moderator by carrying a greater amount of it into the resin containing phase of the reaction mixture. Unexpectedly, this had the effect of greatly increasing the reaction rate and resulted in a high yield of polymer of high viscosity. (Run GB-5)

In further experiments designed to study the effect of water, it was found that dry furfuryl alcohol (Runs GB-8 and GB-9) and dry furfuryl alcohol in dry dioxane (Run GB-12) catalyzed with maleic anhydride reacted at very much lower rates than did furfuryl alcohol in the presence of water. A lower molecular weight polymer was produced in Run GB-8 than in any of the water moderated reactions, but in low yield. Since the reaction rate is very low here, the effect is very probably equivalent to that of a very short reaction time in a water moderated reaction.

Zinc chloride catalyzed dehydrations did not appear promising due both to difficulties in removing inorganic materials from the resin and to the fact that these polymerizations tended to produce higher molecular weight polymers in relatively low yields.

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It appears from the experiments in scaling up the water moderated polymerization that there would be no problem in carrying out the dehydration on a large scale. The hold period at 60°C is quite effective at preventing any significant exotherming during the early phases of the reaction. Although Table 9 reports no perceptible exotherming in either Run GB-22 or GB-23, there was indication that there may have been a very mild exotherm at 60°C in the former run and possibly a very slight exotherm at 100°C in the latter. Lower molecular weight products could be obtained at some sacrifice in polymer yield by shortening the reflux periods.

B. Vapor Phase Polymerization of Furfuryl Alcohol

Vapor phase dehydrations of furfuryl alcohol in which superheated alcohol vapors were brought in contact with gamma alumina or zirconia were carried out as an extension of efforts to polymerize furfuryl alcohol by the Nielsen method. Although efforts to polymerize furfuryl alcohol by these procedures were successful, this does not explain failure to duplicate the Nielsen results in the liquid phase and it must be assumed that the F-110 alumina used is less active than that used by Nielsen.

1. Experimental Procedures

Vapor phase dehydrations were carried out in an apparatus consisting of a three-necked flask fitted with thermometer, mechanical stirrer, and short fractionating column fitted with a distilling head. The column was packed with zirconia or gamma alumina for a distance of about 7 inches and was wrapped with an electrical resistance heating tape so that temperatures could be maintained above the boiling point of furfuryl alcohol. A thermometer

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fitted into the distilling head extended down into the central part of the packing. The alcohol to be dehydrated was charged into the flask and stirred during distillation to prevent bumping. Column temperatures proved difficult to control accurately, but in general were maintained in the region of 170° to 200°C. In Runs GB-9 through GB-11, column temperatures were held in the 230°-250°C range. Water separating from the distillate was discarded and the alcohol periodically returned to the flask. At the conclusion of the run, monomer was vacuum-distilled from the residual mixture in the flask to isolate the resin. Table 10 summarizes results from a series of these polymerizations.

2. Discussion of Results

A study of the data presented in Table 10 indicates that reaction proceeds with considerably greater rapidity over gamma alumina when the catalyst is activated by previous heating and that this activity is retained quite effectively if the activated catalyst is stored in the absence of moisture. Runs GB-29-1 and GB-29-2 both proceeded at a fairly good reaction velocity and it is to be noted that very low molecular weight products resulted--much lower than were obtained from any of the water moderated reactions. Run GB-31 on the other hand, using catalyst without activation, dehydrated very slowly. In fact, no water separation was observed during the first 6.5 hours of distillation. Significantly, the polymer from this run was of much higher molecular weight--comparable in viscosity to products from the water moderated polymerizations.

Runs GB-29-5 through GB-29-8 constitute a study of the properties of the gamma alumina catalyst during prolonged use. The polymer from Run GB-29-5 using activated catalyst was of low viscosity and reaction velocity was good. The catalyst was removed from the column after the run and thoroughly washed with acetone to remove polymer which had not been washed back into the flask by liquid condensates during the dehydration. The alumina was then vacuum

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Table 10.

Summary of Vapor Phase Dehydrations of Furfuryl Alcohol

<u>Run No.</u>	<u>Charge</u>	<u>Catalyst Treatment</u>	<u>Reaction Time</u>	<u>Water Collected</u>	<u>Resin Yield</u>	<u>Viscosity</u>	
						<u>% sol in FA</u>	<u>cps</u>
GB-29-1	300 g. FA 40 g. F-110	F-110 heated 16 hrs. at 1,000°F in air.	14.5 hrs.	12.4 cc	39.7%	100% 90	500 237
GB-29-2	300 g. FA 40 g. F-110	Catalyst is from batch treated as in GB-29-1, but was stored in desiccator 7 weeks after treatment.	10.0	14.3	24.7	100 90	445 250
GB-31	300 g. FA 40 g. F-110	F-110 catalyst used as received	30.5	12.9	44.8	90 65 60	4630 220 135
GB-29-5	300 g. FA 40 g. F-110	Catalyst had been heated in air 16 hrs. at 1,000°F and was then stored 3 weeks in desiccator	4.2	14.2	25.4	100 90	600 212
GB-29-6	300 g. FA 40 g. F-110	Cat. from GB-29-5 was washed with acetone, vac dried, and reused	4.7	13.2	29.6	100 90	1760 525
GB-29-7	300 g. FA 40 g. F-110	Cat. from GB-29-6 was washed with acetone, vac dried, and reused	7.3	14.6	29.3	100 90	8600 3200
GB-29-8	300 g. FA 40 g. F-110	Cat. from GB-29-7 reused without treatment.	12.0	14.4	31.3	100 90	7300 1540
GB-29-9	800 g. FA 40 g. F-110	Catalyst had been heated in air 16 hrs. at 1,000°F and stored 1 day in desiccator	6.7	38.9	31.5	100 90 75	4370 970 206
GB-29-10	800 g. FA 40 g. F-110	Catalyst from GB-29-9 reused without treatment.	6.7	41.3	29.4	100 90 70	12350 3620 200
GB-29-11	800 g. FA 40 g. F-110	Catalyst from GB-29-10 reused without treatment	6.7	41.7	30.8	100 90 75	8040 3160 285
GB-30	300 g. FA 117 g. ZrO ₂	No treatment. Particle size mostly 5 - 14 mesh	8.2	---	25.9	100 90	550 230

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dried and returned to the column for use in the subsequent run. As successive runs were made with this procedure, it is evident that the catalyst progressively lost its activity with the result that reaction velocities dropped and viscosities rose. It is interesting to observe that viscosity of Run GB-29-8 is somewhat lower than that of the polymer from the previous run even though reaction velocity had continued to drop. There had been little accumulation of polymer on the catalyst during Run GB-29-7 and consequently the acetone wash had been omitted prior to Run GB-29-8. The lowered viscosity suggests that the acetone wash may have a deleterious effect on the catalyst and that continued distillation may reactivate it to some extent.

Runs GB-29-9 through GB-29-11 were carried out on a larger scale (though with the same amount of catalyst) and the catalyst was reused successively without any sort of treatment between runs. Reaction velocities remained quite constant throughout the series and viscosities were consistently higher than had resulted from earlier small scale runs with activated catalyst. A vigorous exotherm in the column at the outset of Run GB-29-9 proved that the catalyst was properly activated before the run. One must assume that low viscosity polymer formed initially and that the viscosity of the product rose as catalyst activity declined to some equilibrium value. Viscosities of the products from Runs GB-29-10 and GB-29-11 are about the same, but the produce from GB-29-9 is of lower viscosity, presumably due to the presence of very low molecular weight polymer formed early in the run. It should be noted that the polymers from GB-29-10 and GB-29-11 are of lower viscosity than the product from GB-31 indicating that the catalyst retains

more activity at equilibrium than that possessed by the unactivated gamma alumina. No effect assignable to the higher column temperatures used in these three runs is evident.

The only dehydration carried out with zirconia was Run GB-30. Reaction velocity was good and polymer viscosity was low. This is particularly significant because the catalyst had not been activated in any way. Large scale production of really low viscosity prepolymer by dehydration over activated alumina presents a difficult problem owing to the necessity of reactivating the catalyst or changing it very frequently. It would appear from this one experiment that zirconia may not be subject to these problems. More work was not done with zirconia at this time because of difficulty in obtaining pure zirconia in a suitable particle size.

C. Performance of Furfuryl Alcohol Resin Systems

Ultimately the performance of modified furfuryl alcohol resin systems must be evaluated on the basis of measurement of the characteristics of resin-bonded extruded graphite bodies which at least initially can be unfueled. Unavailability of equipment has delayed this type of evaluation, but measurement of such properties as coking values, gel times, and polymerization exotherms on unfilled resin systems offers a preliminary indication of resin performance.

1. Experimental Procedures & Results

Gel time measurements were carried out at 135°C with a Sunshine Gel Time Meter by the procedure already described in section IV B. Results of

a series of gel time measurements on modified furfuryl alcohol resin systems are summarized in Table 11. Coking value determinations were performed in Vycor sample tubes in a coking furnace assembled by Mr. Peter Gaal. Catalyzed samples in the weight range of 0.5 to 1.0 g were weighed into Vycor sample tubes in the shape of flat-bottomed vials 1.25 in. tall and 0.5 in. inside diameter. Results reported are the average of five determinations and ten samples could be accommodated simultaneously in a graphite block bored out to hold the sample tubes. Determinations were run in an argon atmosphere and temperature of the coking furnace was raised at 30°F per hour to a top temperature of approximately 1560°F. Results of a series of coking value determinations are summarized in Table 12. DTA facilities at the Astronuclear Laboratories were used to locate exotherms in a series of modified furfuryl alcohol resin systems. Unfortunately procedures with this apparatus had not been adequately standardized at the time the measurements reported here were made and these determinations are to be repeated. Table 13 reports some preliminary results.

Results of a shelf life study on maleic anhydride and pyromellitic dianhydride catalyzed furfuryl alcohol resin systems are reported in Table 14.

Table 11
135°C Gel Times of Some Furfuryl Alcohol Resin Systems

<u>Resin</u>	<u>Catalyst*</u>	<u>135°C Gel Time</u>
1. Varcum 8251, Run 49	3.2% MAA	6.1 min. 5.9 min. (Two series of 5 samples each)
2. Varcum 8251, Run 46	3.2% MAA	5.6
3. Varcum 8251, Run 46 100% Solids	3.2% MAA	6.1, 7.0 (Two series of 5 samples each)
4. Varcum 8251, Run 46 100% Solids	3.0% MPTS	18.5
5. Varcum 8251, Run 46	2.0% MPTS	12.4
6. Varcum 8251, Run 46	3.0% MPTS	9.0 min.
7. Varcum 8251, Run 46	2.0% PMDA	18.3
8. Varcum 8251, Run 49	3.2% MAA 1.0% MPTS	5.6
9. Varcum 8251, Run 49	3.2% MAA 2.0% MPTS	4.6 (foamed out of tube)
10. Varcum 8251, Run 49	1.0% MAA 1.0% MPTS	5.6
11. GB-29-1, 100% Solids	3.2% MAA	43.5
12. GB-29-2, 90% sol. in FA	3.2% MAA	24.7
13. GB-29-2, 80% sol. in FA	3.2% MAA	20.3
14. GB-29-2, 65% sol. in FA	3.2% MAA	14.1
15. GB-30, 100% Solids	3.2% MAA	23.2
16. GB-30, 90% sol. in FA	3.2% MAA	19.0
17. GB-31, 100% Solids	3.2% MAA	67.2
18. GB-31, 90% sol. in FA	3.2% MAA	30.1
19. GB-31, 80% sol. in FA	3.2% MAA	21.8
20. GB-31, 65% sol. in FA	3.2% MAA	16.1

*In this table and in tables 12, 13, and 14, MAA indicates maleic anhydride, MPTS methyl p-toluenesulfonate, and PMDA pyromellitic dianhydride.

Table 12

Coking Values of Some Furfuryl Alcohol Resin Systems

<u>Resin</u>	<u>Catalyst</u>	<u>Coking Value</u>
1. Varcum 8251, Run 49	3.2% MAA	48.6%
2. Varcum 8251, Run 49	3.2% MAA	44.0*
3. Varcum 8251, Run 46 100% Solids	3.2% MAA	51.8
4. Varcum 8251, Run 46 100% sol. + 25% dioxane	3.2% MAA	48.5 (based on resin only)
5. Varcum 8251, Run 49	2.0% PMDA	48.5%
6. Varcum 8251, Run 46 100% Solids	3.2% MAA	54.5
7. Varcum 8251, Run 49 100% Solids	3.0% MPTS	53.5
8. GB-19, 100% Solids	3.2% MAA	45.9
9. GB-20, 100% Solids	3.2% MAA	46.4
10. GB-20, 100% Solids plus 50% dioxane	3.2% MAA	45.2 (based on resin only)
11. GB-29-1, 100% Solids	3.2% MAA	50.2
12. GB-29-1, 100% Solids	3.2% MAA	49.4
13. GB-29-1, 90% Solids in FA	3.2% MAA	47.1
14. GB-29-2, 90% Solids in FA	3.2% MAA	45.8
15. GB-29-2, 80% Solids in FA	3.2% MAA	45.2
16. GB-31, 90% Solids in FA	3.2% MAA	46.2

*Top temperatures of the coking furnace were not always adequately controlled. The first and second determinations are values on identical samples with top furnace temperatures of 1435° and 1600°F respectively.

Table 13

Preliminary DTA Studies of Some Furfuryl Alcohol Resin Systems

<u>Resin</u>	<u>Catalyst</u>	<u>Rate of Temp. Rise</u>	<u>Exotherm Peaks</u>
1. Std. Binder & Filler (unfueled)	3.2% MAA	0.5°C/min.	106°C
2. Varcum 8251, Run 49	3.2% MAA	5.0	115°, 119°
3. Varcum 8251, Run 49	3.2% MAA	2.0	104°, 111°
4. Varcum 8251, Run 49	2.0% PMDA	4.0	137°, 158°
5. Varcum 8251, Run 49	3.0% MPTS	1.0	122°, 126°
6. Varcum 8251, Run 49	3.0% MPTS	4.0	147°
7. Varcum 8251, Run 49	3.0% MPTS	4.0	145° (Rpt. run)
8. Varcum 8251, Run 46 100% Solids)	3.0% MPTS	1.0	135°
9. GB-29-2, 90% Sol. in FA	3.2% MAA	4.0	147°

Table 14

Room Temperature Storage Stability of MAA and PMDA-Catalyzed Varcum 8251

<u>Days of Storage</u>	<u>25°C Viscosity</u>	
	<u>Varcum 8251 plus 2% PMDA</u>	<u>Varcum 8251 plus 3.2% MAA</u>
0 days	243 cps.	350 cps.
1	266	562
2	270	640
3	---	665
4	---	663
6	282	---
8	331	745

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2. Discussion of Results

Examination of gel time data in Table 11 indicates a striking increase in resin reactivity (as shown by shorter gel times) as the amount of furfuryl alcohol monomer in a particular resin system is increased. The series of gel time determinations on compositions in the GB-29, GB-30, and GB-31 systems illustrate this clearly as does the comparison between Compositions #4 and #6 where Varcum 8251 catalyzed with 3.0% methyl p-toluenesulfonate is far less reactive with the furfuryl alcohol monomer removed. This effect is also present, but much less striking, when Varcum 8251 is catalyzed with maleic anhydride. Greater reactivity in a resin system is undoubtedly associated with more severe exotherming during cure but severity of exotherms cannot reliably be established from the DTA data now available.

DTA samples reported were run in small cylindrical platinum crucibles with the thermocouple fitted into a receptacle attached to the base of the crucible. Shrinkage of the resin during cure resulted in deterioration of the quality of thermal contact between the sample and the wall of the crucible. Since the degree of contact remaining after gelation of the sample had taken place was not reproducible, it is felt that heights of exotherm peaks of different samples are not comparable. Crucibles now available have the thermocouple contained in a small hollow spike which protrudes from the base of the crucible into the body of the sample. Good contact with this spike should be maintained during resin cure with consequent improvement of the quality of the data. It is felt that location of the temperature region

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of the exotherm is reasonably accurate by the procedure used initially.

The series of gel time determinations carried out on the GB-29-2 and GB-31 compositions indicates that resin reactivity is dependent not only upon proportion of monomer in the resin system, but also upon the mobility of other molecular species which are present in the prepolymer. The viscosity of GB-31 resin was far higher than that of GB-29-2 resin and comparison of a series of samples having identical monomer and catalyst contents shows GB-29-2, the lower viscosity prepolymer, to have a shorter gel time in each case. These gel times, however, are not dramatically shorter as is usually the case when the gel time of a prepolymer containing monomer is compared to that of a 100% solids resin.

Since the goal of the furfuryl alcohol resin modifications reported here is to achieve a composition of suitable viscosity for use as a binder which has minimum volatility and maximum possible freedom from severe exotherms during cure, the use of monomer free prepolymers containing substantial quantities of "dimers" and "trimers" is indicated. Presence of the latter molecular species permits prepolymer viscosities to fall within the usable range and at the same time does not drastically increase the resin reactivity. Further support of this type of composition is the fact that coking values tend to be slightly higher in the absence of furfuryl alcohol monomer.

Dioxane was used as a solvent for Varcum 8251 prepolymer from which monomer had been removed by distillation to determine whether this high

viscosity prepolymer could be used as a graphite bond when its viscosity was lowered to a suitable value by an inert solvent. This might permit lowering the reactivity (and therefore the exotherm peaks) of a resin now commercially available. This procedure tended to lower coking values to some extent. Unexpectedly, it was observed that coke samples from dioxane containing compositions appeared to contain fewer voids than coke samples from resins containing furfuryl alcohol monomer.

A limited amount of work with catalyst systems has shown that pyromellitic dianhydride causes furfuryl alcohol resins to exotherm at higher temperatures than does maleic anhydride. This suggests use of smaller quantities of both catalysts simultaneously in an attempt to spread curing exotherms over a broader temperature range, thereby permitting an accelerated curing schedule. The higher activation temperature of PMDA permits longer catalyzed shelf life as shown by the data of Table 14. It was observed that PMDA-catalyzed resins generally gave more void free coke samples than similar compositions catalyzed with MAA.

VI Recommendations for Future Work

1. Evaluation of many of the compositions reported here must be performed by incorporating them into experimental green mixes which are to be processed by extrusion, cure, and bake. Physical properties of the graphite bodies thus prepared must then be determined. Resin performance data reported here provide only a very preliminary indication of suitability of the resin system as a bond for extruded graphite bodies.

2. More extensive and better controlled DTA analysis of the resin systems reported here is needed.

3. Only a limited amount of work on catalyst systems was performed. DTA studies of other catalysts and combinations of catalysts is indicated. Examination of the correlation between quantity of catalyst used and coking value would be of interest since severity of curing exotherms could be lowered simply by reducing the amount of catalyst.

4. Further study of zirconia-catalyzed vapor phase dehydration of furfuryl alcohol is desirable as this may well be the method of choice for manufacture of low molecular weight prepolymers.

5. Investigation of other resin systems for use as graphite bonds is needed. Furfuryl alcohol resins offer the advantages of high coking value and of becoming thermoset during an early phase of the cure so as to permit the extruded body to retain its shape, but suffer from the inherent disadvantage of being condensation resins which must cure by the elimination of volatile products. If suitable thermosetting addition resins can be found, their failure to split out volatiles should make more void-free graphite bodies possible and it should be possible to greatly speed up curing schedules. A slow cure is an inherent necessity with any condensation resin because reasonable freedom from voids is possible only if time is allowed for volatile molecules to escape from the curing mass by diffusion.

A suggested approach is through study of epoxy novolak systems. Conventional epoxies do not offer sufficiently high coking values, but epoxy

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novolaks resemble phenolic resins which do have good coking values. Since these systems are normally too viscous to be used as graphite bonds, they would have to be used in conjunction with reactive epoxy diluents.

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