

## A Study of the Low Molecular Weight Components of Furfuryl Alcohol Polymers

E. M. WEWERKA, E. D. LOUGHRAN, and K. L. WALTERS,  
*Los Alamos Scientific Laboratory, University of California,  
Los Alamos, New Mexico 87544*

### Synopsis

Low molecular weight components of both an acid-polymerized and a  $\gamma$ -alumina polymerized furfuryl alcohol polymer were separated by gas chromatography utilizing a Porapak type P-S column packing. The identities of the separated polymer components were established by infrared spectroscopy, mass spectrometry, and nuclear magnetic resonance analysis. Volatile constituents found to be common to both furfuryl alcohol resin types were: furfuryl alcohol, water, difurylmethane, difurfuryl ether, and 2,5-difurfurylfuran. Also, 5-furfurylfurfuryl alcohol was found to be present only in the acid-polymerized resin, and 4-furfuryl-2-pentenoic acid  $\gamma$ -lactone was a constituent only of the  $\gamma$ -alumina-polymerized resin. Contrary to expectation, no esters of levulinic acid were found among the low molecular weight components of the  $\gamma$ -alumina-polymerized furfuryl alcohol polymer.

### INTRODUCTION

Furfuryl alcohol polymers are thermosetting resins which have been utilized as binder, coating, and impregnating materials. In addition to exhibiting excellent heat and chemical resistance when cured, furfuryl alcohol polymers also produce relatively large amounts of carbon when subjected to high-temperature pyrolysis.<sup>1</sup> These properties account for the more recent use of furfuryl alcohol resins as binder materials in the manufacture of nuclear-grade graphite. Our interest in the development of improved furfuryl alcohol resin-bonded graphite has led us to further studies of the chemical and physical properties of the resins used in graphite fabrication.

The polymerization of furfuryl alcohol is accompanied by many side reactions which, from a chemical point of view, result in the formation of a heterogeneous product. Thus, to attempt an understanding of the behavior of these polymers when used as graphite binder materials, it is necessary to have some knowledge about their chemical composition.

As it is experimentally difficult to isolate the larger molecules present in furfuryl alcohol polymers, it was decided that by separating and identifying the low molecular weight components of these polymers, much information concerning the chemical composition of the polymers as a whole could nonetheless be gained. Of course, the assumption must be made that the com-

position of the entire polymer is reflected in the composition of its more volatile components. In fact, the low molecular weight components of furfuryl alcohol resins are likely to be of particular importance to us. A recent study concerning the effects of the molecular-size distributions of furfuryl alcohol polymer binders on the properties of graphites made from them<sup>2</sup> indicated that the behavior of these binder materials is determined largely by the amount of lower molecular weight constituents present in the polymer.

Experimentally, the task of isolating the volatile components of furfuryl alcohol polymers in amounts suitable for further characterization appeared to be well suited to gas chromatography techniques.

Furfuryl alcohol polymers are usually made by the polymerization of furfuryl alcohol with a mild, acid catalyst, often in the presence of an inert diluent.<sup>3</sup> The initial polymerization rate of furfuryl alcohol has been shown to be controlled by the pH of the reaction mixture;<sup>3-5</sup> the result of this is that the product of acid polymerization will be composed of similar types of chemical species regardless of the specific acid catalyst used.<sup>6-8</sup> However, Boquist and his co-workers<sup>9</sup> used  $\gamma$ -alumina to effect the polymerization of furfuryl alcohol, and they found that the resulting polymer contained chemical components other than those usually obtained by acid-catalyzed polymerization. Because of these apparent differences in composition, both types of furfuryl alcohol resins are of interest to us.

In previous studies,<sup>6-9</sup> vacuum distillation was employed to separate the low molecular weight components of furfuryl alcohol resins from the whole polymer. The separated resin components were then identified by various analytical methods. However, we found early in our work with these polymers that vacuum distillation is a time-consuming method of isolating polymer components, resulting often in incomplete separations of the desired species and usually making multiple distillation necessary to effect total separation.

A consideration of the studies we desire to conduct with the large number of furfuryl alcohol resins involved in our programs prompted us to turn to gas chromatography with the expectation of realizing a quicker means of separating and identifying their volatile components. (Of course, it is still necessary to remove the more volatile resin components from those of higher molecular weights prior to their injection into the gas chromatograph; for this purpose a simple vacuum distillation works nicely.) In addition to identifying any new components which might be present in the two furfuryl alcohol resin types, we also desired to reestablish the identities of those components which had been previously reported with the modern analytical techniques now available.

This paper describes the development of chromatographic conditions and the use of gas chromatography on a porous polymer column packing, to separate the low molecular weight components of both acid-polymerized and  $\gamma$ -alumina-polymerized furfuryl alcohol resins. Further described are the collection of the isolated components from the chromatograph and their

subsequent identification by infrared spectroscopy (IR), high-resolution mass spectrometry (MS), and nuclear magnetic resonance analysis (NMR).

## EXPERIMENTAL

### Procedures

#### *Furfuryl Alcohol Resin Synthesis*

The acid-polymerized furfuryl alcohol resin was made in a 2000-ml, three-necked, round-bottomed flask fitted with a water-cooled reflux condenser, a thermometer, and a motor-driven, paddle-type stirrer. Furfuryl alcohol (1120 g), maleic anhydride (2 g), and water (400 g) were added to the reaction flask at room temperature, and stirring at 400 rpm was started. The flask was heated to the reflux temperature of the furfuryl alcohol-water azeotrope (92°C) by means of a Variac-controlled heating mantle, and the temperature was held there for 30 min. The polymer was then quickly cooled to 50°C by immersing the flask in ice water; at this point, the product was neutralized to pH 7 with 5% sodium hydroxide solution. After separation and removal of the aqueous phase (a solution of salt water was often used to break the emulsion resulting from product neutralization), residual water was removed from the polymer by heating it with steam in a rotary evaporator under "house" vacuum for a 2-hr period.

The  $\gamma$ -alumina-polymerized furfuryl alcohol resin was made in a manner similar to that described by Nielson.<sup>10</sup> This was done in a 2000-ml, three-necked, round-bottomed flask equipped with a thermometer and an 18-in. air-cooled Vigreux condenser. Furfuryl alcohol (900 g) and 8- to 14-mesh  $\gamma$ -alumina (120 g) were added to the reaction flask, and the mixture was heated at a uniform rate with a heating mantle until a temperature of 170°C was achieved (65 min). During heating, water and some furfuryl alcohol were allowed to escape at the top of the reflux condenser and were not collected. The resulting polymer was cooled to 75°C and then poured through a glass wool filter in order to separate the product from the alumina catalyst. All of the furfuryl alcohol polymers were refrigerated until used.

#### *Polymer Viscosity Measurement*

The polymer viscosities were measured at 25°C with a Brookfield Model LV Syncrelectric viscometer. Each polymer sample was contained in a 1-pint glass bottle which was suspended in a constant-temperature bath for a 1-hr period prior to and also during the time that the measurement was taken.

#### *Vacuum Distillation of Volatile Polymer Components*

The vacuum distillations, which served to separate the more volatile polymer components from those of less volatility, were carried out similarly for both polymer types. The distillations were done from a 1000-ml, three-necked, round-bottomed flask which was fitted with a Variac-controlled

heating mantle, a thermometer, a magnetic stirring bar, and a distilling head. To the latter was connected a water-cooled condenser and a fraction-collecting device. After the addition of the furfuryl alcohol polymer (400 g) to the distilling flask, the system was out-gassed by vacuum pumping and stirring for a 1-hr period. The resin was then slowly heated to 180°C while the system pressure was maintained at 10 to 50 microns. (We had previously determined that 180°C was the maximum temperature to which the resins could be subjected for short periods of time without causing serious component degradation.) Three or four crude fractions were collected during the distillation in order to partially isolate the rest of the volatile resin components from the relatively large amount of furfuryl alcohol that we expected to be present. The collected resin fractions were stored under nitrogen and were refrigerated in air-tight bottles.

Previous experiments had been conducted using a 16-in., air-cooled Vigreux condenser to enhance component separation during sample distillation. Even so, it was found that the separation of the low molecular weight resin components from one another was still incomplete. But more important, as was indicated by the large difference between the flask and head temperatures, a considerable amount of material was suspended in the Vigreux column. Some of this problem could have undoubtedly been solved by the use of a heated distilling column. However, for the sake of simplicity, we abandoned all except a rudimentary separation of the individual resin components by vacuum distillation; and we utilized this technique only to separate the volatile materials from the rest of the resin while causing minimum transitory holdup of them. This was accomplished by removing the Vigreux column from the distillation system altogether.

#### *Gas Chromatography of Furfuryl Alcohol Polymer Components*

We expected to find differences in chemical behavior among the constituents of furfuryl alcohol polymers, so it was difficult a priori to predict which partitioning material(s) might best accomplish the desired separations. Thus, at the onset of this study, a number of column packing materials, which were chosen on the basis of temperature stability and/or liquid substrate polarity, were tested. This was done by noting the effectiveness of each partitioning agent at separating the volatile components of a standard furfuryl alcohol resin sample under a variety of chromatographic conditions. Among those partitioning agents that we investigated were: Apiezon L, 15%; Carbowax 20M, 15%; diethylene glycol succinate, 15%; Squalene, 15%; and SE-30, 4%. Each was packed into a 10-ft-long, 1/4-in.-diam. stainless steel column. All of the liquid substrates were deposited on 60/80 mesh acid-washed Chromosorb W. Porapak types P-S and Q-S porous polymer beads packed into 8-ft-long, 1/4-in.-diam stainless steel columns were also tried. As might be expected, varying degrees of resin component resolution were obtained from the variety of partitioning agents tested; however, Porapak type P-S appeared most promising, and we sub-

sequently developed our chromatographic conditions for this partitioning agent.

The gas chromatography studies were conducted with a Varian-Aerograph Model 1520 gas chromatograph which was equipped with dual thermal-conductivity detectors. The component separations were done with an 8-ft by  $\frac{1}{4}$ -in.-diam. stainless steel column which was packed with 80- to 100-mesh Porapak, type P-S. Another similar column was connected into the reference side of the instrument to provide gas flow balance through the detector. Listed in Table I are the pertinent chromatographic operating parameters used in this study. During sample analysis, the column oven temperature was regulated according to the temperature program which also appears in Table I. Periods of up to 20 min from the time of sample injection were usually required for complete emergence of the resin components, after which an additional period of 20 min at 285°C was usually allowed for column burnout prior to cooling the oven again to the starting temperature.

TABLE I  
Gas Chromatography Operating Parameters

Sample and reference columns, 8 ft $\times$ $\frac{1}{4}$ in. stainless steel, Porapak type P-S		
Carrier gas, helium		
Sample and reference column carrier gas flow, 150 ml/min		
Injector pressure, 30 psi		
Injector temperature, 290°C		
Detector temperature, 295°C		
TC detector filament current, 150 mA		
Detector outlet temperature, 220°C		
Chart speed, 10 in./hr		
Oven temperature program		
Mode	Temperature, °C	Duration, min
1. isothermal	90	5
2. heat	to 285	5
3. isothermal	285	30

Ordinarily, for analytical work, resin samples of 8  $\mu$ l were injected into the chromatograph; however, when the separated components were to be collected, 100- $\mu$ l samples were used. (We have since constructed a 12-ft by  $\frac{3}{8}$ -in.-diam. column packed with 80- to 100-mesh Porapak type P-S with which we are able to separate polymer samples of up to 500  $\mu$ l in a manner suitable for collection.)

A simple technique was used to collect the separated resin components at the detector outlet. The gaseous components were condensed into air-cooled, open-ended glass capillary tubes which were coupled to the detector outlet by a short Teflon sleeve. The emerging samples condensed as droplets in the capillary tube (or tubes, if more than one was required for a given fraction) until the sample was collected, whereupon both ends of the tubes were flame sealed. In some cases, if the samples were to be analyzed imme-

diately, the material which had been collected was allowed to flow from the lower end of the capillary tube directly onto the surface of a salt plate or into an NMR tube. During sample collection, component condensation was promoted by evaporative cooling of the capillary tube provided by wiping its surface with an acetone-soaked tissue.

#### *Infrared Analysis of Furfuryl Alcohol Polymer Components*

The infrared analysis of the furfuryl alcohol polymer components was carried out with a Perkin-Elmer Model 621 infrared spectrophotometer. Samples were prepared for analysis by compressing several drops of material between the surfaces of two potassium bromide plates.

Infrared spectrophotometer operating parameters were: slit program, 1000; gain, 4.2; attenuator speed, 1100; scan time, 20 min; suppression, 6; scale expansion, 1×; and source current, 0.8 amp.

#### *Nuclear Magnetic Resonance Analysis*

The NMR studies were done with a Varian Model A-60A spectrometer at ambient temperature (35°C). Samples were run either as pure liquids or as solutions in carbon tetrachloride, with tetramethylsilane added as an internal standard.

#### *Mass Spectrometry Analysis*

Fragmentation patterns of the separated components were obtained using a Consolidated Electrodynamics Corporation (CEC) 21-103 mass spectrometer equipped with a heated oven and a liquid introduction system. The source was operated at 250°C and 70 volts ionizing voltage. The ionizing current was varied depending on the sensitivity required for qualitative identification, but was set at 15 microamperes when comparing total ionization per micron sample pressure. A CEC 21-110B mass spectrometer equipped with the precise mass measurement system was employed where precise mass measurements were needed for identification of fragment and/or parent ions.

### **Materials**

The furfuryl alcohol used for this study was Eastman White Label, the maleic anhydride was MCB standard quality, and the 8- to 14-mesh  $\gamma$ -alumina was Grade F-10 manufactured by Alcoa.

The gas chromatography columns packed with liquid substrates were obtained from Varian-Aerograph. Porapak partitioning agents were purchased from Waters Associates.

## **RESULTS AND DISCUSSION**

### **Background**

As mentioned earlier, the isolation and identification of many of the low molecular weight components of furfuryl alcohol polymers have been pre-

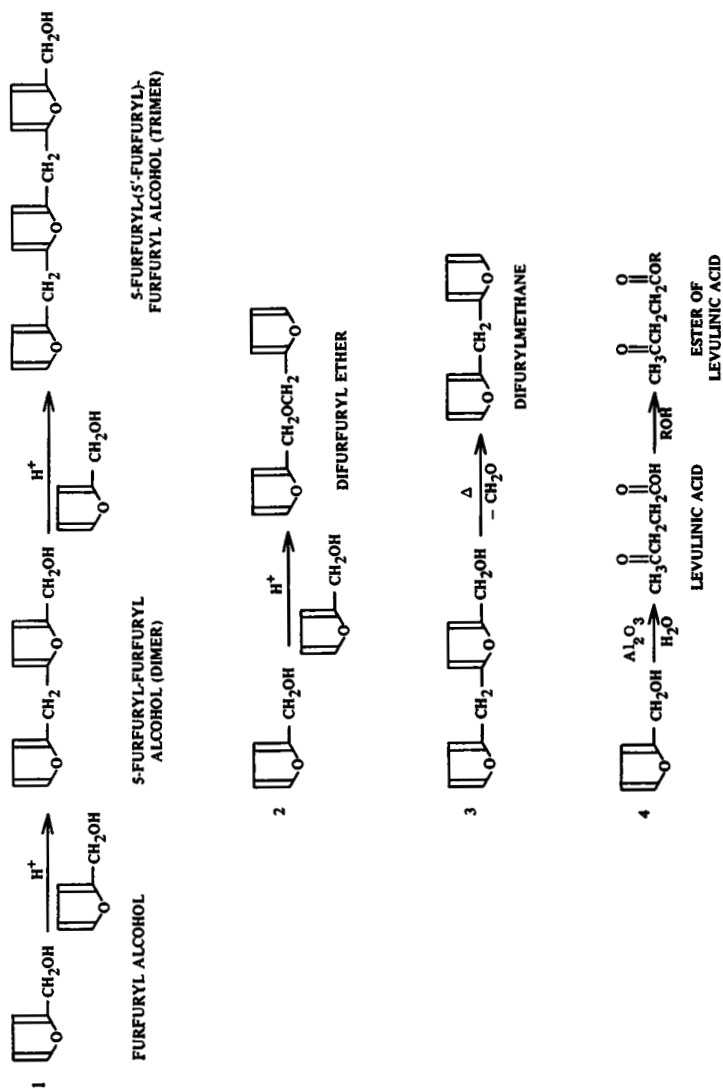


Fig. 1. Reactions of furfuryl alcohol in the presence of polymerization catalysts.

viously reported. Although the results of these studies differ to some extent, an indication of the kind of chemical species to be expected in such polymers was obtained from them. At this point, a short review of the current state of knowledge in this area will provide useful background.

Most of the previous studies of furfuryl alcohol resin components were done with the acid-polymerized polymer. As is expected from a reaction mixture containing an aromatic-type alcohol and an acid catalyst, numerous chemical species result.<sup>6-8</sup> Reactions (1) through (3) of Figure 1 account for the major low molecular weight components which have been isolated from acid-polymerized furfuryl alcohol resins. The situation is complicated somewhat, as Conley and Metil<sup>11</sup> report that acid-polymerized furfuryl alcohol polymers also contain appreciable amounts of products resulting from oxidation and ring cleavage reactions of some of the polymer components.

The corresponding product distributions of  $\gamma$ -alumina-polymerized furfuryl alcohol resins<sup>9</sup> differ significantly from those of the acid-polymerized resins. Levulinic acid, a known ring cleavage product of furfuryl alcohol, which apparently forms only in minor amounts, if at all, during the acid polymerization of furfuryl alcohol, is thought to be a major intermediate in the reactions taking place during the  $\gamma$ -alumina-polymerization of furfuryl alcohol. This conclusion results from the fact that Boquist and his co-workers<sup>9</sup> isolated significant amounts of what they believed to be esters of levulinic acid (or of related acids) from  $\gamma$ -alumina-polymerized resins, see reaction (4) in Figure 1. The importance of this reaction mode, during the  $\gamma$ -alumina polymerization of furfuryl alcohol, was reported by Boquist's group to be further substantiated by the absence of components in the reaction product which contained free hydroxyl groups, such as the "dimer" or "trimer" species. It was concluded that the latter species were present only in the form of esters. Although analytical results were incomplete,  $\gamma$ -alumina-polymerized resins were reported to also contain unreacted monomer, difurylmethane and difurfuryl ether, as do acid-polymerized resins.

### Gas Chromatography of Furfuryl Alcohol Polymer Components

An acid-polymerized and a  $\gamma$ -alumina-polymerized furfuryl alcohol polymer, both of about 300-centipoise viscosity, were utilized for this study. Prior to GC analysis, the volatile resin components were separated from the bulk polymer by vacuum distillation wherein those components which distilled up to 180°C at minimum system pressure were separated into several crude fractions (see experimental section). Each of these fractions was subjected to GC analysis.

Figure 2 is a composite chromatogram containing each of the volatile components that were separated from the acid-polymerized resin. The identities of the components were established by IR, MS, and NMR analyses. The position of the water band was established by the injection of water samples into the chromatographic system.



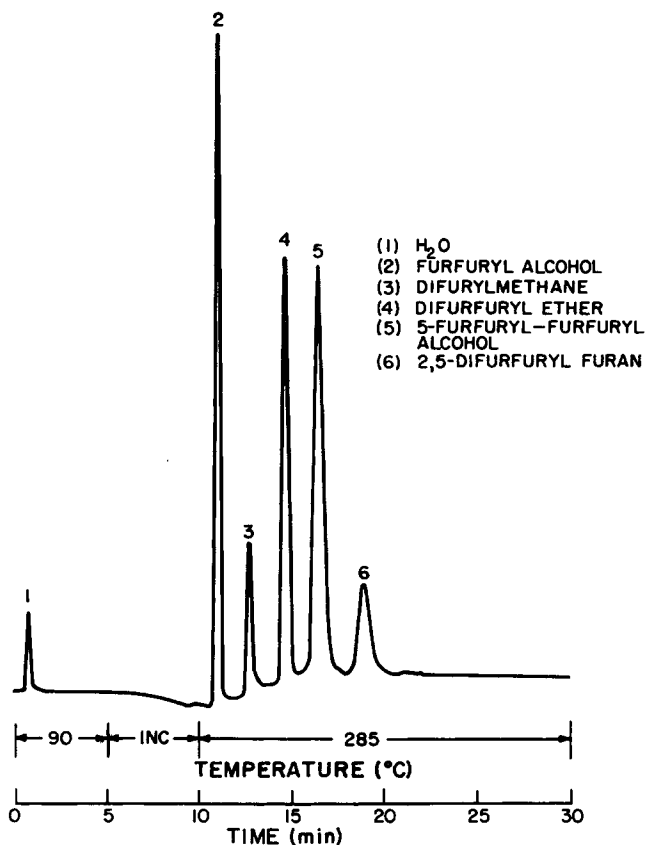


Fig. 2. Gas chromatogram of the volatile components of acid-polymerized furfuryl alcohol resin.

As can be seen from Figure 2, no unexpected major products were found among the low molecular weight components of the acid-polymerized resin. (The component 2,5-difurfurylfuran is the next higher homolog of difurylmethane, and it would be expected to have formed in the same manner as did difurylmethane.) Moreover, considering that no special precautions were taken to exclude oxygen either during distillation or GC analysis, it is interesting to note that no appreciable amounts of oxidation products appear to be present. For that matter, considering the numerous chemical possibilities for such a system, the lack of a significant number of minor components of any kind in the low molecular weight region of the polymer is noteworthy.

The absence of extraneous bands in the NMR spectra of the components indicates that each of the major chromatographic peaks represents a single, relatively pure component. Also, the fragmentation patterns obtained from mass spectrometry could generally be interpreted on the basis of the structures assigned to the components. (Several of the components showed

a tendency to discolor rapidly to a light shade of yellow or brown as they were collected from the GC. This behavior was probably caused by undetectable amounts of highly chromophoric impurities which were either present in the samples as collected or which were formed by the interaction of the isolated materials with their environments.)

A chromatogram composed of the species found in the low molecular weight region of the  $\gamma$ -alumina-polymerized furfuryl alcohol resin is shown as Figure 3. Several of the resin components that were found in the acid-polymerized furfuryl alcohol resin, i.e., furfuryl alcohol, difurylmethane, difurfuryl ether, 2,5-difurfurylfuran, and water, were also present in the  $\gamma$ -alumina-polymerized resin. These resin components were identified by

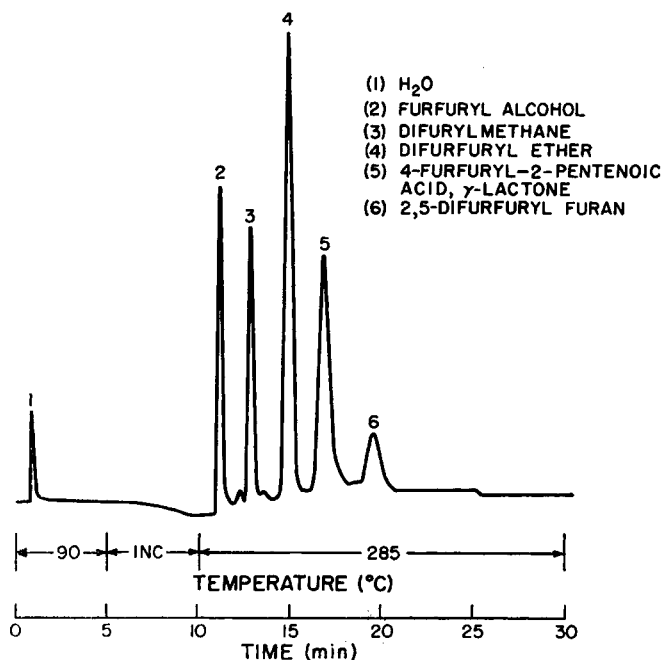
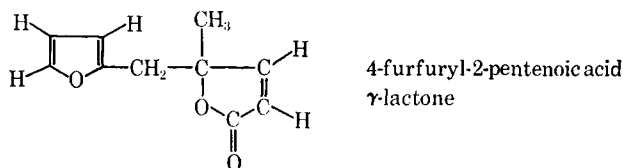


Fig. 3. Gas chromatogram of the low molecular weight components of a  $\gamma$ -alumina-polymerized furfuryl alcohol polymer.

comparing their infrared spectra with the spectra of the previously identified constituents from the acid-polymerized resin. No furfuryl alcohol dimer (5-furfurylfurfuryl alcohol) was isolated from this polymer; however, in an analogous position on the chromatogram, we found a component that, based on IR, NMR, and MS data, we identified as 4-furfuryl-2-pentenoic acid  $\gamma$ -lactone (PAL). This component was not present in the acid-polymerized resin and has not, apparently, been previously considered to be a furfuryl alcohol polymer component. (The presence of the lactone component is not an isolated incident. We found it to be present in a commercial  $\gamma$ -alumina-polymerized furfuryl alcohol polymer as well as in several

other experimental alumina-polymerized resins of differing viscosities which were prepared in our laboratory.)



Conley and Metil<sup>11</sup> discussed the possible presence of a lactone species in a thermally polymerized furfuryl alcohol resin, but they did not have this particular lactone in mind.

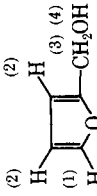
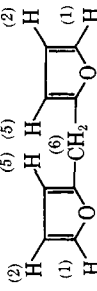

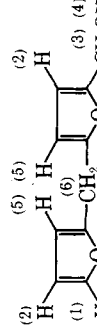
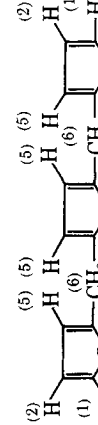
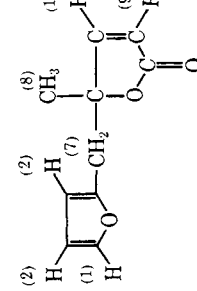
Of considerable interest is our failure to locate an ester (or esters) of levulinic acid among the volatile constituents of the  $\gamma$ -alumina-polymerized furfuryl alcohol resin. Unfortunately, sufficient information on which to base an explanation of this apparent difference between our work and that of Boquist's group is not available.

A comparison of the characteristic properties of PAL with those reported by the IIT group to represent an ester of levulinic acid does not show conclusively whether or not we are even considering the same component. Also, because little is known about the effects of experimental conditions during the  $\gamma$ -alumina-polymerization of furfuryl alcohol on the composition of the resulting polymer, it is not possible to state whether differences in experimental conditions could result in the preferential formation of either PAL or levulinic esters during resin polymerization.

Considering the boiling point of the material reported to be an ester of levulinic acid, it is unlikely that we would have failed to isolate this material during our study had it been present in our resin. So, it appears that either we are dealing with a polymerization system that, under certain circumstances, can result in the formation of differing resin components or that a structural assignment has been erroneously made to a common resin component. Clearly, further study of the chemistry involved in the  $\gamma$ -alumina-polymerization of furfuryl alcohol must be undertaken before an answer to this question can be given.

An examination of Figures 2 and 3 reveals that peak no. 5 of both figures, representing furfuryl alcohol dimer in the case of the acid-polymerized resin and PAL in the  $\gamma$ -alumina-polymerized resin, appear on their respective chromatograms in nearly identical positions with respect to elution times. Further experiments showed that when both components were present in the same sample, they were not resolved. The failure of our chromatograph to resolve these two components would be a serious shortcoming if we were to deal with materials containing both components. Fortunately, we have found no evidence, based on MS, NMR, or IR studies, that the two components ever occur together in any appreciable amounts in the resin types that we have studied. Thus, it appears that, as long as we are concerned with the components of either acid-polymerized furfuryl alcohol

TABLE II  
Assigned Nuclear Magnetic Resonance Chemical Shifts ( $\delta$  Values) and Multiplicities  
of Low Molecular Weight Constituents of Furfuryl Alcohol Polymers<sup>a</sup>

	H <sub>1</sub>	H <sub>2</sub>	H <sub>3</sub>	H <sub>4</sub>	H <sub>5</sub>	H <sub>6</sub>
	7.38 M	6.28 M	4.48 S	4.99 S	—	—
	7.23 M	6.20 M	—	—	6.03 M	3.93 S
	7.35 M	6.27 M	4.42 S	—	—	—
	7.27 M	6.20 M	4.42 S	4.50 S	5.98 M	3.90 S
	7.25 M	6.22 M	—	—	5.98 M	3.91 S
	H <sub>1</sub>	H <sub>2</sub>	H <sub>7</sub>	H <sub>8</sub>	H <sub>9</sub>	H <sub>10</sub>
	7.37 M	6.25 M	3.11 S	1.43 S	5.95 D	7.57 D

<sup>a</sup> S = singlet; D = doublet; M = multiplet.

polymers or  $\gamma$ -alumina-polymerized polymers alone and not with mixtures of the two, the column system and chromatographic conditions we have described will perform satisfactorily.

### Nuclear Magnetic Resonance Studies

The configuration of hydrogen atoms of the low molecular weight components of furfuryl alcohol polymers is such that NMR was of considerable value in identifying these materials. The assigned chemical shifts for the identified polymer components appear in Table II. Chemical shift assignments were made by referring to NMR data for compounds<sup>12,13</sup> which contain proton environments similar to those of the resin components. Also given in Table II is the multiplicity resulting from band splitting.

Compelling evidence for the structure of PAL was particularly obtained from NMR data. The presence of the furfuryl group is well established by comparison of the spectrum of PAL with the NMR spectra of the other resin components. The chemical shift of the methyl hydrogen singlet ( $\delta = 1.43$ ) is such as to indicate that the methyl group is attached to a quaternary carbon atom. Also, the presence of the conjugated ethylenic group of PAL is supported by a symmetrical pair of doublets with identical splitting ( $J = 5.8$  cps) which appear at substantially different positions in the spectrum ( $\delta = 5.95$  and  $7.57$ ). These bands have been assigned to resonances of the two hydrogen atoms attached to the neighboring ethylenic carbon atoms. The positions and splitting of these bands indicate that each of the ethylenic protons exist in an environment that differs widely from the other and that there are no protons attached to the atoms adjacent to each end of the ethylenic group.

Only the spectrum of PAL showed any evidence of NMR bands due to extraneous impurities. These low-intensity impurity bands, which appeared between 1.7 and 4.8 ppm, could not be assigned to a molecular structure; however, they are not due to furfuryl alcohol dimer and do not appear to be due to levulinic acid or its esters.

### Infrared Spectroscopy Studies

The infrared spectra, or the main-peak band positions, of many of the furfuryl alcohol resin components have been previously reported.<sup>9,14</sup> We obtained good agreement between our spectra and those data appearing in the literature. However, the IR spectra of PAL and 2,5-difurfurylfuran have not been reported previously.

Interpretation of the infrared spectrum of PAL is complicated by the presence of the numerous bands due to the furfuryl group. However, corroborative evidence for the  $\alpha,\beta$ -unsaturated  $\gamma$ -lactone structure can be obtained by an examination of the 1600- to 1800- $\text{cm}^{-1}$  region of the spectrum.

A strong carbonyl stretching band peaking at 1755  $\text{cm}^{-1}$  is found in the IR spectrum of PAL. The relatively high frequency of the band appears to be characteristic of lactone or ester carbonyl groups.<sup>15</sup> However, more substantial evidence for the origin of this peak is provided by the fact that

the carbonyl band of PAL is nearly identical, with respect to peak shape and position, to that of the similar molecule, 4-methyl-2-pentenoic acid  $\gamma$ -lactone, as reported by Angell et al.<sup>16</sup> Qualitatively, the carbonyl band of PAL also appears similar to those of several other  $\alpha,\beta$ -unsaturated  $\gamma$ -lactones reported by Angell's group. However, caution must be exercised when making the latter comparisons, since the spectrum of PAL (and of 4-methyl-2-pentenoic acid  $\gamma$ -lactone) were recorded from thin films of pure sample, while the spectra of the other lactones were examined as solutions.

Of further interest is a weak band appearing in the spectrum of PAL at  $1603\text{ cm}^{-1}$  which can be attributed to the conjugated double bond in the lactone ring. Again, the spectra of the substituted  $\alpha,\beta$ -unsaturated  $\gamma$ -lactones reported by Angell and his co-workers proved useful for comparison purposes. In nearly all instances, including, of course, 4-methyl-2-pentenoic acid  $\gamma$ -lactone, a weak band near  $1600\text{ cm}^{-1}$  is observed in the spectra of these lactones, providing further evidence for the existence of the unsaturated lactone ring of PAL.

The infrared spectrum of 2,5-difurfurylfuran would be expected to resemble that of its homolog, difurylmethane. In fact, all of the bands of 2,5-difurfurylfuran, with the exception of three medium-intensity bands found at  $1562$ ,  $976$ , and  $790\text{ cm}^{-1}$  are found in the spectrum of difurylmethane. It is reasonable to assume that these bands are attributable to excitations associated with the center furan ring of 2,5-difurfurylfuran.

### Mass Spectrometry Studies

Each separated polymer component was subjected to mass-spectral analysis where molecular structure information was obtained utilizing both precise mass measurements and fragmentation patterns. Such information, coupled with NMR and IR data, proved sufficient to identify the furfuryl alcohol polymer components. In general, the mass spectra of the resin components obtained in the study agreed with the limited information available in the literature.<sup>17,18</sup>

Because of its uniqueness, particular attention was given to the behavior of PAL when subjected to electron fragmentation. Precise mass measurement established its empirical formula as  $\text{C}_{10}\text{H}_{10}\text{O}_3$ . Also, the major fragment ions of PAL supported the proposed structure. There were, however, no unique peaks in the spectrum that based on MS analysis alone would establish the identity of PAL unequivocally.

The behavior of furfuryl alcohol polymer components when subjected to electron bombardment is of considerable interest to us and will be the subject of a later publication.

### SUMMARY

Gas chromatography on a Porapak type P-S partitioning agent has been shown to be a useful method of separating the low molecular weight components of furfuryl alcohol polymers. Sufficient resolution was obtained

so that the polymer components could be collected and subsequently identified by infrared, nuclear magnetic resonance, and mass-spectrometric analyses. It is expected that the low molecular weight constituents of furfuryl alcohol resins will reflect the composition of the higher molecular weight material. Such information about the resin constituents will be of value in exploring the behavior of these polymers when they are utilized as binders in the manufacture of graphite.

The authors are appreciative of the assistance throughout the course of this study of Mr. Tomas G. Sanchez of LASL Group CMF-13. We additionally wish to thank Dr. Michael D. Coburn and Mr. Frank M. Muse of LASL Group GMX-2 for their assistance in the collection and interpretation of the NMR data.

This work was done under the auspices of the United States Atomic Energy Commission, and with the support of the National Aeronautics and Space Administration.

### References

1. C. H. Riesz and S. Susman, *Proceedings of the Fourth Conference on Carbon*, Pergamon Press, New York, 1960, p. 609.
2. J. M. Dickinson and E. M. Wewerka, *Carbon*, **8**, 249 (1970).
3. A. P. Dunlop and F. N. Peters, *The Furans*, Reinhold, New York, 1953, p. 220.
4. T. Shono and Y. Hachihama, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **56**, 520 (1953).
5. J. Mistrik and S. Bobula, *Chem. Zvesti*, **15**, 625 (1961).
6. A. P. Dunlop and F. N. Peters, *Ind. Eng. Chem.*, **34**, 814 (1942).
7. Y. Hachihama and T. Shono, *Technol. Rept. Osaka Univ.*, **4**, 413 (1954).
8. K. Takano, *Nippon Kagaku Zasshi*, **79**, 955 (1958); *C. A.*, **54**, 4530e (1960).
9. C. W. Boquist, E. R. Nielson, H. J. O'Neil, and R. E. Putecher, *WADD Tech. Rept. 61-72*, Vol. XV, Armour Research Foundation, Chicago, 1963.
10. E. R. Nielsen, U.S. Pat. 2,681,896 (1954).
11. R. T. Conley and I. Metil, *J. Appl. Polym. Sci.*, **7**, 37 (1963).
12. L. M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed., Pergamon Press, New York, 1969.
13. N. S. Bhacca, D. P. Hollis, L. F. Johnson, E. A. Pier, and J. N. Shoolery, *High Resolution NMR Spectra Catalog*. Vols. I and II, Varian Associates, Palo Alto, 1962 and 1963.
14. K. Takano, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **82**, 373 (1961).
15. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., Wiley, New York, 1958, p. 178.
16. C. L. Angell, B. S. Gallagher, R. Ito, R. J. D. Smith, and R. N. Jones, *The Infrared Spectra of Lactones*, NRC Bulletin No. 7, National Research Council, Ottawa, 1960.
17. M. Stoll, M. Winter, F. Gautschi, I. Flament, and B. Willhalm, *Helv. Chim. Acta*, **50**, 628 (1967).
18. *Catalog of Mass Spectra Data*, American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa. 1947 to 1960.

Received January 20, 1971