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Chemistry

AEC RESEARCH AND DEVELOPMENT REPORT

MASTER

CHARACTERIZATION OF POLYFURFURYL
ALCOHOL RESINS

C. R. Schmitt

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE Y-12 PLANT

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

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Nuclear Division

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ABSTRACT

Various physical and chemical test methods and analyses were investigated and evaluated for their suitability in distinguishing differences in different types and batches of commercial, partially polymerized furfuryl alcohol resins. The methods studied included optical and electron microscopy, infrared analysis, water and alcohol film spreadability, thermogravimetric-differential thermal analysis, gel permeation chromatography, centrifugation, ultraviolet fluorescence, halogenation, X-ray radiography, cryogenic X-ray diffraction, and ultrasonic attenuation.

Most tests failed to show significant differences in various batches; however, molecular weight, differential thermal analysis, and film spreadability tests showed significant differences.

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SUMMARY

Laboratory investigations were made of various physical and chemical test methods that might be useful for distinguishing differences in various types and batches of commercially procured, partially polymerized furfuryl alcohol resins.

Optical and electron microscopy showed the presence of small polymer particulates ($\sim 15\mu$) in batches of two types of commercial Varcum that were examined. These particulates could be removed from the polyfurfuryl alcohol resin by high-speed centrifugation.

Low-density carbon foam specimens that had been made from different fractions of centrifuged polyfurfuryl alcohol resin indicated that significant improvements in the compressive strength and other properties of the foam are possible by fractionation of the liquid resin into controlled gradients of molecular size and molecular weight by high-speed centrifugation techniques.

Other characterization test methods studied included: infrared analysis, thermogravimetric-differential thermal analysis, gel permeation chromatography, ultraviolet fluorescence, water and alcohol film spreadability, halogenation, X-ray radiography, cryogenic X-ray diffraction, and ultrasonic attenuation.

INTRODUCTION

Interest in low-density carbon honeycomb and carbon foam as structural materials and the use of various extruded resin-bonded bodies as nuclear reactor materials has prompted an investigation of the physical and chemical properties of the polyfurfuryl alcohol resins used for the preparation of these materials. The fabrication of carbon honeycomb⁽¹⁾ uses a polyfurfuryl alcohol resin (Varcum, Type 8251)^(a) as an impregnant material prior to coking, which has a viscosity of approximately 200 - 300 centipoise. For the fabrication of carbon foam, ^(2 - 4) a more viscous type of polyfurfuryl alcohol resin (Varcum, Type 8266) having a viscosity of approximately 7,000 - 14,000 centipoise is used in a polyurethane foam formulation prior to coking. Although viscosity is one physical property which affects the quality of these coked materials, it is only one of many which needs to be controlled. Other important properties of the polyfurfuryl alcohol resins which also affect the final quality, uniformity, and strength of these coked materials include: acidity, water content, and hydroxyl number, and these also need to be controlled. The viscosities and molecular size distribution of furfuryl alcohol resin binders were also shown^(5 - 8) to be important properties which greatly affect the fabrication and physical or mechanical properties of extruded resin-bonded and graphitized bodies made from them.

Investigation of various means of strengthening the low-density carbon foam materials made at the Oak Ridge Y-12 Plant^(b) was of primary interest. Recently, ⁽⁹⁾ it was shown that hole and indentation-type structural defects in the cell walls were present in the foams while these foams were still in the uncoked condition, and it was indicated that better characterization of the raw materials from which these foams are made, together with improved control of mixing and formulation variables, might prevent or eliminate some of these abnormalities. Thus, the primary objective of this study was to investigate and determine various physico-chemical characteristics of the polyfurfuryl alcohol resins to form some basis for the development of a more comprehensive quality control specification to permit the fabrication of more uniform, reproducible, and trouble-free low-density, high-strength carbon foam and honeycomb products of acceptable quality.

(a) A product of Reichhold Chemicals, Inc-Varcum Chemical Division, Niagara Falls, New York.

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

INVESTIGATION OF THE POLYFURFURYL ALCOHOL RESINS

EVALUATION OF NEW AND AGED VARCUM 8251

Optical and Electron Microscopy

Both a "new" and an "old" lot of liquid polyfurfuryl alcohol resin (Varcum, Type 8251), having a viscosity of approximately 300 centipoise, were examined by optical and electron microscopy to discern any differences that might be useful for characterizing different batches of this material so that a set of quality control specifications, tests, and analyses might be formulated. The new lot of Varcum 8251 was approximately three months old; the old lot had been stored at room temperature (25° C) for approximately 18 months.

A suspension of the Varcum in a furfuryl alcohol monomer^(c) was prepared by ultrasonic dispersion and then centrifuged. Solid particulates were found which were re-suspended in ethyl alcohol and centrifuged several times until all color in the ethyl alcohol had disappeared. The amounts of solids removed from equal volumes of new and old Varcum 8251 are compared in Figures 1 and 2. The starting material in each case is shown in the tube at the left and the collected solids after centrifuging on the right. The solids appeared to be an orange-to-yellow color when suspended in ethyl alcohol, and straw colored when dried. Some shrinkage of the particles occurred at room temperature after the ethyl alcohol had evaporated.

Particle-size measurements were made on particles in the dry state from material dispersed on glass microscope slides. Particle-size distribution data on the centrifuged particles for the two Varcum 8251 batches are given by the graph of Figure 3. These data, obtained with a Zeiss particle analyzer from photomicrographs, (10) showed that the average sizes of the particles in the new and old Varcum resins were 13 and 16 microns, respectively; maximum diameters of the particles in the new and old Varcum resins were 23 and 35 microns, respectively.

Optical and electron microscope examination of the solids showed that the new lot of Varcum contained a large number of chain-like particles and small spherical particles which were soft and rubbery. Spherical particles were also found in the old lot of Varcum, but these particles were harder and more perfect spheres. Photomicrographs of solid spherical particulates separated from the new and old Varcum batches are presented in Figure 4 and 5, respectively.

A summary of the physical and chemical analyses on the new and old lots of liquid polyfurfuryl alcohol resin (Varcum 8251) is given in Table 1. These data indicate that there is no significant differences between these two batches of material with

(c) Manufactured by the Quaker Oats Company-Chemicals Division, Chicago, Illinois.

M-4647

Figure 1. SOLIDS CENTRIFUGED FROM A "NEW" BATCH OF VARCUM 8251.

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Figure 2. SOLIDS CENTRIFUGED FROM AN "OLD" BATCH OF VARCUM 8251.

Figure 3. PARTICLE-SIZE DISTRIBUTION OF SOLID PARTICULATES IN "NEW" AND "OLD" LOTS OF VARCUM 8251 (Logarithmic Plot)

regard to density, percent solids, water content, aldehyde, or coke residue after heating in argon to 1, 400° C.

Infrared Spectra

An infrared scan of the new and old lots of Varcum was made and compared to that of freshly distilled furfuryl alcohol which is the monomer material from which the Varcum was prepared by the vendor. The infrared spectra for these materials, as seen in Figure 6, showed no significant differences between the new and old Varcum. Both of these partially polymerized resin materials, however, had infrared spectra which were considerably different from the freshly distilled furfuryl alcohol monomer.

Halogenation Tests

Halogenation studies were conducted to determine if Varcum 8251 could be characterized by the amount of halogen consumed, thus reflecting the degree of unsaturation. In this case only the olefinic double bonds were considered to be present. Of the classical halogenation procedures developed for the analysis of vegetable and animal oils and fats, two were chosen as being most appropriate to Varcum: iodine monochloride (ICI) and pyridine sulfate dibromide ($C_5H_5N-H_2SO_4 \cdot Br_2$). These reagents were reacted with the two samples of Varcum designated as "new" and "old".

Iodine monochloride, 0.1 N concentration in glacial acetic acid, was the first reagent tested. Upon adding this reagent to a chloroform solution of Varcum (0.03 - 0.08 gm Varcum in 20 - 25 mls solvent) an immediate formation of black particulate matter resulted, possibly due to polymerization and/or oxidation. Nevertheless, a series of aliquots of these two Varcum samples was prepared. Each aliquot was immediately placed in a light-free environment upon the addition of the monochloride reagent and removed after one hour. Potassium iodide was added prior to titrating with 0.1 N sodium thiosulfate. Due to the black color, it was necessary to use a pH meter with platinum-silver bromide electrodes to detect the end point. There was a wide deviation, entirely unpredictable, between aliquots of each of these samples.

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Figure 4. PHOTOMICROGRAPH OF PARTICLES FROM A "NEW" BATCH OF VARCUM 8251. (Particles Separated by Centrifugation; 160X)

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Figure 5. PHOTOMICROGRAPH OF PARTICLES FROM AN "OLD" BATCH OF VARCUM 8251. (Particles Separated by Centrifugation; 160X)

Table 1
COMPARATIVE PHYSICAL AND CHEMICAL PROPERTIES OF SAMPLES
FROM NEW AND OLD LOTS OF VARCUM 8251

	Liquid Furan Resin	
	New Lot	Old Lot
Viscosity (centipoise at 25° C)	314	280
Density (at 24.3° C)	1.198	1.197
Percent Solids ⁽¹⁾	53.9	52.6
Percent Aldehyde (as furfural)	1.9	1.9
Percent Water (by Karl Fischer method)	0.64	0.56
Saponification Number ⁽²⁾	19.6	15.4
Hydroxyl Number	210	221
Percent Coke Residue ⁽³⁾	22.53	23.25
Molecular Weight (osmometry method)	242	272
Infrared Analysis	(4)	(4)
Fluorescence	None Observed	None Observed

(1) Based on residue weight after heating resin in an open cup for three hours at 135° C.

(2) Milligrams of potassium hydroxide consumed per gram of sample.

(3) Based on heating resin in an argon atmosphere to 1,400° C over a 24-hour period.

(4) See Figure 6.

Figure 6. INFRARED SPECTRA OF DISTILLED FURFURYL ALCOHOL AND "OLD" AND "NEW" BATCHES OF VARCUM 8251.

Thus, differentiation between the "new" and "old" batches of Varcum 8251 by iodine consumption could not be made.

Pyridine sulfate dibromide, 0.1 N in glacial acetic acid, was the second reagent tested. This reagent when added to a chloroform solution (0.1 – 0.8 gm Varcum in 20 – 25 ml solvent) of the sample did not cause black particles to form, and the relatively light color permitted a visual end-point detection. Again, however, reproducibility with one batch of Varcum was poor and unpredictable, though experimental techniques were carefully controlled.

The deviation between the "new" and "old" batches of Varcum was not significant; thus, it was concluded from these experiments that the bromination approach to Varcum characterization was not sufficiently sensitive to be of much value.

EVALUATION OF VARCUM 8266

Optical and Electron Microscopy

Two batches of liquid polyfurfuryl alcohol resin (Varcum, Type 8266), which were known to provide carbon foam materials of "normal" and "low" characteristics, designated as normal-strength foam (NSF Varcum) and low-strength foam (LSF Varcum), respectively, were also examined by various physical and analytical techniques to evaluate those methods that might be useful for preparing a quality control specification for the Varcum 8266 which has a viscosity of approximately 7,000 centipoise.

Using a centrifugal separation technique involving partial dilution of the extremely viscous liquid Varcum with approximately 50 volume percent furfuryl alcohol monomer, solid particulates were collected from the NSF and LSF Varcum and examined by optical and electron microscopy. The total yield of solid particulates from 1.0-milliliter samples of both the NSF and LSF Varcum was approximately the same; ie, 0.12 to 0.15 milliliter. When viewed in bulk, the collected particles from the NSF Varcum were straw-yellow to orange-yellow in color; whereas, the collected particles from the LSF Varcum were brown to brown-black. Photomicrographs showing typical dispersed particles from the NSF and LSF Varcum are given in Figures 7 and 8, respectively.

As shown in Figure 7, large particles from the NSF Varcum appear optically to be individual, rounded units having smooth surfaces. An electron micrograph of some of the typical large particles removed from the NSF Varcum is seen in Figure 9. An electron micrograph showing a tubular structural form of a particle that was common to both NSF and LSF Varcum is shown in Figure 10. This type of resin particle appears to consist of rolled-up tubes of thin films of resin. An electron micrograph showing typical particles found in the LSF liquid Varcum is presented in Figure 11. These particles appear to be agglomerate masses of connected particles. Agglomerated particles of this general form and appearance were only found in the LSF liquid Varcum.

A particle-size distribution analysis of ethanol-washed solid particulates removed from the NSF and LSF Varcum 8266 batches is reported in Table 2. These data

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Figure 7. PHOTOMICROGRAPH OF PARTICLES FROM NSF VARCUM 8266. (Particles Separated by Centrifugation; 160X)

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Figure 8. PHOTOMICROGRAPH OF PARTICLES FROM LSF VARCUM 8266. (Particles Separated by Centrifugation; 160X)

PEM-200-9321

Figure 9. ELECTRON MICROGRAPH OF PARTICLES REMOVED FROM NSF VARCUM 8266. (25,800X)

PEM-200-9319

Figure 10. ELECTRON MICROGRAPH SHOWING TUBULAR-TYPE PARTICLES FOUND IN NSF AND LSF VACUUM 8266. (13, 200X)

(a) PEM-200-9325

(b) PEM-200-9318

Figure 11. ELECTRON MICROGRAPHS OF INTERCONNECTED PARTICLE CLUSTERS THAT ARE TYPICAL OF LSF VARCUM 8266. (13, 200X)

Table 2
ZEISS PARTICLE-SIZE DISTRIBUTION OF ETHANOL-WASHED SOLIDS
REMOVED FROM NSF AND LSF VARCUM 8266

Percent $\leq$ the Given Diameter ⁽¹⁾	Particle Diameter (microns)	
	NSF Resin ⁽²⁾	LSF Resin ⁽²⁾
10	5.5	7.0
25	7.0	8.8
50	9.0	11.0
75	11.5	13.0
90	13.6	15.5
100	17.0	21.0

- (1) This signifies the percent of the particles having a particle diameter equal to or smaller than the corresponding numbers shown in the particle diameter column.
- (2) Quality of Varcum is based on the quality and characteristics of the carbon foam castings produced from the resin.

indicate that particles having a slightly larger diameter are associated with the LSF Varcum, which presumably is associated with its more highly agglomerated condition.

Water and Alcohol Film Spreadability

A film-spreadability test for characterizing the NSF and LSF batches of the highly viscous liquid Varcum was also developed. Definitive differences in the two batches of resin have been observed using distilled water and ethyl alcohol as suspending agents. The NSF resin showed a smooth, continuous film in which the particles were more highly interconnected; whereas, the LSF resin showed a rough-edged, non-homogeneous film of partially isolated particles. Figures 12 and 13 are photographs showing the typical appearance of films formed by suspending some of the NSF and LSF Varcum in distilled water.⁽¹⁰⁾

Results on the resin film-spreadability test in distilled water, as shown in Figures 12 and 13, appear to be reproducible. For this test, a glass Petri dish (9 cms in diameter) was half filled with distilled water and a small globule of Varcum placed in the center of the dish. A resin film formed on the water and became enlarged due to differences in surface tension. The Petri dish was covered and allowed to stand for 24 hours. An environmental reaction occurred involving Varcum, air, and possibly water, resulting in the polymerization of a thinned-out film of resin on the liquid surface. As seen in Figures 12 and 13, substantial differences in the visual appearance of the films were obtained for the NSF and LSF liquid resins.

Thermogravimetric-Differential Thermal Analyses

Comparative Mettler thermogravimetric-differential thermal analytical data obtained on the NSF and LSF liquid Varcum 8266, as given in Figure 14, also showed definite differences in these two batches of materials. The NSF resin exhibited an

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Figure 12. APPEARANCE OF NSF VARCUM 8266 RESIN FILM FORMED IN DISTILLED WATER.

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Figure 13. APPEARANCE OF LSF VARCUM 8266 RESIN FILM FORMED IN DISTILLED WATER.

Figure 14. THERMOGRAVIMETRIC-DIFFERENTIAL THERMAL ANALYSES OF THE NSF AND LSF VARCUM 8266.

exotherm at 268° C; whereas, the LSF resin exothermed at a significantly lower temperature (240° C). Secondary exotherms also occurred at 343 and 340° C for the NSF and LSF resins, respectively. These data are in general agreement with molecular weight, hydroxyl number, and other data obtained on the NSF and LSF summarized in Table 3. The comparative Mettler thermogravimetric-differential

Table 3
COMPARATIVE PHYSICAL AND CHEMICAL ANALYSES OF
NSF AND LSF VARCUM 8266

	Varcum 8266	
	NSF	LSF
Viscosity (centipoise)	7,000	7,700
Acid Number	1.7	1.7
Hydroxyl Number	140	152
Hydroxyl Value (%) ⁽¹⁾	3.85	4.56
Percent Water (by Karl Fisher method)	0.47	0.51
Average Diameter of Ethanol-Washed Solids Removed by Centrifugation (microns) ⁽²⁾	9.0	11.0
Molecular Weight, As-Received (average) ⁽³⁾	385	372
Molecular Weight, Acetone-Rinsed Solids (average) ⁽³⁾	1,041	944
Differential Thermal Analysis, Exotherm Temperature (° C)	268	240
Film-Spreadability Test (distilled water suspension)	Smooth, Pinhole-Free, Homogeneous	Irregular, Nonhomogeneous, Containing Pinholes
Film-Spreadability Test (ethyl alcohol suspension)	Slow Rate of Coloration	Rapid Rate of Coloration
Cryogenic X-Ray Diffraction (-80° C)	Amorphous	Amorphous
Ultraviolet Spectra	(4)	(5)

(1) Conducted by the ORGDP Laboratory using a modified procedure.

(2) By a Zeiss microscope method.

(3) By osmometry method.

(4) See Figure 15.

(5) See Figure 16.

thermal data, shown in Figure 14 for the NSF and LSF Varcum 8266, were obtained by heating a 309-milligram quantity of resin in a platinum crucible under flowing argon at a controlled heating rate of 4° C per minute.

Ultraviolet Fluorescence

Ultraviolet fluorescence studies were made of the NSF and LSF Varcum 8266, but no fluorescence of these materials in the as-received condition from the vendor was observed. After removing the solid particulates from both Varcum batches by diluting with furfuryl alcohol and centrifuging, the solid particulates exhibited some fluorescence under ultraviolet radiation. Ultraviolet spectra of tetrahydrofuran solutions of the solids removed from the NSF and LSF Varcum are shown in Figures 15 and 16, respectively. These spectra did not indicate any significant differences between the two Varcum batches.

Figure 15. ULTRAVIOLET SPECTRA OF SOLIDS FROM NSF VARCUM 8266. (Dissolved in Tetrahydrofuran)

Figure 16. ULTRAVIOLET SPECTRA OF SOLIDS FROM LSF VARCUM 8266. (Dissolved in Tetrahydrofuran)

Cryogenic X-Ray Diffraction

A preliminary cryogenic X-ray diffraction study of the NSF and LSF Varcum 8266 was made to ascertain whether any differentiation between these two materials could be observed using low-temperature X-ray diffraction techniques. Liquid nitrogen was used as the cooling agent for the low-temperature diffractometer attachment to attain a temperature of -80°C as the diffractometer scan was made. Preliminary results showed both types of Varcum 8266 to be amorphous at this temperature.

Ultrasonic Tests

Ultrasonic attenuation, capacitance, and microwave dielectric measurements on NSF and LSF batches of Varcum 8266 were also investigated, but these methods will require further study before becoming useful for Varcum quality control.

For the ultrasonic attenuation tests⁽¹¹⁾ with Varcum, the ultrasonic velocity and critical angle of reflection properties were evaluated first. Equal liquid depths of the NSF and LSF Varcum 8266 in a tube were analyzed for a comparative loss of intensity of the first reflection of a wave produced by an immersed 2.25×10^8 hertz, lead titanite-zirconate transducer. This test gave a relative measure of attenuation between the two materials. Since the wave path length was equal for both liquid samples, the comparative velocity was measured by observing the amount of time required for a wave to return to the transducer. Neither velocity nor attenuation was found to vary measurably between the two Varcum batches.

Critical angle of reflection measurements were obtained by covering the Varcum with a layer of water; and, using this method to couple the transducers and Varcum, the intensity of the reflected signal from the surface of the Varcum was observed as the angle of the transducer was varied. The angle at which the ultrasonic signal reached minimum amplitude was noted and found to be equal for each lot.

The dielectric properties of each lot of Varcum were observed using microwaves and capacitance techniques.⁽¹¹⁾ Capacitance was measured by the use of a parallel-plate capacitor and capacitance bridge. A series of readings was made, but these values were found not to vary between the two Varcum lots tested. Next, microwave energy at a frequency of 1×10^{10} hertz as transmitted by a wave guide impinged upon the surface of the Varcum. The energy was either attenuated or reflected, causing standing waves which were recorded on the X-Y recorder. The response was the same for each lot. It was found, however, that microwave dielectric measurements could readily distinguish between water, furfuryl alcohol monomer, and Varcum.

CHARACTERIZATION OF VARCUM 8251 AND 8266

Centrifugation Studies

A study was made of the characterization of Varcum 8251 and 8266 by centrifugation. Samples of Varcum 8251 and 8266, both undiluted and after diluting with 50 volume percent furfuryl alcohol monomer, were centrifuged at 20,000 rpm at the ORGDP Biophysical Limnology Laboratory to determine the gradients in density and molecular weight at various liquid depths in the centrifuge tube.

Density determinations were made after centrifugation by removing aliquots of the gradient solution at various liquid depths using a band recovery apparatus⁽¹²⁾ equipped with a motor-driven syringe and a 22-gauge, blunt-point needle. For Varcum 8251, liquid density gradient values from 1.181 to 1.185 gms/cc were obtained at liquid depths of 10/32 and 60/32 inch in the centrifuge tube. A variation of density with the liquid depth of Varcum 8251 is indicated in Figure 17. Variation of density with liquid depth of a 50 volume percent Varcum 8251-50 volume percent furfuryl alcohol monomer mixture is illustrated by the graph of Figure 18. Figure 19 shows the variation of liquid density with refractive index for a 50 volume percent Varcum 8251-50 volume percent furfuryl alcohol monomer mixture after centrifuging at 20,000 rpm. Variation of the average molecular weight of Varcum 8251 and 8266 at various liquid depths after centrifuging at 20,000 rpm is given in Table 4.

Figure 17. CENTRIFUGATION DENSITY GRADIENT FOR VARCUM 8251.

Figure 18. CENTRIFUGATION DENSITY GRADIENT FOR A 50 VOLUME PERCENT VARCUM 8251-50 VOLUME PERCENT FURFURYL ALCOHOL MIXTURE.

Figure 19. VARIATION OF DENSITY WITH REFRACTIVE INDEX FOR A 50 VOLUME PERCENT VARCUM 8251-50 VOLUME PERCENT FURFURYL ALCOHOL MIXTURE AFTER CENTRIFUGATION.

As Table 4 indicates, somewhat erratic results were obtained in attempting to correlate the average molecular weight by osmometry with the liquid depth of centrifuged Varcum 8266. It is believed that some correlation of molecular weight or molecular size with liquid depth may be obtained by refinements of the molecular weight method or by gel permeation chromatography analyses of the various centrifuged polymer fractions.

Table 4
VARIATION OF LIQUID DEPTH OF VARCUM IN A CENTRIFUGE TUBE
WITH MOLECULAR WEIGHT

Liquid Depth (inch)	Average Molecular Weight ⁽¹⁾	
	Varcum 8251	Varcum 8266
10/32	229	391
20/32	230	386
30/32	237	397
40/32	233	373
50/32	245	379
60/32	245	391

(1) By osmometry. Precision of the analytical method estimated to be ± 2.5 per-cent.

Fractionated Varcum Foam

Two carbon foam specimens were made using two different fractions of centrifuged Varcum 8266 in the polyurethane foam formulation⁽²⁾ and compared after coking at 1,000° C in an inert gas atmosphere. The carbon foam made with the heavy centrifuged fraction which contained a high percentage of polymer particulates was badly deformed in appearance, exhibited a nonuniform cell structure, and showed a very low compressive strength of approximately 25 psi. In contrast, carbon foam made with the centrifuged fraction from which the polymer particulates had been removed showed a more uniform cell structure, a density of 0.050 gm/cc, and a compressive strength of 75 psi (using unbonded platens and tested parallel to the direction of rise of the foam). These results indicate that significant improvements in the compressive strength and other structural properties of the foam are possible by fractionating the liquid Varcum into controlled gradients of molecular size and molecular weight by high-speed centrifugation techniques. Methods for predicting the trajectories in centrifuged force fields of particles having diameters from one to fifty microns were reported by Burson,⁽¹³⁾ and experimental results were shown to be in excellent agreement with the theoretical predictions. Thus, the fractionation of Varcum into particulate-free gradients of controlled molecular size and weight should not be very difficult.

Gel Permeation Chromatography

Typical gel permeation chromatograms of Varcum 8266 and 8251 and furfuryl alcohol monomer are given in Figure 20. By using the chromatographic method, the molecular size distribution of the partially polymerized furfuryl alcohol resin can be readily compared since the larger sized polymer molecules require larger elution volumes to elute them from the gel column system. As seen in Figure 20, a single molecular peak was found at an elution volume of 41 milliliters for the furfuryl alcohol monomer, which corresponds to the presence of a single molecular species; ie, the furfuryl alcohol monomer. Distinct differences were noted in the chromatograms of Varcum 8266 and 8251 that are indicative of the various polymer fractions of discrete molecular size and the presence of some monomer furfuryl alcohol.

Figure 20. TYPICAL GEL PERMEATION CHROMATOGRAMS OF VARCUM 8266 AND 8251 AND FURFURYL ALCOHOL MONOMER.

Gel permeation chromatographic studies were made on four batches of Varcum 8266 that were known to produce large differences in the quality of production-scale, low-density carbon foam castings when these resins were used with the same polyurethane foam formulation. A summary of the molecular size distribution of these resins, arbitrarily designated as LSF, NSF, and "high-exotherm" foam (HEF Varcum) resin types, is given in Table 5. Physical and chemical analyses, comparing the NSF and HEF batches of Varcum 8266, are reported in Table 6. An inspection of the data in these two tables shows that no significant differences exist that might account for observed differences in the polyurethane foam casting behavior for these batches of Varcum.

Table 5
MOLECULAR SIZE DISTRIBUTION OF VARCUM 8266 BY GEL
PERMEATION CHROMATOGRAPHY

Varcum Designation(1)	NSF	NSF	LSF	HEF Exotherm(2)
Drum Number	84875	810885	84873	810874
Molecular Size (A)	Percent	Percent	Percent	Percent
10 - 30	37.17	38.01	38.96	37.53
31 - 45	17.68	17.13	17.67	18.01
46 - 80	17.67	17.28	17.11	17.27
81 - 155	14.94	15.15	14.98	15.533
156 - 345	9.96	10.12	9.39	9.69
346 - 560	1.73	1.68	1.50	1.68
Over 560	0.86	0.64	0.39	0.29

- (1) Quality of the Varcum is based on the quality and characteristics of the carbon foam castings produced.
 (2) High exotherm (HEF) refers to the excessive internal heat that is developed by the carbon foam castings.

Table 6
COMPARATIVE PHYSICAL AND CHEMICAL ANALYSES OF NSF AND
HEF VARCUM 8266

Varcum Designation(1)	NSF	HEF(2)
Drum Number	810885	810874
Density (gms/ml)	1.2231	1.2093
Hydroxyl Number(3)	135.9	136.4
Acid Number	2.0	2.0
Percent Water (by Karl Fischer)	0.49	0.54
Molecular Weight (osmometry)	-	369

- (1) Quality of the Varcum is based on the quality and characteristics of the carbon foam castings produced.
 (2) High exotherm (HEF) refers to the excessive internal heat that is developed by the carbon foam castings.
 (3) Obtained by a Y-12 method, ASTM Designation D1638-61T.

Solubility Studies

Several organic solvents were tested for general solubility purposes. Liquid Varcum 8251 and 8266 dissolved readily in nitrobenzene, dimethylformamide, tetrahydrofuran, chloroform, toluene, and trichloroethylene.

Cloud-Point Studies

Attempts to characterize the old and new batches of Varcum 8251 and the NSF and LSF batches of Varcum 8266 of higher viscosity by cloud-point or freezing-point determinations were unsuccessful. Furfuryl alcohol monomer forms clear solutions in water; but, upon cooling, a point is reached when such an aqueous solution clouds due to the insolubility of the alcohol at a certain temperature. Cloud-point determinations are, therefore, used to designate the quality of the furfuryl alcohol monomer. Concentrations of the Varcum as low as five volume percent,

while apparently clear, were so highly colored they made it impossible to determine an end-point measurement of clouding or freezing with any certainty.

X-Ray Radiography Tests

X-ray radiography studies were made on Varcum 8251 and 8266 to determine whether polymer particulates which have been identified in Varcum would settle out after prolonged settling. After a prolonged settling period (six weeks at 25° C) under quiescent conditions, the radiographs showed no detectable density gradient between the top and bottom portions of the settling tubes. X-ray radiographs of NSF and LSF Varcum 8266 before and after a six-weeks settling period at 25° C were made (Figure 21).

EVALUATION OF THE DUREZ POLYFURFURYL ALCOHOL RESINS

Physical and chemical characterizations of three other commercially available liquid polyfurfuryl alcohol resins^(d) were also evaluated. Physical and chemical analytical data which characterize these resins (Durez D-14383, D-16470, and D-18719) are summarized in Table 7. Gel permeation chromatograms of the three Durez polyfurfuryl alcohol resins which show large differences in molecular size distribution are given in Figures 22 through 24.

DISCUSSION

The commercial liquid polyfurfuryl alcohol resins used in this study are partial polymerization products of furfuryl alcohol. The formation of thermosetting, partially polymerized liquid resins from furfuryl alcohol in the presence of acidic substances has been known since the nineteenth century.⁽¹⁴⁾ The polymerization of furfuryl alcohol is somewhat complex in that several competing reactions and interactions between reaction products can occur.

According to Dunlop and Peters,⁽¹⁵⁾ furfuryl alcohol heated in the presence of an acidic catalyst is subject to three competing reactions to form a variety of products such as: water, 5-furfuryl-furfuryl alcohol, furfuryl ether, levulinic acid, formaldehyde, and di-2-furylmethane.

The initial and predominant reaction is intermolecular dehydration involving the hydroxyl group of one molecule and the active alpha-hydrogen atom of another

(d) Obtained from the Hooker Chemical Corporation - Durez Division.

Figure 21. X-RAY RADIOGRAPHS OF NSF AND LSF VARCUM 8266 AFTER SIX WEEKS SETTLING AT 25° C.

Table 7
PHYSICAL AND CHEMICAL ANALYSES OF DUREZ
FURFURYL ALCOHOL RESINS

Resin Number	D-14383	D-16470	D-18719
Vendor's Viscosity Designation	Medium	Low	Low
Viscosity (centipoise at 25° C)	350	200	200
Density (gms/ml at 25° C)	1.177	1.209	1.214
Acid Number	1.0	0.8	0.9
Hydroxyl Number ⁽¹⁾	260	148	158
Percent Solids ⁽¹⁾	77.9	59.3	59.7
Percent Water (by Karl Fischer)	0.49	0.87	1.48
Average Molecular Weight ⁽²⁾	356	274	275
Molecular Size (A) ⁽³⁾	Percent	Percent	Percent
< 10	-	0.84	1.76
10 - 30	22.02	58.49	57.83
31 - 45	20.51	19.93	19.18
46 - 80	21.13	13.98	14.70
81 - 155	12.66	6.07	6.91
156 - 345	13.47	0.73	1.35
346 - 560	5.62	-	-
561 - 1,000	3.34	-	-
1,000 - 2,100	1.07	-	-
6,100	0.14	-	-
48,000	0.03	-	-

(1) By a Y-12 method, ASTM Designation D1638-61T.

(2) By osmometry.

(3) By gel permeation chromatography.

Figure 22. GEL PERMEATION CHROMATOGRAM OF DUREZ RESIN D-14383. (Elution Volume Shown by Numerals)

Figure 23. GEL PERMEATION CHROMATOGRAM OF DUREZ RESIN D-16470. (Elution Volume Shown by Numerals)

Figure 24. GEL PERMEATION CHROMATOGRAM OF DUREZ RESIN D-18719. (Elution Volume Shown by Numerals)

molecule.⁽¹⁶⁾ Further reaction in the same manner leads to higher-molecular-weight condensation products in which furan rings are linked together by methylene bridges in a linear chain. To a small extent, furfuryl ether is also found; and formaldehyde, resulting from thermal decomposition, is always found in the reaction mixture.⁽¹⁶⁾ Experimental evidence indicates that the formaldehyde recondenses with the intermediate products, and this is conceived to be one way in which the chains become crosslinked.⁽¹⁶⁾ The linkages most likely to be present in cured furfuryl alcohol resins are:

Analyses of Varcum polyfurfuryl alcohol resins for acid number, hydroxyl number, viscosity, percent solids, and water content by the Karl Fischer method have been made routinely for several years at the Oak Ridge Y-12 Plant Laboratory in accordance with a modified ASTM procedure (ASTM Designation D 1638-61T). Although extreme variations in the results obtained by any of these analytical methods were partially indicative of the resin quality with respect to the final product being made, in the case of low-density carbon foam the most reliable criterion of resin quality was the hydroxyl number. As emphasized in Table 3, the viscosity, acid number, and water content of two batches of the manufacturer's lot of Varcum 8266 were all approximately the same; yet, these same two batches exhibited widely different performance characteristics when used to make low-density carbon foam. Thus, the primary objective of this investigation was to initiate, evaluate, and develop other suitable quality control tests or analyses that would enable the formulation of a more comprehensive quality specification for Varcum 8251 and 8266.

The hydroxyl number results from the Y-12 Plant Laboratory, as reported in Table 3, were checked by submitting samples of the NSF and LSF Varcum 8266 to the

ORGDP Laboratory for independent determinations. This laboratory also used the same general method of Ogg, et al,⁽¹⁷⁾ which is based on esterification with acetic anhydride. A pH meter was used for the end-point detection. The method is claimed to react with all hydroxyl groups except those on tertiary carbon atoms and 2, 4, 6-trisubstituted phenols. Although the method of calculation used by the ORGDP Laboratory is different in that the hydroxyl value of the Varcum resin is expressed as percent, good general agreement was obtained between the two laboratories inasmuch as the LSF resin showed the higher hydroxyl value which would indicate that it was in a lower state of polymerization.

As shown by the experimental results, several new characterization tests (such as optical and electron microscopy, centrifugation, gel permeation chromatography and average molecular weight, and film spreadability in water and ethyl alcohol) show considerable promise for differentiating between polyfurfuryl alcohol resins having variant quality characteristics, as judged from their performance in the fabrication of carbon materials.

As exemplified by the data presented in Table 3, two batches of Varcum 8266 which consistently gave normal and low-quality carbon foam castings, showed no significant difference in viscosity, acid number, or water content. However, the molecular weight, differential thermal analysis, and film spreadability tests showed significant differences in these two batches of resin.

As Figure 6 shows, a distinctive absorption band is present in the infrared scans of both samples of Varcum at approximately $1,700\text{ cm}^{-1}$, but is not present in the infrared scan of monomer furfuryl alcohol. This band is indicative of a carbonyl group ($\text{C}=\text{O}$) and suggests the presence of levulinic acid (4-oxopentanoic acid),^(e) a known possible intermediate product involved in the polymerization of polyfurfuryl alcohol resin. Levulinic acid can be formed by hydrolytic ring cleavage of furfuryl alcohol when heated in the presence of an acidic catalyst by the following reaction:

The data, presented in Table 3, are in agreement with the theoretical considerations regarding reasons for the difference in quality between the NSF and LSF Varcum.

(e) Name approved by the International Union of Chemistry.

The analytical data indicate that a primary difference between these two materials is that the LSF Varcum 8266 is in a less highly polymerized state than the NSF resin. This difference is evidenced by the higher hydroxyl number, lower average molecular weight of the as-received resin and acetone-washed solids in the resin, and higher rate of coloration (ie, presumably by extraction) upon exposure to ethyl alcohol for the LSF resin.

Although the ultraviolet spectra, shown in Figures 15 and 16, of solids separated from the Varcum 8266 resins after dissolving in tetrahydrofuran do not show significant differences between the NSF and LSF resins, additional and perhaps differential ultraviolet spectra of Varcum solids should be obtained in future characterization studies before this method is abandoned.

Gel permeation chromatography is a good method for determining the molecular distribution of a polymer according to molecular size.^(18 - 19) Using tetrahydrofuran as a carrier solvent for the polyfurfuryl alcohol resin, a sample was passed through a series of five 4-foot-long columns filled with crosslinked polystyrene gels of different pore sizes. The smaller-sized polymer molecules are able to diffuse more rapidly into the gel matrix and thus have longer retention times than the larger polymer molecules, and require different elution volumes.

Gel permeation chromatography only provides information concerning the distribution of molecular size. Since polymer molecules having the same size are not necessarily of the same molecular weight, a different analytical method (ie, vapor-phase osmometry) was needed to determine polymer molecular weights. In future studies, molecular weight data should be correlated with specific fractions of eluates obtained from gel permeation chromatography to obtain a more meaningful characterization of polyfurfuryl alcohol polymers, and such studies are currently in progress.⁽²⁰⁾

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