FINAL REPORT

HPLC CHARACTERIZATION OF PHENOL-FORMALDEHYDE RESOLE RESIN USED IN FABRICATION OF SHUTTLE BOOSTER NOZZLES

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Prepared for

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ABSTRACT

A reverse phase High Performance Liquid Chromatographic method was developed to rapidly fingerprint a phenol-formaldehyde resole resin similar to Durite® SC-1008. This resin is used in the fabrication of carbon-carbon composite materials from which Space Shuttle Solid Rocket Booster nozzles are manufactured. A knowledge of resin chemistry is essential to successful composite processing and performance. The results indicate that a high quality separation of over 35 peaks in 25 minutes were obtained using a 15 cm Phenomenex LUNA C_8 bonded reverse phase column, a three-way water-acetonitrile-methanol nonlinear gradient, and UV detection at 280 nm.

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I. INTRODUCTION

The performance of Solid Rocket Booster nozzles used to assist the Space Shuttle fleet into low-Earth orbit is related in a fundamental manner to the chemistry of the phenolic resin system used to fabricate carbon-carbon composite material from which these nozzles are manufactured. Recent events during launch have led to questions relative to the initial quality of this resin. A greater than anticipated burn of selected carbon-carbon composite parts was noted on at least two shuttle launches. The possible contribution of the phenolic resin is one of the factors being considered to explain this phenomenon.

The objective of the present research is to develop a High Performance Liquid Chromatography (HPLC) analytical technique to rapidly separate the phenolic resin system into components such that quality can be tracked and documented. HPLC is unchallenged in its ability to separate complex mixtures. The technique is also uniquely suited for quantifying and enabling the identification of key resin components. Thus, HPLC can provide insight into fundamental chemistry pertinent to resin behavior.

A high quality separation with over 35 peaks in less than 25 minutes was obtained using a Phenomenex LUNA C_8 reverse phase chromatographic column and a three-way nonlinear water-acetonitrile-methanol gradient. The parameters established in this study can be further developed into an efficient quality control tool for resin characterization.

A. Phenol-Formaldehyde Resins

Phenol-formaldehyde or phenolic resins are one of the oldest synthetic polymers to achieve widespread application. First processed by Baekeland in the 1890s (1), phenolic resins became popular in the 1920s and 1930s as heat-resistant molded appliance parts and as jewelry under the trade name "Bakelite" (2). Phenolic resins are formed by the acid or base catalyzed reaction of phenol and formaldehyde and are currently used in the production of automotive products, building materials, and selected aerospace components. Resorcinol and alkyl-substituted phenols are used in specialty resins. Properties of interest to the final produce include superior fire resistance, low smoke generation, and resistance to chlorinated solvents.

Phenolic resins form thermoset polymers; once polymerization or cure takes place, the final product will not melt or flow. Extensive crosslinking results from multiple reactive sites on the phenol monomer. Since crosslinked systems are difficult to characterize, the exact molecular structure of cured resin has not been definitely established. The addition of fibers or fabrics to form composite materials make phenolic resins extremely versatile. They constitute a major thermoset polymeric commodity with production exceeding 70 kilotons annually worldwide (2).

Phenolic resins are categorized by the ratio of phenol to formaldehyde and by the method used to achieve catalysis.

1. **Novolac Resins.** Novolac phenolic resins are acid catalyzed prepolymers with an approximate molecular weight of 2000 g/mole. They are thermoplastic until cured and relatively stable at room temperature in the absence of additional formaldehyde. Novolacs cure with the addition of both formaldehyde and heat to yield a crosslinked network polymer. These resins are commonly used in the production of automotive products.

2. **Resole Resins.** Resole resins are base catalyzed prepolymers having excess formaldehyde. Resins typically consist of phenol, formaldehyde and mono-, di-, and tri-substuted phenyl adducts. A typical low molecular weight oligomer is shown in Figure 1. Resole resins are reactive systems which cure with the addition of heat to yield a crosslinked molecular structure. Changes in resin chemistry can occur at room temperature. Resole resins are commonly used as adhesives in the production of plywood. Resorcinol-substituted phenolic resins are one of the starting monomers commonly used in the manufacture of high performance carbon-carbon composite materials.

3. **Base Catalyzed Reaction Mechanism.** The material studied in this research was a base catalyzed resole resin. As shown in Figure 2, the reaction mechanism probably occurs in three primary steps. The first step likely involves a condensation reaction between resonance-stabilized phenol and formaldehyde. The second step then yields the formation of methylene or ester linkages which bridge phenyl rings. These oligomers then cure with heat in the final step to yield a crosslinked or "infinite" molecule. Since this final product is insoluble, its exact molecular structure is difficult to characterize.

4. **Phenolic Resins.** This brief discussion points to the complexity of phenol-formaldehyde resole resins. Not all resole resins are alike. Depending on the chemistry of the monomers, their stoichiometry, and initial reaction conditions, a complex mixture of species is usually present in a typical resin. The chemistry of this heat-sensitive material can also change with time. These phenomena can adversely affect processability and performance. Thus, the chemical characterization of phenolic resins is not a trivial matter.

B. Characterization

Current methods for characterizing phenolic resins used in aerospace application include gel permeation chromatography, infrared spectroscopy, gas chromatography, nuclear magnetic resonance spectroscopy and high performance liquid chromatography. Mechin (3, 4) and Bourdreau (5) developed HPLC separation techniques and isolated fractions for NMR analysis. Figure 3 shows a chromatogram obtained by Bourdreau (5) on a base catalyzed phenolic resin. The numbering of peaks in the figure corresponds with numbering in Bourdreau's original report. Figure 4 gives the molecular structure of seven peaks in Figure 3. Bourdreau determined the molecular structure of at least 30 peaks in the chromatogram (5). While this separation is outstanding, the 2.5 hour analysis time is undesirable. The present research focused on achieving an acceptable separation in less time.

1. **High Performance Liquid Chromatography.** HPLC is an analytical technique which separates components in a mixture at the molecular level. All forms of chromatography are dependent on a stationary phase and a mobile phase. Separation is achieved based on the relative preference of sample components for these two phases.

With HPLC, a silica gel-like material serves as the stationary phase and a liquid serves as the mobile phase. The small particle stationary phase is tightly packed into a narrow-diameter stainless steel tube or column. Due to the pressure drop associated with HPLC columns, pressure is required to force the liquid phase through the column of a reasonable rate. This feat is achieved using a high pressure pump.

HPLC is conveniently divided into two disciplines: normal phase chromatography and reverse phase chromatography. The normal phase technique utilizes a polar stationary phase such as silica gel and a nonpolar mobile phase such as isooctane.

Reverse phase chromatography utilizes a nonpolar stationary phase and a polar mobile phase. Active polar –OH groups on the surface of silica gel are replaced with chemically bonded nonpolar groups such as normal alkyl chains. Water and accetonitrile are common reverse phase mobile phases. Many variations on these two techniques are practiced.

Two types of elution are common in HPLC analysis. In isocratic analysis, the concentration of polar or nonpolar solvents in the mobile phase remains constant throughout the separation. In gradient elution analysis, the polarity of the mobile phase is systematically changed. Gradient elution for normal phase chromatography involves changing the mobile phase polarity from non-polar to more polar. Mobile phase polarity for reverse phase gradient elution changes from polar to less polar. Gradient elution allows better control of component selectivity and often results in improved resolution. The effect of gradient elution in liquid chromatography is similar to that of temperature programming in gas chromatography.

Analyte detection is often achieved using ultraviolet (UV) absorption although detection based on refractive index, mass spectroscopy, infrared, and electrochemical principles are also used. With UV detection, a detector wavelength is selected where the mobile phase does not absorb. The sample peak is then detected as it elutes the column. The UV signal is attenuated, especially with specimens such as phenolic resins which are highly conjugated. Qualitative and quantitative information is obtained from elution volume or retention time and peak area. Other techniques such as NMR or mass spectroscopy must be used to establish the chemical identify of an eluted peak.

A more detailed description of HPLC can be found in numerous textbooks on the subject.

2. **The Present Chromatographic Approach.** Based in large part on previous work, reverse phase HPLC was chosen for this research. Selected C_{18} and C_8 bonded phase columns were evaluated and several polar mobile phases were examined. A UV detector was used. Gradient elution was eventually employed because this technique enabled the analysis of the widest range of sample components.

II. EXPERIMENTAL

A. Materials

The resole-type phenolic resin used in this study was similar to Durite® Phenolic Resin SC-1008, manufactured by Borden Chemical, Inc., Columbus, OH. Typical properties for Durite® SC-1008 are given in Table I.

A similar resin system containing 5μm chopped carbon fiber (Fiberite, Inc., Winona MN) was also examined. This material, designated HT-672, contained approximately 30-60% phenolic resin and 10-30% carbon fiber in isopropanol. HT-672 was an opaque, glassy, black viscous liquid.

Both resin specimens were shipped in dry ice from the NASA-Langley Research Center via commercial overnight delivery. They were maintained below 10°C prior to analysis.

B. Sample Preparation

1. Solubility Study. The solubility of Durite® SC-1108 was visually observed in various solvents at selected pH. For this preliminary evaluation, approximately 0.01g of resin was placed in 0.8 ml centrifuge tubes containing 0.5 ml of solvent. The tube was capped and manually shaken for 5-10 seconds. Results are summarized in Table II.

2. Chromatographic Specimens. Neat Durite® SC-1008 was used for all HPLC development research. The chromatographic specimen was prepared by weighing resin on an analytical balance and then diluting to the desired ppm level (100-1000 ppm) with the appropriate solvents. The sample was then filtered through an ISO-DISC P-252 25-mm PTFE membrane syringe filter with a 0.2μm pore size.

3. Extracted Specimen. A chromatographic sample was extracted from the fiber-containing HT-672 resin by dissolving approximately 0.001g of resin in 5 ml of acetonitrile in a neoprene centrifuge tube. After centrifuging for 5 minutes, a 20μl aliquot of supernatant was filtered and analyzed. Carbon fiber was recovered by decanting the supernatant. The solid residue was washed with methanol, allowed to dry, and optically characterized at the Langley Research Center.

4. Heated Specimen. Ten milliliters of 1000 ppm neat resin in acetonitrile was divided into two 5 ml samples. One sample was maintained at room temperature while the second sample was heated slowly to 100°C and allowed to cool to room temperature. The two specimens were analyzed under identical conditions.

C. Chromatography

1. Instrumentation. Analyses were performed using a Hewlett-Packard 1050 Series High Performance Liquid Chromatograph equipped with a variable wavelength UV detector. Sample was delivered with either a Rheodyne (Cotati, CA) Model 7125 Manual Injector with a 20μl sample loop or a Hewlett-Packard 1050 Series Auto Injector. A Hamilton (Reno, NV) 25μl syringe was used to fill the manual injector loop.

Chromatograms were recorded using a Hewlett-Packard 3394A Integrator. A chromatograph equipped with a Perkin-Elmer 410 LC Pump and a Perkin-Elmer Series 235 Diode Array Detector was used to conduct selected analyses.

2. **Analytical Columns.** Table III lists all high performance chromatographic columns and summarizes their properties. They were manufactured by Phenomenex (Torrence, CA) and made available to this study by various sources.

3. **Mobile Phase.** All mobile phase and sample solvents were HPLC grade and obtained from Fisher Chemical. Methanol, acetonitrile, tetrahydrofuran, and water solvents were filtered using a 0.4μm PTFE filter and vacuum degassed. Mobile phase reservoirs were washed weekly with soap and water.

5. **Method Development.** All separations development work was conducted at room temperature on neat Durite® SC-1008 resin.

a. Isocratic Elution. Isocratic analyses utilized the 15 cm Prodigy column, partial loop-filled manual injection (less than 20μl), 1.0 ml/min flow rate, and 255 nm UV detection.

b. Linear Gradient Elution. The polarity of the mobile phase was changed in a linear fashion using a solvent programmer which was an integral part of the Hewlett-Packard 1050 Series HPLC. The solvent gradient was programmed from high polarity (high water/low organic phase content) to low polarity (low water/high organic phase content). The high organic phase concentration was maintained for 5 to 10 minutes at the end of the gradient before returning to initial conditions. The column was allowed to equilibrate at the initial polarity between analyses. Sample injection, flow rate, and UV detection were the same as for the isocratic technique.

c. Nonlinear Gradient Elution. Initial nonlinear gradient analyses were based on work reported by Bourdreau (5). In general, a slow ramp from 1-5% to 20-30% organic phase was followed by a rapid ramp to 100% organic phase. A 5 to 10 minute hold at this composition was included with each analysis before the mobile phase was returned to initial conditions for column equilibration. Sample was delivered manually or using the auto injector. UV detection at 254 nm and a 1.0 ml/min flow rate were also employed.

d. Photo Diode Array Detection. This technique simultaneously monitored the absorption of sample components from 195 to 370 nm and served as an aid in selecting the optimum detector wavelength for a particular specimen. Several analyses were conducted using the Perkin-Elmer chromatograph and non-linear gradient elution conditions.

6. **Column Purging.** Analytical columns were periodically purged in an effort to maintain a low-noise background and eliminate ghost peaks. The cleaning technique, developed by Kazakevich (6), employed three solvents of varying polarity. Initially, 100% water was pumped through the column at 1.0 ml/min. The mobile phase was then switched to 100% methanol or acetonitrile and, finally, to tetrahydrofuran. A final purge at 100% water completed the cycle. Each new mobile phase composition was maintained for a 3 minute interval. This procedure was repeated until an acceptable background was obtained. Columns were occasionally inverted and flushed with 100% methanol.

III. RESULTS AND DISCUSSION

HPLC is an ideal technique for the characterization of thermally unstable complex mixtures such as phenolic resin systems because analyses are conducted at room temperature. However, a successful separation often results only after a significant amount of time is spent "problem solving" and optimizing various chromatographic parameters. Such was the case with this research. Much of this work was conducted during the summer of 1997 in the Chromatography Laboratory at Virginia Tech. Officially, 250 hours of work were charged to this grant by a student assistant (Jennifer H. Brown). However, the assistant is estimated to have spent over 500 hours on the project. Approximately 275 chromatographic "runs" were conducted at Virginia Tech, of which, about 95% were gradient elution analyses. Diligence was ultimately rewarded. The following discussion is a concise summary of our work.

A. Resin Solubility. The solubility of neat resin was examined in several chromatographic solvents. Results of this inspection are given in Table II. The resin was insoluble in nonpolar solvents such as hexane. This property eliminated normal phase chromatography as a potential analytical method. The material was soluble in methanol, tetrahydrofuran, and slightly soluble in acetonitrile, three standard reverse phase solvents. Solubility at various pH levels was also investigated in the event that the pH of the mobile phase had to be manipulated to enable an acceptable separation. This option turned out to be unnecessary.

B. Isocratic Elution. A 15 cm Prodigy C_{18} reverse phase column, 1.0 ml/min flow rate, and UV defection at 255 nm were selected as initial chromatographic parameters. A simple isocratic elution analysis was the logical first attempt at achieving a separation. Isocratic analyses were conducted using 50/50, 40/60, and 25/75 water/methanol (MeOH) as the mobile phase. Three typical chromatograms obtained are given in Figure 5. These chromatograms exhibit poor resolution and offer little information useful for quality control purposes.

C. Linear Gradient Elution. As anticipated, a simple linear gradient provided an improved separation. Figures 6 and 7 show chromatograms obtained using gradients from 50/50 H_2O/MeOH to 100% MeOH and 90/10 H_2O/MeOH to 100% MeOH respectively. Figure 8 gives similar results for a water/acetonitrile (ACN) gradient. Column, flow rate, and detector wavelength parameters remained the same as for the isocratic analyses. The chromatogram shown in Figure 8 represented a dramatic improvement over previous attempts and established acetonitrile as the mobile phase of choice for this work. About 18 peaks are observed in the chromatogram. However, solubility studies using acetonitrile suggested that, perhaps, all the sample was not being analyzed with this solvent.

D. Nonlinear Gradient Elution. The development of nonlinear gradients proved to provide additional information. Peak resolution was improved and the number of peaks increased from approximately 18 to 35. Results varied depending on the gradient selected and solvent. In general, gradients involving methanol provided results inferior to those obtained with acetonitrile. Figures 9 and 10 give typical H_2O/MeOH and H_2O/ACN nonlinear gradient analyses.

E. Evaluation of Initial Results. Results obtained at this point in our research were deemed "workable" for quality control purposes. On July 30, 1997, a progress report was submitted to the Technical Officer at the Langley Research Center describing our research. A copy of that report is included in Appendix A. A separation with 39 peaks in 30 minutes was documented. We then began to pursue other details considered pertinent to this project.

F. Resin Extraction From HT-672. The HT-672 carbon fiber-containing resin is similar to the actual resin used to produce carbon-carbon composites. Since all HPLC analyses had been conducted on neat Durite® SC-1008 resin, a comparison of samples extracted from HT-672 with the neat resin was necessary to ensure that SC-1008 was a good representative for the carbon-containing resin. Figure 11 shows chromatograms obtained under identical conditions for both neat and extracted specimens. Since the chromatograms were essentially identical, we were confident that work could continue on neat resin only.

G. Heated Samples. Since resole resins are reactive systems, changes in chemistry can occur with time. This phenomenon was demonstrated for SC-1008 by analyzing unheated and heated specimens under identical chromatographic conditions. The preparation of these two samples is discussed in the Experimental section of this report. Figure 12 shows results of this brief study. A large reaction peak was observed after approximately 8 minutes in the chromatogram of heated resin. While not within the scope of our research to follow changes in resin chemistry, we are confident that our chromatographic technique can effectively track resin reaction state.

H. Optimizing UV Detector Wavelength. A Photo Diode Array detector was used as an aid in selecting the optimum UV wavelength for this resin. This detector essentially scanned each chromatographic peak from 195 to 370 nm. A careful analysis of information generated using this technique determined that 280 nm was the preferred wavelength for this work. Figure 13 compares chromatograms of the same sample obtained at 280 nm and 255 nm detector wavelengths. Absorbance at 280 nm was dramatically increased over that observed at 255 nm.

I. LUNA C_8 Column and Three Solvent Gradient Elution. Additional chromatographic columns described in Table III were then evaluated. The LUNA C_8 column produced the highest quality chromatogram from a resolution vs. time perspective. The C_8 column resembled the C_{18} columns but was less "nonpolar" because the bonded alkyl groups were shorter in length. A three-way water-acetonitrile-methanol

gradient was also investigated. We felt more confident including methanol because the resin was completely soluble in that solvent. Thus, more of the sample could likely be chromatographed.

Figure 14 represents the best separation obtained in our research. Approximately 35 peaks were eluted in 25 minutes. We feel the chromatographic conditions associated with this separation are appropriate to quality control the phenolic resin.

J. Additional Comments. Poorly resolved peaks eluting between 20 and 25 minutes in Figure 14 are likely oligomer. Should future work be deemed appropriate, an initial solid phase extraction should be investigated as a means of eliminating this fraction from the sample. The extracted fraction could then be analyzed by Gel Permeation Chromatography. However, its contribution to resin quality may be difficult to establish. The elimination of oligomer would significantly simplify the HPLC characterization of the material.

Future work should also establish how much of the sample is actually being analyzed and how much is remaining on the column. While our chromatograms were quite reproducible, column efficiency deteriorated with time which necessitated periodic regeneration and purging. This question could be answered by collecting the effluent from several runs, evaporating the mobile phase, and weighing the dried residue. Since the amount of sample injected will be known, a comparison of "before" and "after" results would settle the issue.

The identification of various peaks in Figure 14 was not within the scope of the present work. A liquid chromatograph operating under conditions developed in this study and interfaced with a mass spectrometer (LC/MS) should satisfactorily address this problem. However, we feel that key peaks in Figure 14 can be matched with key peaks in Figure 5, which were identified (5). Thus, we have an appreciation for the chemical identity of most peaks in the chromatogram.

K. A Perspective. We are confident that the results of this study are of benefit to the NASA-Langley Research Center and justify the modest funds expended. However, the benefits to Emory & Henry College are immeasurable. Jennifer H. Brown successfully defended an Honors Thesis submitted this Spring in partial fulfillment of her requirements for the Degree of Bachelor of Science (7). Jennifer also presented a summary of her work in April at ScienceFest 98, an undergraduate science symposium sponsored by the Natural Science Division at Emory & Henry College (8). Copies of these works are included with this report.

Ms. Brown also gave a paper on this work at the 1998 Pittsburg Analytical Conference in New Orleans (9), a first for an Emory & Henry College student at an international technical conference. The lessons Jennifer learned as a result of this project will have a profound impact on her. Finally, the Principal Investigator gave a talk at the Annual Meeting of the Virginia Academy of Science in May at George Mason University (10). Copies of key PittCom and VAS slides are also included with this report.

Approximately $1000 remains unspent from this grant. A one-year no-cost extension was requested on June 3, 1998 (See Appendix B), and subsequently approved. Hopefully additional students can be exposed to the excitement of research with these remaining funds.

IV. SUMMARY

The high performance liquid chromatographic analysis of a phenol-formaldehyde resole resin was studied in detail. The resin was similar to the material used to fabricate carbon-carbon composite materials from which Space Shuttle Solid Rocket Booster nozzles are manufactured.

A high quality separation of over 35 peaks in 25 minutes was obtained using a Phenomenex LUNA C_8 bonded phase column, a three-way water-acetonitrile-methanol non-linear gradient, and ultraviolet detection at 280 nm. These parameters can be further developed to provide quality control and reaction state information on the resin.

V. ACKNOWLEDGEMENTS

We express appreciation to Dr. Terry L. St. Clair and the NASA-Langley Research Center for providing the opportunity and funding to pursue this work. Terry is a valued friend, colleague, and mentor. We also acknowledge the wonderful cooperation provided by Prof. Harold M. McNair, a loyal friend, at Virginia Tech. We thank the Friends of the Sciences and the Natural Science Division at Emory & Henry College for their financial support of Jennifer H. Brown at Virginia Tech during the Summer of 1997, and for funds enabling her to attend the Pittsburg Analytical Conference this Spring in New Orleans. We deeply appreciate the continued support of Dr. James M. Dawsey, Dean of the Faculty at Emory & Henry.

Much of this report is the work of Jennifer H. Brown, a recent graduate of Emory & Henry College. It is with a sincere feeling of loss and sadness but also with a renewed faith in our future that we send Jenny off to continue her development in graduate school with Prof. McNair at Virginia Tech.

VI. REFERENCES

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TABLE I. SELECTED PROPERTIES OF DURITE® SC-1008

Solids @ 135°C (%)	60-64
Solvent	isopropanol
Free Formaldehyde (%)	0.6-2.0
Free Phenol (%)	11-18
Viscosity @ 25°C (cps)	180-300
pH at 25°C	7.0-8.5
Get Time @ 135° (min)	11-18
Color	golden yellow

TABLE II. SOLUBILITY OF DURITE® SC-1008 IN SELECTED SOLVENTS

Solvent	Soluble	Comments
Methanol	Yes	Clear Solution
Methanol, pH 9.1	Yes	Clear Solution
Methanol, pH 8.9 buffer	Yes	Clear Solution
Methanol, pH 3.2	Slightly	White Ppt. Formed
Acetonitrile	Slightly	Cloudy Solution
Tetrahydrofuran (THF)	Yes	Pale Yellow Solution
THF, pH 11.2	Yes	Clear Solution
THF, pH 8.2 buffer	Yes	Clear Solution
THF, pH 3.5	Yes	Clear Solution
Hexane	No	Imiscible
Water	No	Waxy Layer Formed
Water, pH 8.5	No	Waxy Layer Formed
Water, pH 6.9 buffer	No	Waxy Layer Formed
Water, pH 2.8	No	Waxy Layer Formed

TABLE III. ANALYTICAL COCUMNS

Identity	Length (cm)	Particle Size (μ)	Pore Size (A)	Bonded Phase	Source
Prodigy	15	5	100	C_{18}	H.M. McNair VPI & SU
Prodigy	10	5	100	C_{18}	H.M. McNair VPI & SU
Columbus	15	5	100	C_{18}	NASA-Langley Research Center
Luna	15	5	100	C_8	Y. Kazakevich, Seton Hall Univ

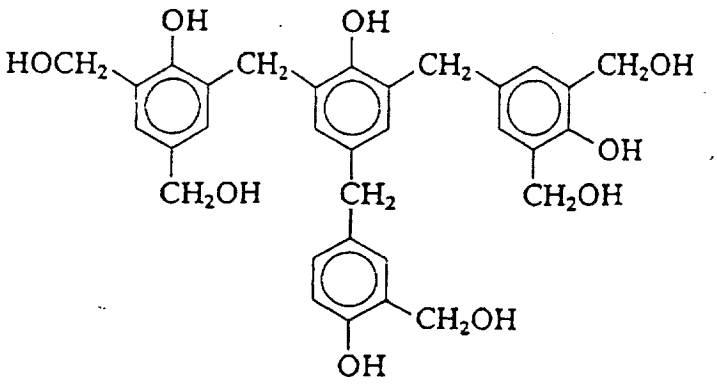

Figure 1. A typical low molecular weight phenolic resole oligomer.

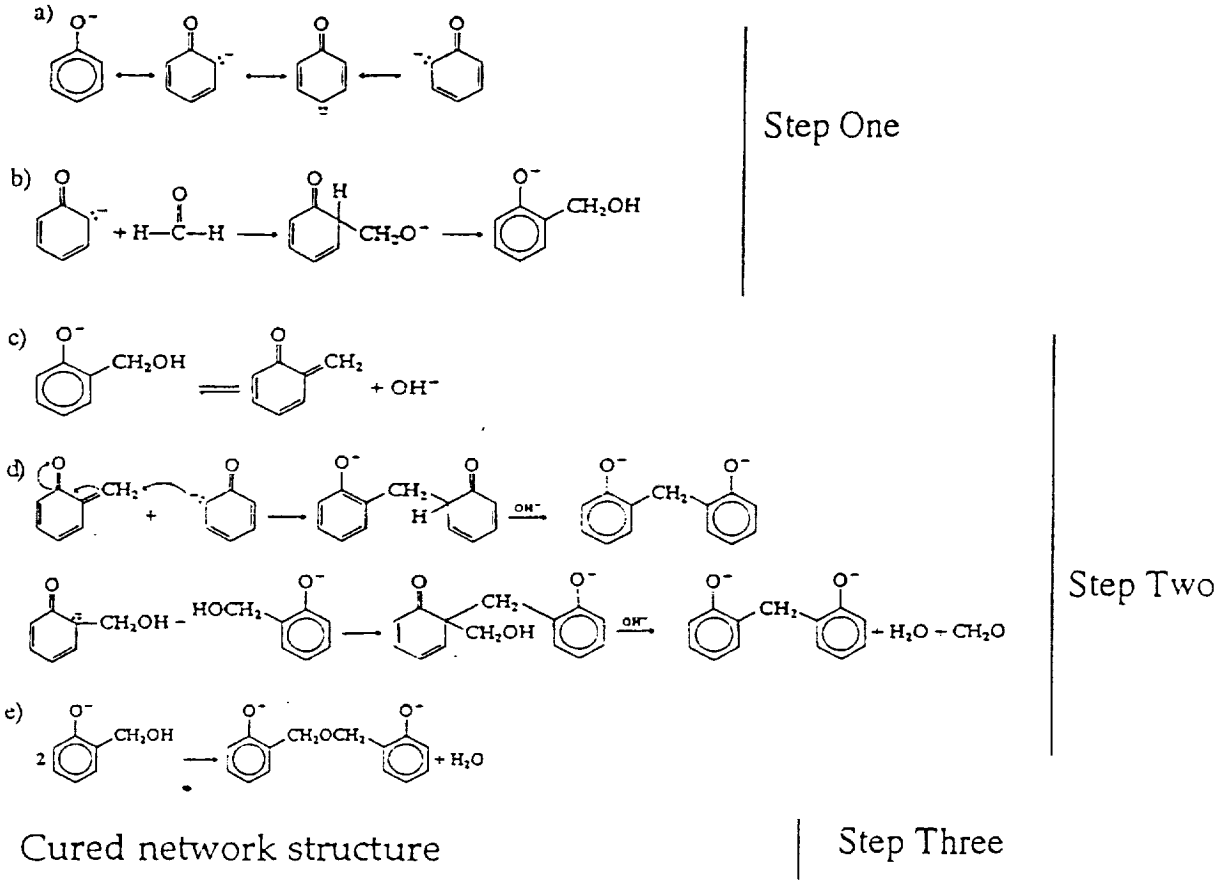

Figure 2. Elementary mechanism for the addition of formaldehyde to phenol. a) deprotonation of phenol resulting in resonance stabilization, b) reaction of phenol with formaldehyde, c) regeneration of OH, d) two routes for the formation of methylene bridges, e) formation of either linkages.

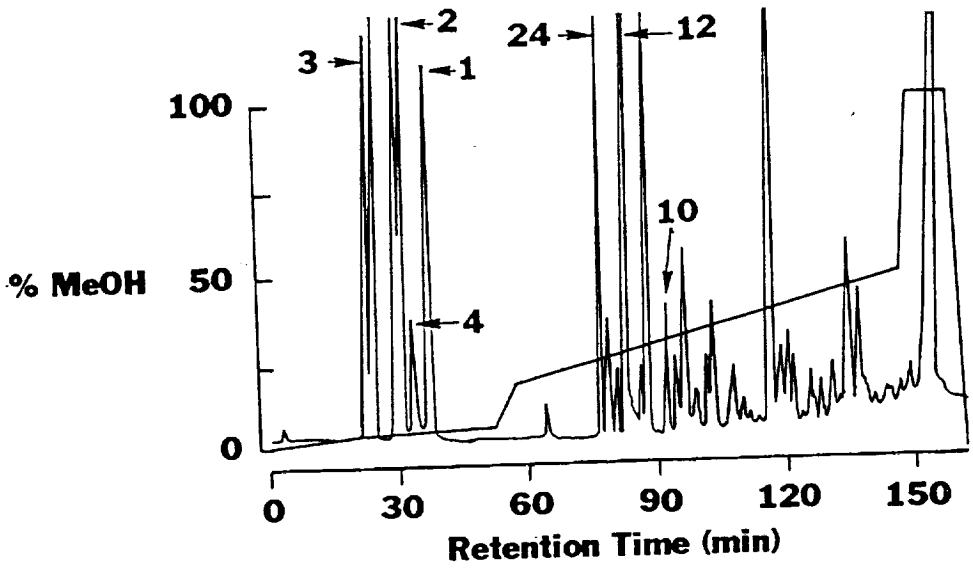

Figure 3. HPLC separation of base catalyzed phenolic resin (5).

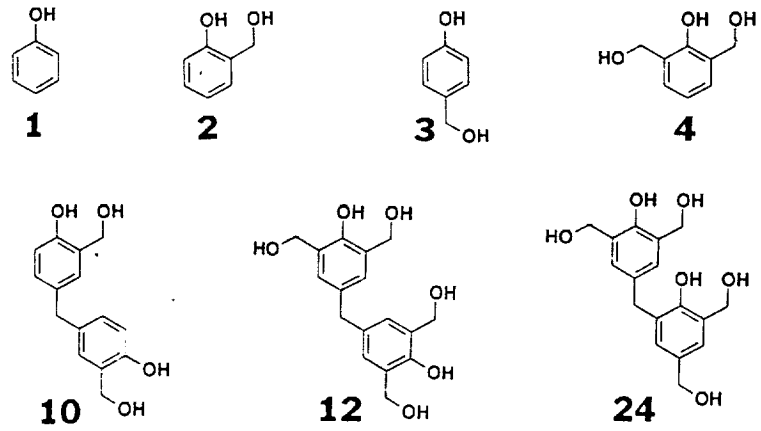

Figure 4. Identification of selected peaks in Figure 3.

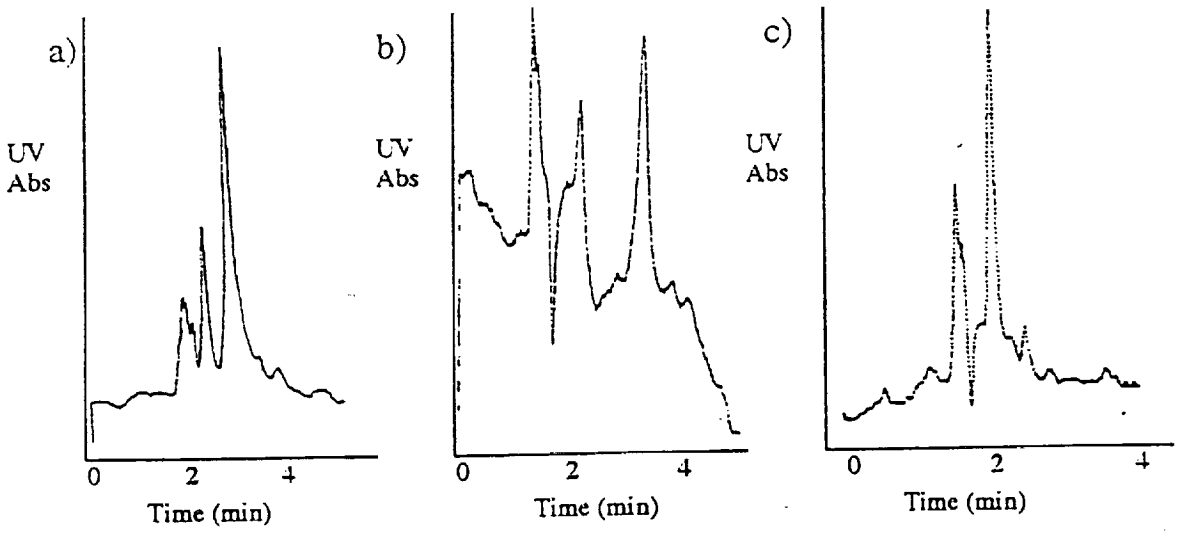

Figure 5. Isocratic HPLC analysis using Prodigy C_{18} column, 1.0 ml/min flow rate and 255 nm UV detector wavelength. b) 50/50 H_2O/MeOH, b) 40/60 H_2O/MeOH, c) 25/75 H_2O/MeOH.

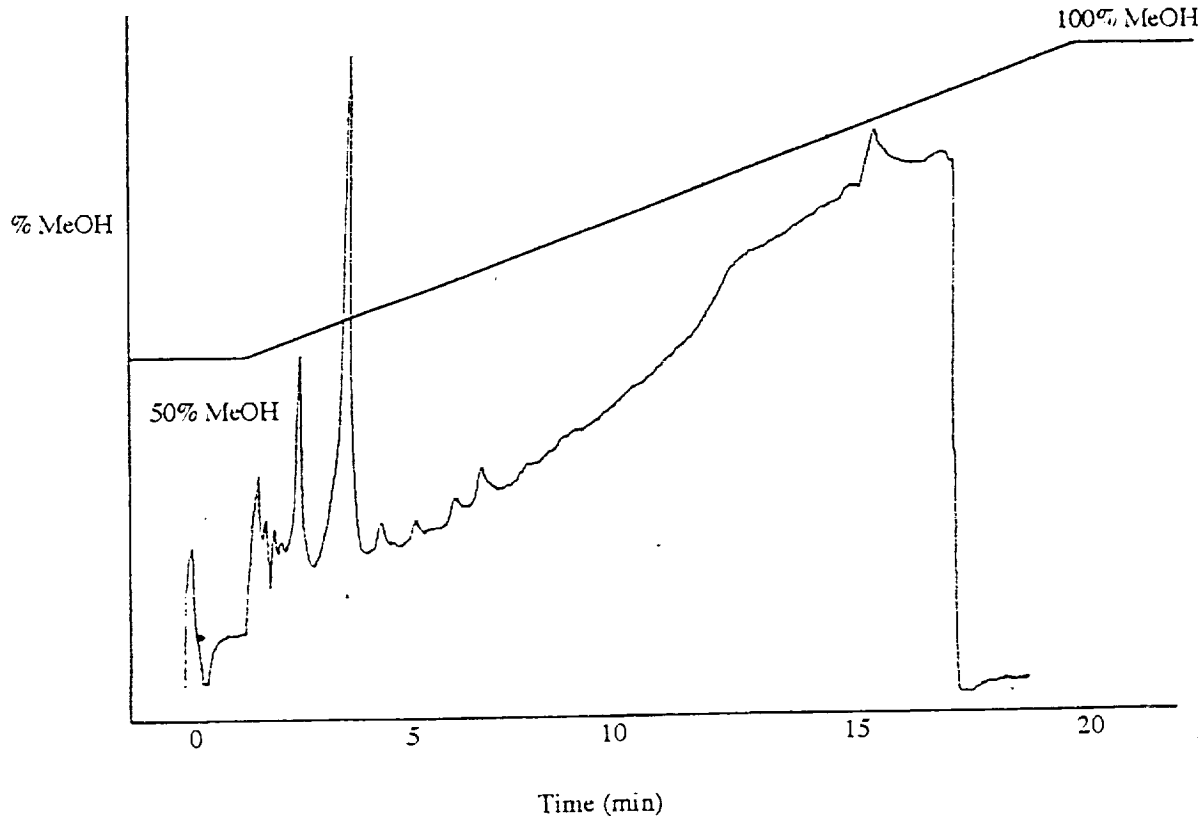

Figure 6. Linear gradient elution analysis. 50/50 H_2O/MeOH to 100% MeOH in 20 minutes using Prodigy C_{18} column.

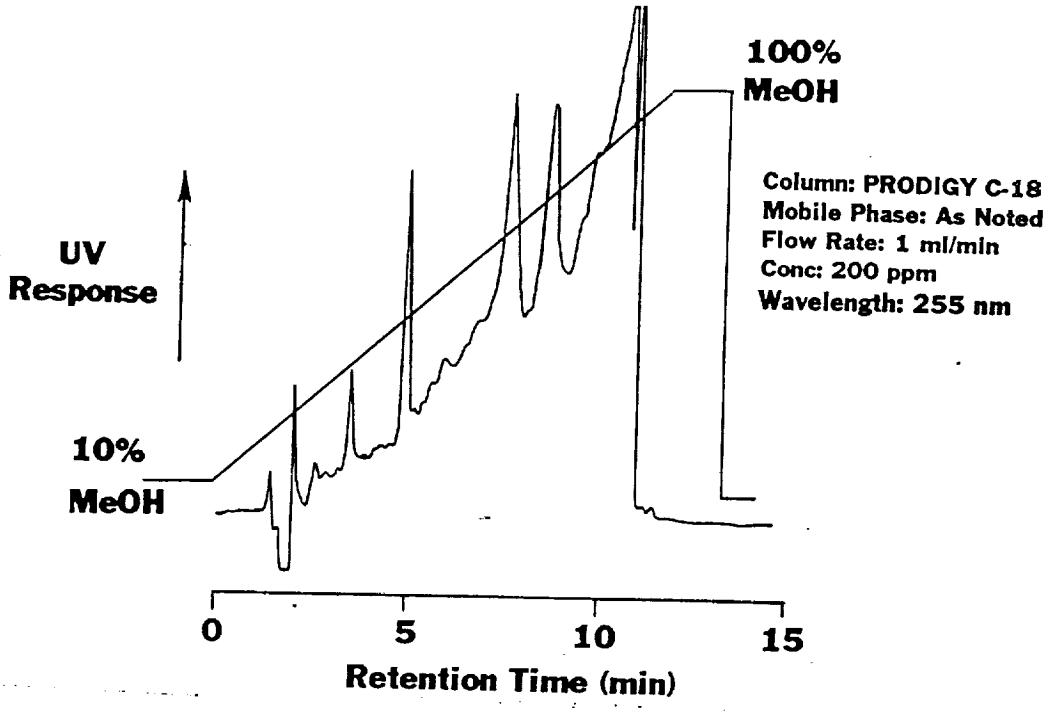

Figure 7. Linear gradient elution analysis. 90/10 H_2O/MeOH to 100% MeOH in 10 minutes using the Prodigy C_{18} column.

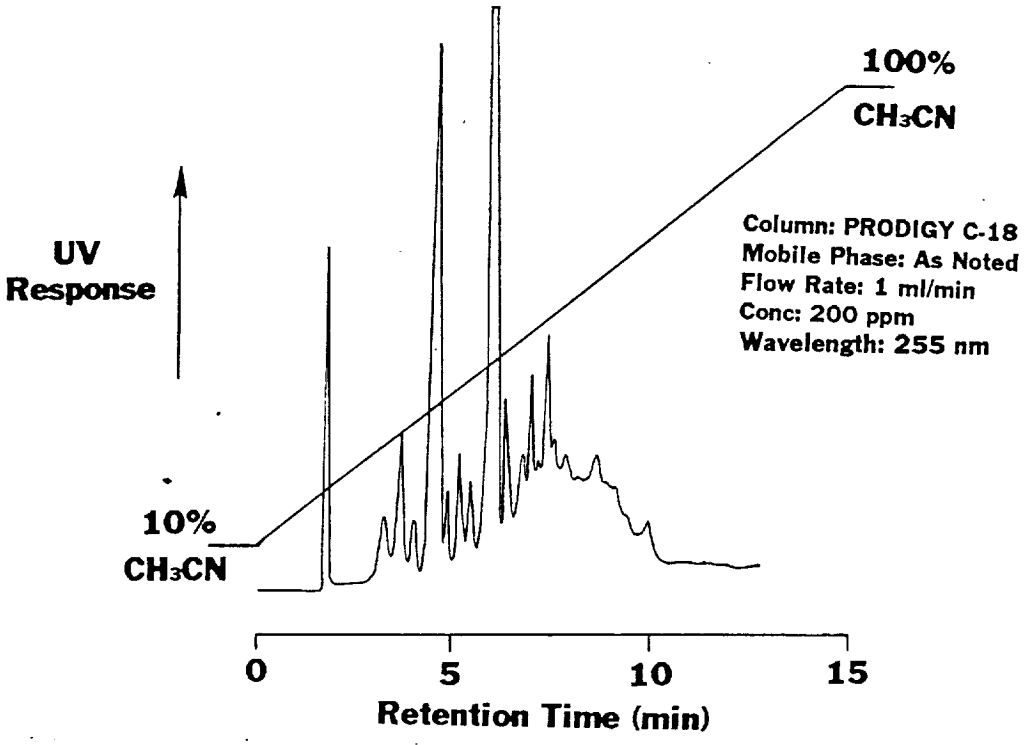

Figure 8. Linear gradient elution analysis. 90/10 H_2O/ACN to 100% ACN in 15 minutes using the Columbus C_{18} column.

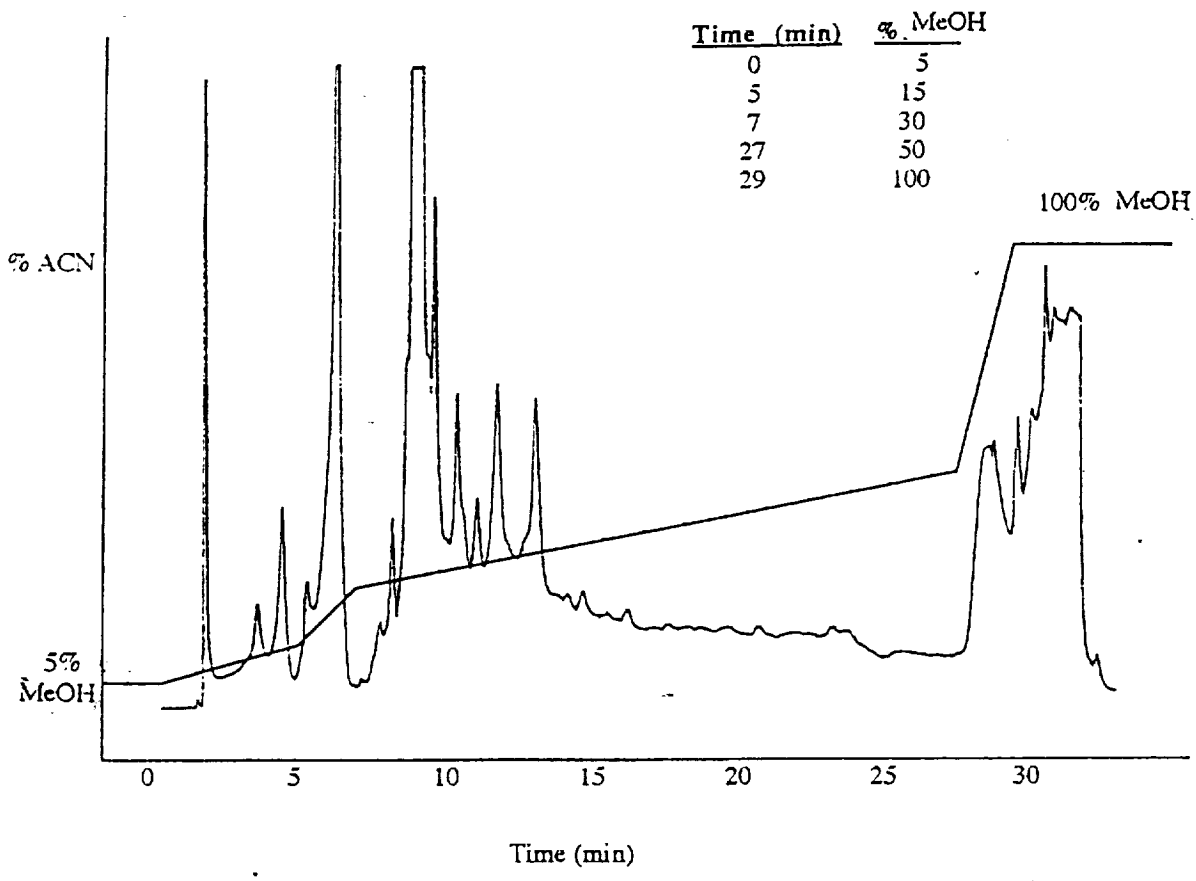

Figure 9. Nonlinear H_2O/MeOH gradient using Columbus C_{18} column.

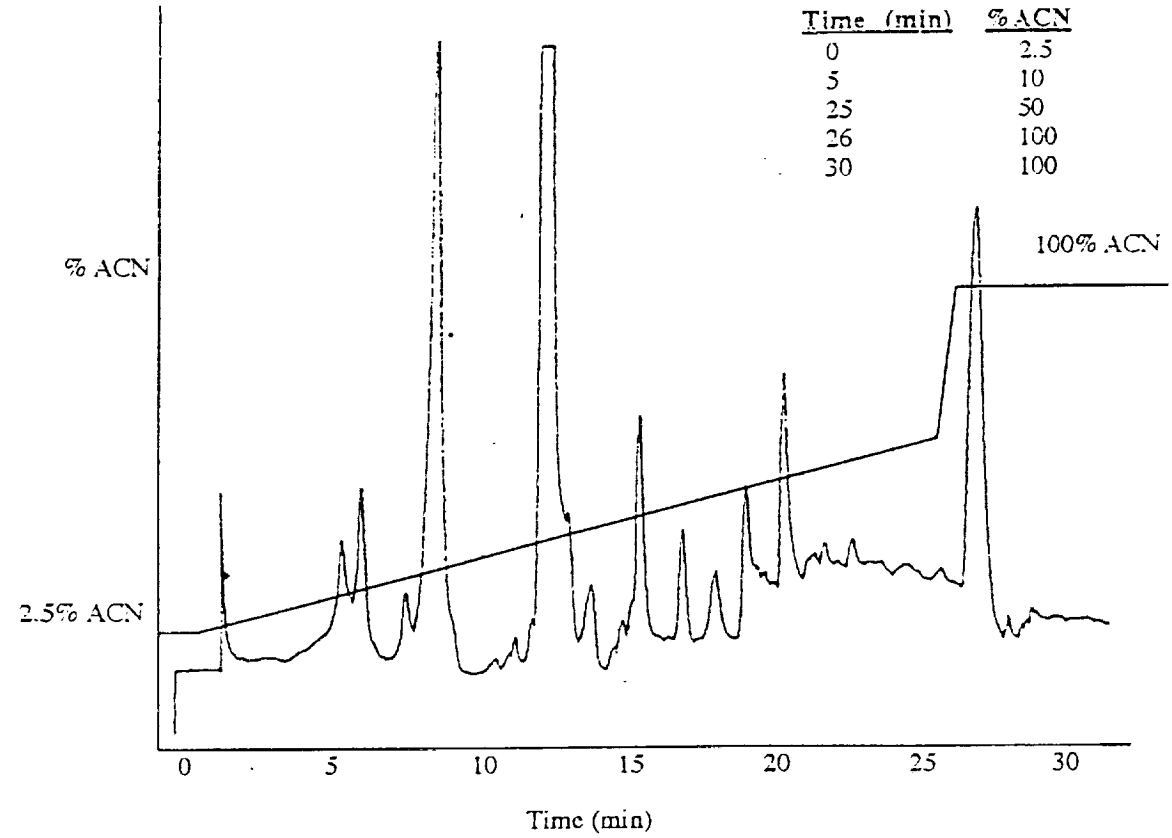

Figure 10. Nonlinear H_2O/ACN gradient using Columbus C_{18} column.

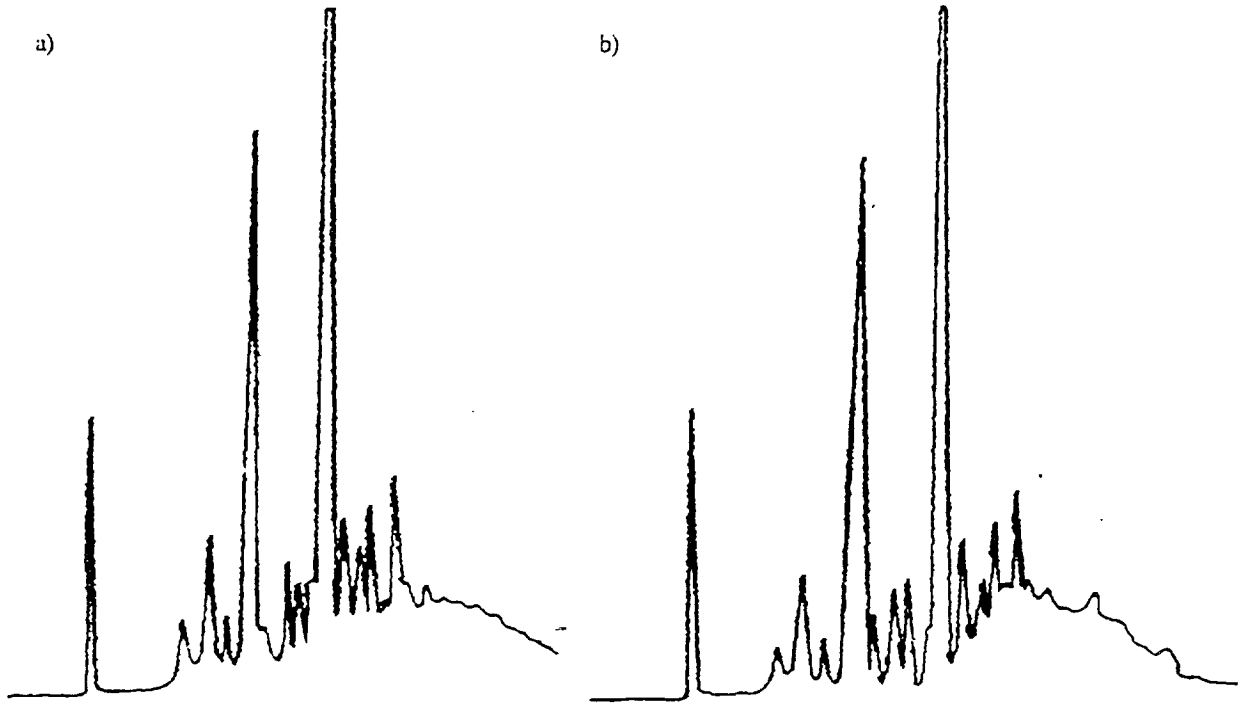

Figure 11. Comparison of neat and extracted resin. a) neat Durite® SC-1008, b) resin extracted from HT-672. Column: Prodigy C_{18}, Mobile Phase: Linear Gradient, 10-100% ACN in 15 minutes, UV Detector: 255 nm.

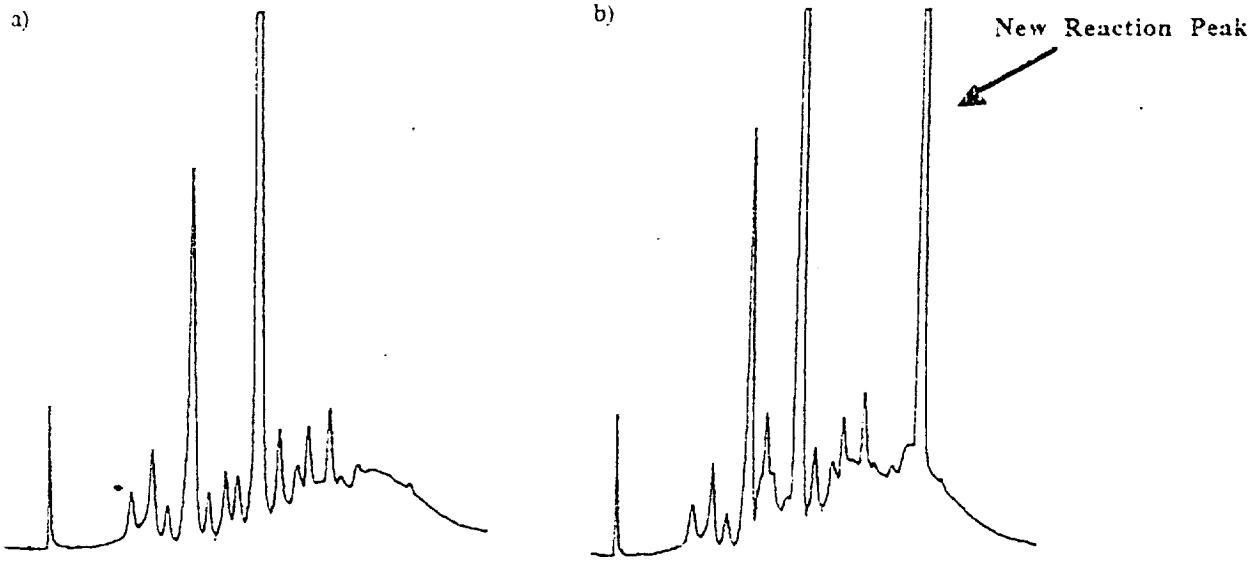

Figure 12. Comparison of unheated and heated Durite® SC-1008 Resin. a) unheated neat sample. b) sample heated to 100°C and cooled. Column: Prodigy C_{18}, Mobile Phase: Linear Gradient, 10-100% ACN in 15 minutes, UV Detector: 255 nm.

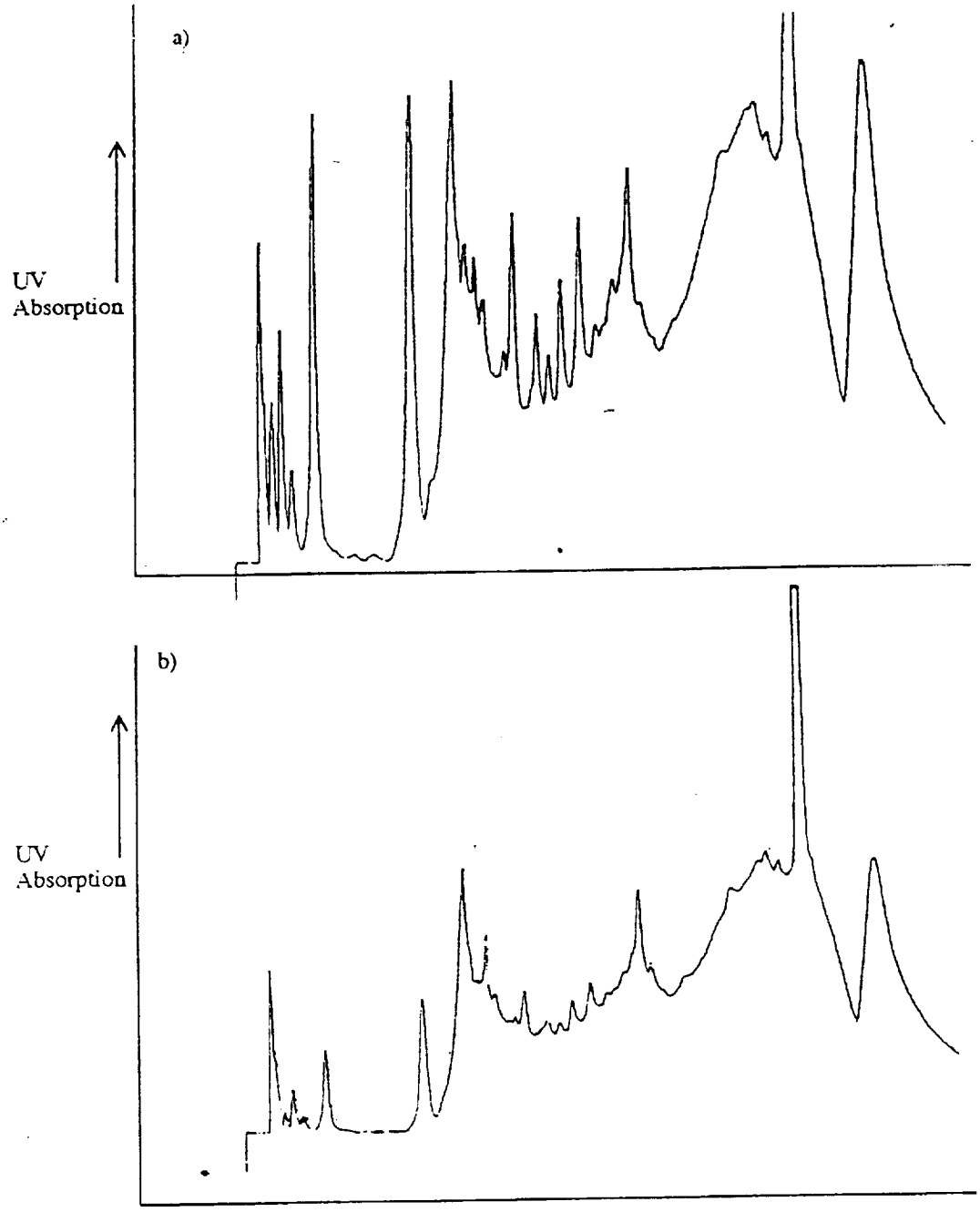

Figure 13. Comparison of UV absorption for Durite® SC-1008 under identical chromatographic conditions. a) 280 nm, b) 255 nm.

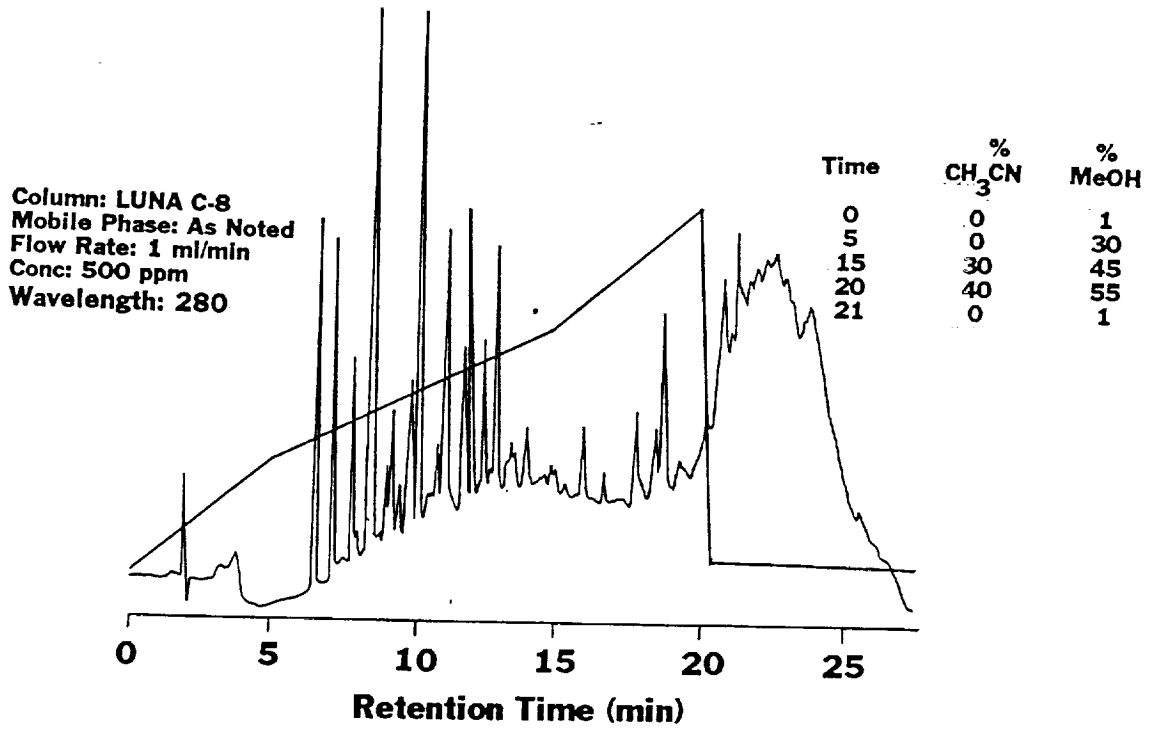

Figure 14. Three-solvent nonlinear gradient elution analysis of phenol-formaldehyde resole resin. Column: LUNA C_8, Mobile Phase: H_2O/ACN/MeOH, Flow Rate: ml/min, Size: 20 μl (100 ppm), UV Detector: 280 nm.

EMORY & HENRY COLLEGE
FOUNDED 1836

MEMORANDUM

July 30, 1997

TO: **Terry L. St. Clair, Technical Officer**
Head, Composites and Polymers Branch

FROM: **Philip R. Young, Principal Investigator**
Dept. Of Chemistry, Emory & Henry College

SUBJECT: **Progress Report on NASA Grant NAG-1-1943 for the Period June 9 - July 31, 1997**

REFERENCE: **HPLC Characterization of Phenol Formaldehyde Resole Resin Used in Fabrication of Shuttle Booster Nozzle**

NASA Grant NAG-1-1943 was awarded on June 6, 1997. A "kick-off" meeting was held at Virginia Tech on June 9. In attendance were Prof. Harold M. McNair of VPI & SU; Dr. Yuri KazaKevich, Visiting Summer Professor from Seton Hall University; Jennifer H. Brown, rising senior at Emory & Henry College; and Philip R. Young. Jennifer formally began work in Prof. McNair's Chromatography Laboratory on June 10.

The first two weeks were spent getting a Hewlett Packard 1050 High Performance Liquid Chromatograph up and running, analyzing standard mixtures, and learning the theory and practice of HPLC. During this time, specimens arrived from the NASA-Langley Research Center and various sampling techniques were investigated.

We elected to pursue a reverse phase separation using a C-18 column and a water-acetonitrile mobile phase. Numerous chromatographic analyses were conducted in an effort to optimize the gradient elution separation and satisfactory progress was achieved.

Figure 1 gives the chromatogram of the best separation obtained to date on Durite Phenolic Resin SC-1008. This separation was obtained using the following conditions:

Sample:	Durite SC-1008
Concentration:	1000ppm in acetonitrile, filtered through a Supelco 25mm PTFE membrane with a 0.2μm pore size
Size:	20μl
Flow Rate:	1.2ml/min

Column:	Phenomenex Prodigy 5-ODS-2, 5μ 150 X 4.60mm Serial Number 109462
Detector:	UV at 255nm
Mobile Phase:	Water-Acetonitrile

Gradient:	Time, min.	% ACN
	0	2.5
	2	15.0
	15	40.0
	20	50.0
	21	95.0
	25	100.0

Note that at least 39 peaks were resolved in 30 minutes. This is considerably faster than the 150 minute separation of approximately 30 components reported in the literature (B. Mechin, D. Hanton, J. LeGoff, and J. Tanneur, Polym. J.. 20 (4), 333 (1984). As noted later in this report, we feel this separation can be improved. However, if no such improvement is possible, the chromatographic separation associated with Figure 1 should be sufficient to quality control the phenolic resin system used to fabricate carbon-carbon composite rocket nozzles.

A carbon-fiber containing specimen designated HT-672 was also obtained from Langley. The resin was isolated by dissolving approximately 0.002g of the specimen in 5 ml of acetonitrile and centrifuging. Analysis of the supernatant under conditions listed for Figure 1 yielded a result virtually identical to Figure 1. Thus, for the present, we assume that the phenolic resins in SC-1008 and HT-672 are identical. However, we can pursue any minor variations in the future if desired. The effects of adding carbon fiber appear to be minimal.

We noted that SC-1008 is not completely soluble in acetonitrile. The recovered insoluble portion is a glassy solid at room temperature and may be oligomer. Since the resin is completely soluble in methanol, we are currently optimizing a separation using a water-methanol gradient. The result, hopefully, will be an improvement over the chromatogram given in Figure 1.

Several additional issues will be investigated before Ms. Brown leaves Virginia Tech on August 15:

1. We know that SC-1008 is a reactive system. Thus, the resin must be refrigerated during storage. Peaks change when the resin is stored at room temperature or heated. We intend to conduct a preliminary kinetic study where resin chemistry is monitored with "out" time at RT. Peaks which change, appear, or disappear will be noted.

2. When chromatograms fail to reproduce, either the sample is changing, the column is changing, or both. We intend to follow column quality by monitoring the number of theoretical plates while conducting the kinetic study.

3. We are compiling a bibliography on the chromatographic analysis of phenolic resins.

Future work will investigate the identification of key peaks in Figure 1.

NASA-Langley was billed for the following on July 21, 1997:

$2,000.00	Technical Support at VPI & SU
1,666.00	Support for J. Brown (2 months)
600.00	Living Expenses for J. Brown (2 months)
$4,266.00	

I intend to spend an additional $2,500.00 of the $8,143.00 budget by September 15, 1997.

I am satisfied with the initial progress on this grant. The cooperation between Virginia Tech, the Langley Research Center, and Emory & Henry College has been superb. This summer has been a wonderful opportunity for Jennifer Brown to work in the facilities of a major university. Prof. McNair has allowed Jennifer to participate in several short courses offered at Virginia Tech. She is learning a lot of practical chemistry and will make valuable contributions to this grant during the 1997-98 school year.

I intend to visit Langley with the next month to discuss this research. Your comments and advice will be appreciated.

Philip R. Young

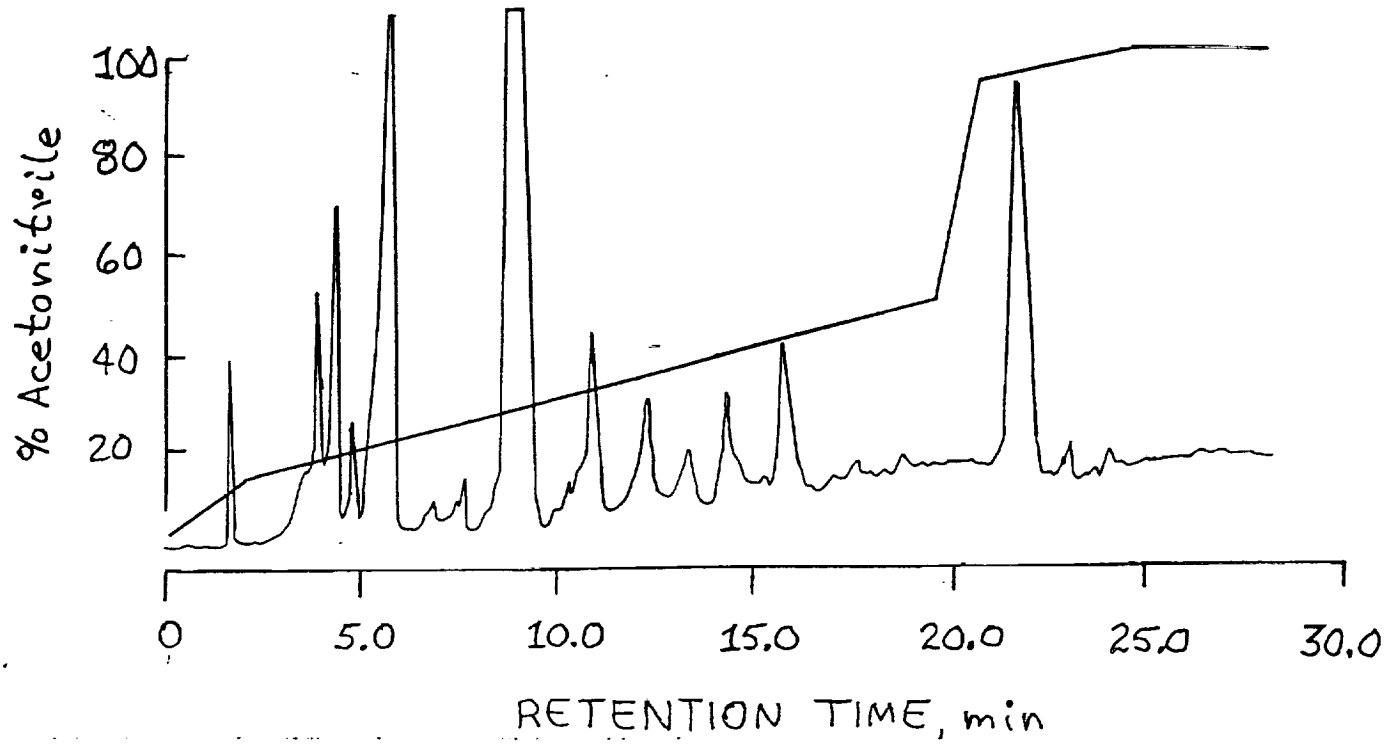

Figure 1. HPLC separation of phenol formaldehyde resole resin SC-1008. Chromatographic conditions are summarized in this report.

APPENDIX B

EMORY & HENRY COLLEGE
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MEMORANDUM

June 3, 1998

TO: Terry L. St. Clair, Technical Officer
Head, Composites and Polymers Branch

FROM: Philip R. Young, Principal Investigator
Dept. of Chemistry, Emory & Henry College

SUBJECT: Request for No-Cost Time Extension

REFERENCE: NAG-1-1943; HPLC Characterization of Phenol Formaldehyde Resole Resin Used in Fabrication of Shuttle Booster Noozle

The referenced grant had effective and expiration dates of 6/5/97 and 6/4/98, respectively. Thus, it is about to expire. While we have successfully met the objectives of this grant, approximately $1200 remains unspent, primarily because I charged no time to the effort. I request a 1-year no-cost time extension in order to spend the remaining funds. This action will enable me to introduce additional students to the characterization of advanced materials.

I am presently preparing a comprehensive report on this research. I am pleased to report that Jennifer H. Brown, the undergraduate student who worked with me, made a presentation on March 2, 1998, at the Pittsburg Analytical Conference in New Orleans. She also gave a talk at the Emory & Henry College Science Fest '98 on April 15, and successfully defended an Honors Thesis entitled "Characterization of Phenol-Formaldehyde Resole Resin by Reverse Phase High Pressure Liquid Chromatography" prior to her graduation this May. I also gave a talk on this work at the 76th Virginia Academy of Science Meeting last week at George Mason University. I personally feel that NASA's funds are being used effectively.

Your attention to this request will be appreciated. We continue to be grateful for the opportunities and support you have provided.

Philip R. Young
James Earl Copenhaven Professor in Chemistry

Emory & Henry College
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