shown in Figure 2 is obtained. In this case the combining ratio is 1.

Data from experiment 1 in which the ceric concentration is varied are shown in Figure 3, plotted from Equation 8, taking $p = 1$. The curve is linear except for the two lower points at ceric concentrations less than $3.86 \times 10^{-2} M$. At these lower concentrations, the assumption that $c_o \gg c_c$ is not valid, and, therefore, the curve deviates from linearity.

Details of experiments are summarized in Table III. In all cases (except experiment 1), a linear plot was obtained over the entire concentration ranges shown, using unity as the combining ratio.

Values of K for every alcohol were considerably lower in the solutions containing nitric acid, and this is the result of the formation of ceric nitrate complex ions, which reduce the concentration of the complexing species (see equation defining K'''). A comparison of the K values obtained for the three butanols shows that they are all of the same magnitude. Ethylene glycol, however, presents a definite anomaly, as the K values in both perchloric and nitric acid solutions are considerably larger than the corresponding values for the butanols. This may be because of the formation of a stable chelated ring, as the disposition of the electron donor oxygen atoms are such that a five-membered ring may form

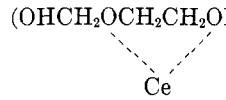

Table III. Summary of Experiments

Experiment	$HClO_4$ concn., M	HNO_3 concn., M	$Ce(ClO_4)_4$ concn., $M \times 10^2$	$(NH_4)_2$-$Ce(NO_3)_6$ concn., $M \times 10^2$	Alcohol concn., $M \times 10^2$	K
tert-Butanol						
1	1.62		2.750–22.00		10.00	13
2		2.00		2.086	17.01–123.7	0.6
sec-Butanol						
3	1.69		2.341–16.39		2.943	11
4		2.00		1.982	4.025–64.40	1
n-Butanol						
5	1.69		3.277–16.39		3.051	16
6		2.00		1.982	3.400–54.40	1
Diethylene glycol						
7	1.69		2.341–16.39		2.033	40
8		2.00		1.982	3.680–58.88	3

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Quantitative Gas Liquid Chromatography of Mononuclear Hydroxymethylphenols as Acetate Esters

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▶ **A new method for analyzing complex resole prepolymer systems is presented. Under anhydrous conditions, phenol and hydroxymethylated phenol derivatives are quantitatively converted to the acetate esters by treatment with acetic anhydride in the presence of an organic base at room temperature. All of the acetylated mononuclear resole components are sufficiently stable and volatile to permit their separation by gas liquid chromatography. The complex acetylated mixtures are resolved using temperature-programming techniques in conjunction with an ionization detector. Certain aspects of the quantitative method are discussed in detail, and special emphasis is given to sample preparation procedures. Proton magnetic resonance is used to confirm the validity of the method.**

RESOLES, as a type of phenolic prepolymer (*14*), have many industrial uses since they can be cross-linked to give thermoset plastics with desirable properties. These prepolymers are usually prepared by reaction of one mole or more of formaldehyde per mole of phenol under base-catalyzed conditions (*10*). The reaction is complex, since a multitude of mono- and polynuclear hydroxymethylated phenols can be formed. However, many commercially important resole prepolymers are mainly composed of mononuclear components. The problem of analyzing these prepolymers has been formidable because of their complexity and instability. A number of analytical procedures have been applied to determining the prepolymer structure, but only a small percentage of the methods provides a quantitative (or even qualitative) determination of one or more of the individual components present.

Unreacted formaldehyde in a resole can be accurately determined chemically (*18*). Unreacted phenol has been determined by methods employing steam distillation (*8*), infrared spectrometry (*16*), and, more recently, gas liquid chromatography (GLC) (*17*). Thus far, the only successful method for the individual hydroxymethylated phenols has been the use of paper chromatographic techniques, as applied by Freeman (*5*), Reese (*13*), and others (*10*). The latter method makes possible the determination of the common mononuclear and many of the dinuclear components of the resole system. Although the methods reported in the literature are successful to varying degrees, some are limited in applicability and many have inherent limitations with respect to rapidity and accuracy of the measurements.

The fact that resole systems are usually reactive and heat-sensitive has prevented their direct analysis by a number of otherwise potentially useful techniques. Derivative formation may impart the required stability and convert the resoles to a highly desirable

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form. Before present day GLC techniques were available, Barthel (*3*) effected a partial separation of an acetylated resole resin by high-vacuum fractionation. Martin (*11*) accomplished a similar separation using trimethyl silyl ether derivatives of a resole. Numerous investigators have used the esters as derivatives for elucidating the structure of both resinous and nonresinous phenolic products (*10*). Esterification has been widely used with resoles, because both the methylol and phenolic hydroxyl groups are readily esterified with acid anhydrides with few side reactions (*3*, *10*).

The current literature contains several examples where ether or ester derivatives of complex phenolic mixtures can be resolved more effectively by GLC than can the parent phenols (*7*, *9*, *12*, *15*). Capillary column GLC has been useful for separations involving complex mixtures because of the ease with which the necessary resolutions can frequently be attained. Nonlinear absorption effects have been noted, particularly when phenolic mixtures are separated using capillary columns; but this column type has been used efficiently for the separation of derivatives of phenolic mixtures free of undesirable hydroxyl groups (*7*).

Utilizing GLC temperature-programming techniques, a sensitive ionization detector coupled with a capillary-type column coated with a highly thermally stable substrate, the acetate derivatives of resoles can be effectively resolved. In the method described below, acetate esters of phenol, 2-hydroxymethylphenol (2-HMP), 4-hydroxymethylphenol (4-HMP), 2,6-dihydroxymethylphenol (2,6-DHMP), 2,4-dihydroxymethylphenol (2,4-DHMP), and 2,4,6-trihydroxymethylphenol (2,4,6-THMP) are accurately determined. Related components, such as the acetylated hydroxymethylphenol hemiformals, are also resolvable and are identified. Complete and quantitative functional group analyses on any complex resole or its acetate may be performed by recently developed proton magnetic resonance (PMR) methods (*19*). Although PMR does not reveal the identity of the individual molecular species present, the quantitative number average structures determined by PMR provide a rapid, independent way of checking the certainty of the GLC analytical method.

EXPERIMENTAL

Apparatus. An Aerograph Model 600B gas chromatograph, adaptable for manual temperature programming, and a Brown recorder, Class 15 (1-mv., 1-second response), were used. The 600B was equipped with a hydrogen flame detector. Nitrogen was used as the carrier gas. A flowmeter at the inlet was calibrated in terms of milliliters of nitrogen per minute, measured at the effluent of the column after conditioning and before making the connection to the detector. Peak areas were determined manually using a planimeter and, in some cases, electronically using a CEC 34-310 Chromad integrator equipped with an automatic zero corrector.

Chromatographic Column. The column was coiled copper, 25 feet long with 0.125-inch o.d. and 0.030-inch wall. This coil was cleaned, using a 20% aqueous solution of nitric acid, followed by thorough rinsing. The internal wall was given a preliminary coating with a 5% Siliclad solution (Clay-Adams, Inc., New York, N.Y.), followed by washing with distilled water and drying for 1 hour at 100° C. under a nitrogen stream. The column was then coated with SE-30 substrate using a 4% solution in chloroform, purged with nitrogen at room temperature, and conditioned for 24 hours at 250° C. under a nitrogen purge. Finally, the column was conditioned at 300° C. with a nitrogen purge until a steady base line was obtained.

GLC Operating Conditions and Sample Analysis. Preliminary settings prior to sample injection for the 600B were as follows: hydrogen flow to ionization detector = 20 cc. per minute; injector block temperature = 235° C.; oven temperature = 80° C. or less; input impedance = 10^7; output sensitivity = 10×; flow rate = 15 ml. of nitrogen per minute. When the above conditions were established, the oven Variac was set at a predetermined output, and when the oven temperature reached 100° C., a 2-μl. sample solution was injected into the chromatograph. The oven power setting was such that the chromatograph followed a reproducible nonlinear temperature-programming cycle to 300° C. (average temperature rise, 5.5° to 6.0° C. per minute). Accuracy and precision of the method were critically dependent on the instrument conditions at the time of sample injection.

Procedures for Sample Preparation. A. Freeze-Drying Aqueous Resoles under Neutral Conditions. A typical resole system (30 to 70% aqueous solution) was diluted to approximately a 5% solids level and neutralized to a pH of 6 to 7. Enough diluted solution was then freeze-dried to give 2.5 to 3.0 grams of solid residue. Preferably, the dehydrated resin was immediately acetylated or, during any intervening period, it was maintained at a temperature of 0° C., or below.

B. Freeze-Drying Aqueous Resoles under Basic Conditions with Hemiformal Cleavage. The unreacted formaldehyde level of the resole being analyzed was measured using the hydroxylamine method (*18*). A sample of the resole was diluted to a 5% solids level with water. The diluted solution was chilled to 0° to 5° C. and pyridine bisulfite reagent was added (1 ml. of reagent per 0.2 gram of formaldehyde) with stirring. With the temperature maintained below 5° C., the solution was allowed to equilibrate 10 minutes, and sufficient 20% NaOH was then added to convert the resole completely to its salt form. A large enough sample of the treated solution to give 2.5 to 3.5 grams of dehydrated residue was immediately freeze-dried. The dehydrated product was kept at 0° C., or below, and immediately acetylated.

C. Acetylation Procedure. The dehydrated resole or its salt (2.5 to 3.5 grams) was treated with a mixture of 20 ml. of acetic anhydride and 5 ml. of dry pyridine, at a temperature of 0° C. The mixture was shaken, strictly maintaining the temperature below 10°C., until all the resin dissolved and there was a lightening in solution color. In the case of resole salts, a precipitate of sodium acetate formed after the resin dissolved. After the initial reaction, the acetylation mixture was allowed to warm to room temperature and to stand 1 hour, or more (acetylations were usually left overnight). Approximately 100 ml. of ice water were combined with the acetylation mixture in a 500-ml. separatory funnel. Ether was added to give a clean separation of the organic phase from the aqueous phase after equilibration. If a clean separation was accomplished, the aqueous layer was withdrawn and rejected. In a few cases, solubility limitations necessitated the use of dichloromethane in place of ether. A cold-water wash, a dilute acid wash (2% HCl), and two saturated bicarbonate washes were applied to the organic phase. The organic phase was dried over magnesium sulfate and then filtered. The ether (or dichloromethane) was flash-evaporated from the organic phase, under vacuum at room temperature, to yield a viscous resole acetate sample suitable for examination by GLC or PMR. The nonselective, manipulation losses by this procedure were usually less than 10%.

Resoles, Reagents, Standards, and Area Correction Factors. Sample solutions generally consisted of about 10% (w./v.) acetylated resole in acetone. The solution also contained 0.80% benzyl acetate as a primary internal standard and, in some cases, 1.00% of bis(4-acetoxy-3,5-dimethylphenyl)methane as a second standard.

Area correction factors (ACF) were determined for the six mononuclear resole acetate components relative to benzyl acetate or bis(4-acetoxy-3,5-dimethylphenyl)methane by the internal standard technique. The ACF values (Table IV) represent the slope obtained from a least square plot of component concentration in grams per 100 ml. of acetone solution *vs.* the ratio of the component peak area to the internal standard peak area. The standard concentrations were constant at 0.80% for benzyl acetate and at 1.00% for bis(4-acetoxy-3,5-dimethylphenyl)methane.

The compounds 2-HMP (Eastman Organic Chemicals) and 3-HMP and 4-HMP (Aldrich Chemicals) were purified by recrystallization and 2,6-DHMP, 2,4-DHMP, and 2,4,6-THMP were synthesized following standard procedures reported in the literature (*10*). The purified hydroxymethyl-

phenols were acetylated by a procedure similar to procedure C. Acetylated components were purified by fractional distillation to 100% purity, as confirmed by GLC. Benzyl and phenyl acetate (Eastman Organic Chemicals) assayed 100% by GLC. Bis(4-hydroxy-3,5-dimethylphenyl)methane dimer was prepared by the method of Auwers (*2*). The acetylated dimer was purified by recrystallization from a methanol-water mixture (m.p. 146° C.). The physical properties of the model acetate compounds are summarized in Table III.

Model ether compounds, 2,2'-dihydroxydibenzyl ether and 4,4'-dihydroxydibenzyl ether, were prepared by literature methods (*10*) and acetylated by procedure C.

The pyridine bisulfite reagent was prepared by treating a cold solution of pyridine (1.0 mole) and water (1.1 moles) with SO_2 gas (*1*).

Resole A was prepared by heating an aqueous solution containing phenol (1 mole), formaldehyde (1 mole), and $Ca(OH)_2$ (0.05 mole) at 64° C. for 4 hours. The product was neutralized and freeze-dried. Resole A acetate was prepared from the dehydrated resin by procedure C.

Resole B was prepared by heating an aqueous solution containing phenol (1 mole), formaldehyde (3 moles), and NaOH (1 mole) at 30° C. for 5 hours. The resulting resin was diluted, freeze-dried, and acetylated under different sets of conditions (see discussion).

PMR Analyses. The PMR data were obtained with a Varian Associates Model A-60 spectrometer. PMR integral data were taken electronically and results presented are the averages based on five, or more, independent determinations of the PMR integrals. The errors shown are standard deviations from these averages. The experimental PMR procedures, spectral interpretations, and calculation of results have been described in detail (*19*).

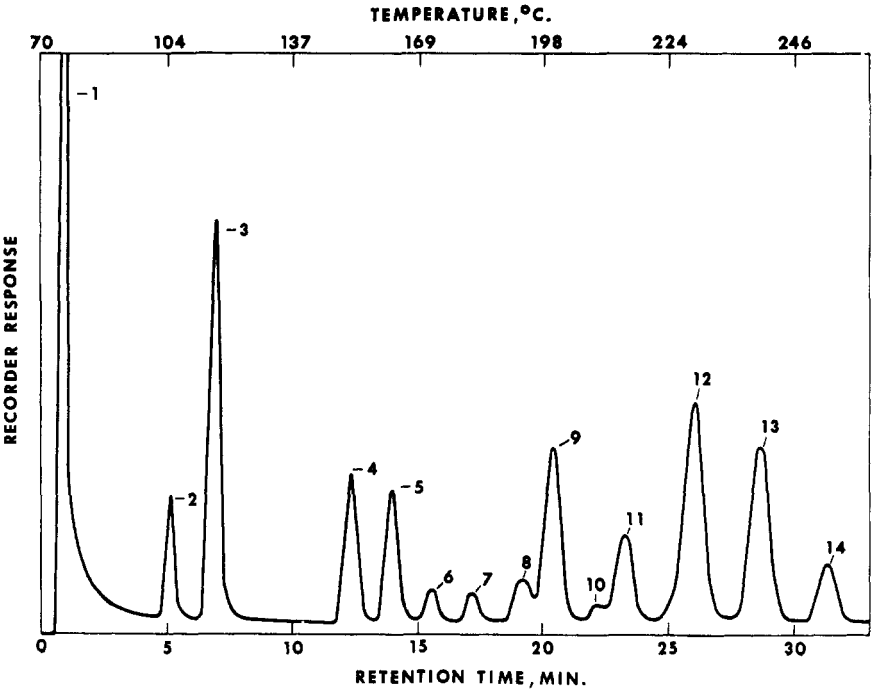


Figure 1. Analysis of resole prepolymer system

1. Solvent, acetone
2. Phenyl acetate
3. Benzyl acetate standard
4. 2-HMP diacetate
5. 4-HMP diacetate
6. 2-HMP monohemiformal diacetate
7. 4-HMP monohemiformal diacetate
8. 2,6-DHMP triacetate
9. 2,4-DHMP triacetate
10. 2,6-DHMP monohemiformal triacetate
11. 2,4-DHMP monohemiformal triacetate
12. 2,4,6-THMP tetraacetate
13. 2,4,6-THMP monohemiformal tetraacetate
14. 2,4,6-THMP dihemiformal tetraacetate

Temperature-programmed from 70° C. Conditions otherwise as described in text

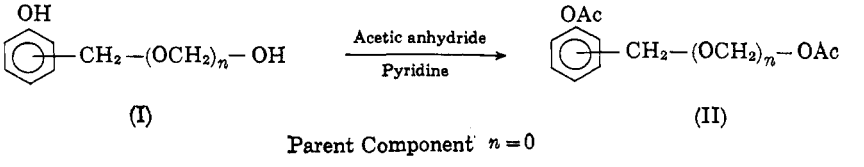
DISCUSSION

Analyzable Resole Samples. The formation of a stable derivative of a resole prepolymer is apparently a requirement of the analytical GLC method. If the analytical method is to be of value, the derivative formation must be quantitative and must not affect the decomposition or advancement of the resin, unless the reactions taking place are determinable. The acetate, trifluoroacetate, and trimethylsilyl ether derivatives of a resole could all be formed and all had sufficiently high vapor pressures and thermal stability to allow the lower molecular weight components to be separated by GLC techniques. However, the resole acetates are formed quantitatively under mild conditions and are much easier to handle and to isolate in a pure form in comparison to the other two types of derivatives.

Many resole prepolymers exist as dilute aqueous solutions and, in order to acetylate such a system effectively, most of the water has to be removed. Removal of water by freeze-drying at low temperatures under controlled conditions results in essentially no resin advancement. The only detectable changes are loss of some unreacted phenol and uncombined formaldehyde. Sodium phenate is not lost under mild freeze-drying conditions, so if a resole is totally converted to its salt form, all phenolic components can be retained in the system.

The freeze-drying operation leaves a dehydrated resin with any titratable formaldehyde (via hydroxylamine, *18*) tightly bound as benzyl-type hemiformals or benzyl-terminated polyformals (I). Acetylation with acetic anhydride in the presence of an organic base will stabilize these species as esters (II). Consequently, a chromatogram of an acetylated resole system may show one or more daughter peak for each parent peak (Figure 1). The daughter components differ in composition from the parents by nCH_2O units and have a greater retention time. More than one formaldehyde molecule can be involved in equilibrium with a given parent molecule if the parent has more than one hydroxymethyl substituent, or if a polyoxymethylene side-chain (benzyl-terminated polyformal) is involved (I; $n>1$). In general, most resole prepolymers contain only a small percentage of unreacted formaldehyde. Consequently, acetylated monohemiformal derivatives of a given parent component are the only ones present in significant amounts (Figure 1). Benzyl-terminated polyformals are not detected in such cases by GLC or PMR (*19*).

Isomeric acetylated hemiformals derived from the same parent hydroxymethylated phenol are observed as a



single chromatographic peak. Acetylated phenyl-type hemiformal groups and other plausible functionalities were not detected by either GLC or PMR (*19*). Polyoxymethylene oligomers, as their diacetates, are resolved by GLC. However, these components are not present in acetylated resole systems which are freeze-dried prior to acetylation (*19*).

A dehydrated resole sample was analyzed structurally by PMR before and after acetylation. The results (Table I) strikingly confirm that other than in total esterification of both the methylol and phenolic hydroxyl groups, the described acetylation procedure does not modify the basic resin structure. The degree of polymerization remains constant. Although there are some manipulation losses during the preparation and isolation of the acetylated samples (procedure C), PMR checks before and after acetylation also confirm that fractionation of the multicomponent mixtures is not occurring to a measurable degree. By using model compounds, it was also verified that the described acetylation method does not alter dibenzyl ether–type bridges.

The presence of parent components and the related hemiformal derivatives obviously complicates the GLC analysis (Figure 1). It is desirable to cleave hemiformal groups prior to acetylation, so that only parent components are detected and analyzed (Figure 2). Cleavage of these groups is accomplished by acetylation in the presence of an acid catalyst at elevated temperatures, or by consuming the formaldehyde involved in the hemiformal equilibrium by forming an amine bisulfite addition product before acetylation. In some instances the former method results in undesirable resin modification. The formation of an amine bisulfite addition product with formaldehyde removes the hemiformal interference, without producing any undesirable reaction products or resin modification.

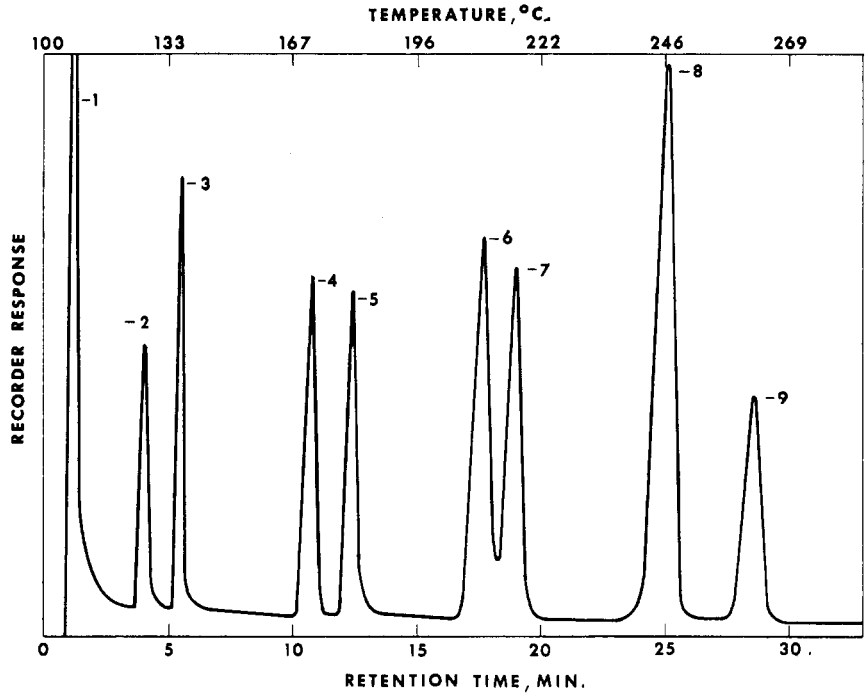


Figure 2. Identification of hydroxymethylphenol acetates, hemiformal-free

1. Solvent, acetone
2. Phenyl acetate
3. Benzyl acetate primary standard
4. 2-HMP diacetate
5. 4-HMP diacetate
6. 2,6-DHMP triacetate
7. 2,4-DHMP triacetate
8. 2,4,6-THMP tetraacetate
9. Bis(4-acetoxy-3,5-dimethylphenyl)methane standard

Table I. PMR Evaluation of Acetylation Procedure[a]

Structure	Resole A	Resole A (Ac)
Aromatic hydrogens per aromatic ring	3.72 ± 0.07	3.75 ± 0.02
Hydroxymethyl groups per aromatic ring	1.14 ± 0.03	1.12 ± 0.01
Methylene bridges per aromatic ring	0.06 ± 0.01	0.06 ± 0.01
Average degree of polymerization, *n*	1.06	1.07
Molecular weight	136 (OH) 233 (Ac)	232 (Ac)

[a] Results reveal formaldehyde–phenol ratio greater than unity because of the loss of some free phenol during freeze-drying of neutralized Resole A.

Table II. PMR and GLC Evaluation of Sample Preparation Methods

	PMR values for Resole B acetates[a]			GLC values[a,b]
Structure	Ac-1	Ac-2	Ac-3	Ac-3
Aromatic hydrogens per aromatic ring	2.76 ± 0.04	2.80 ± 0.05	2.82 ± 0.04	2.83
Benzyl-type hemiformal groups per ring, R_{HF}	0.58 ± 0.04	0.77 ± 0.04	0	0
Hydroxymethyl groups per aromatic ring, R_{HM}	1.63 ± 0.05	1.45 ± 0.04	2.16 ± 0.04	2.16
Total R_{HF} + R_{HM}	2.21 ± 0.08	2.22 ± 0.08	2.16 ± 0.04	2.16
Methylene or dibenzyl ether bridges per ring	0	0	0	—
Molecular weight (Ac)[c]	295	296	292	292

[a] Structure values less phenyl acetate contribution.
[b] GLC structure values calculated from data in Table VI.
[c] Number average molecular weights, less phenyl acetate and hemiformal contributions.

A PMR analysis check was made on special Resole B (100% mononuclear components) to ascertain if different methods of sample preparation affect the basic resin structure (Table II). An aqueous solution of Resole B was treated in three ways: (1), the resin was freeze-dried at a pH of 6; (2) the resin was totally converted to its salt form with base and freeze-dried; and (3) the resin was treated with an excess of pyridine-bisulfite complex, converted to its salt form with base, and then freeze-dried. The three dehydrated residues were acetylated by the described procedure to give samples Ac-1, Ac-2, and Ac-3, respectively. The three acetates differ in the number of hydroxy-

methyl substituents which are hemiformulated. Ac-3 is completely void of hemiformals, because of the effective pretreatment with the amine bisulfite reagent. The difference between Ac-1 and Ac-2 in hemiformal concentration is related to the pH of the original resole solution before freeze-drying. Since the pH also influences the extent to which phenol is lost during freeze-drying, the samples vary in residual phenol content. Structural agreement among the three samples, less the contributions from free phenol and hemiformal groups, is within experimental error. Particularly noteworthy is the fact that none of the methods of treatment resulted in resin advancement—e.g., methylene bridge formation.

GLC Analysis Development. Of the substrates listed in the literature, the silicone oils and greases seemed especially applicable to the separation of high-boiling esters at high operating temperatures. SE-30, a methyl silicone, and SE-52, a methyl phenyl silicone, give especially good performance over the wide temperature range required for separating the various esterified resole components. Golay-type coated capillary columns with large diameters (0.125-inch o.d.), are very effective in separating components with widely different boiling points, in a reasonable time, without decomposition (*4*, *6*). Since the sensitive ionization detector permits the use of minute sample injections this type of column is efficient, even in lengths of only 25 feet. Copper columns which are precoated with an inert silicone (Siliclad) coating before substrate deposition seem to perform better without contributing to component decomposition. Although component decomposition is negligible in the column, acetylated benzyl-type hemiformals are decomposed at injection block temperatures above 250° C.

Figure 2 shows a chromatogram of a resole acetate mixture free from hemiformal derivatives obtained using the conditions described in the experimental section. The components are well resolved, except for a slight overlap of the 2,6-DHMP and 2,4-DHMP esters. The components are eluted in an increasing order of molecular weight. Isomeric components are separated in the order of boiling point, with the ortho-substituted isomer being eluted first. Retention times relative to benzyl acetate are given in Table III. Peak identification is based on the respective retention times of the pure acetate model compounds. If the meta isomer (3-HMP) is present, it will be eluted simultaneously with the 4-HMP component, using the described conditions (Table III). By modifying the temperature-programming cycle, the 2-, 3-, and 4-HMP isomers can be resolved. However, the 3-HMP component was not detected in any of the resole systems examined in this study, in agreement with results obtained independently by paper chromatography (*5*, *13*).

Relative retention times of the simple methylene-bridged dimers and dibenzyl ethers are also shown in Table III. Dibenzyl ether compounds are not detected in any typical resole prepolymer system which has been prepared by normal base-catalyzed conditions (*13*). PMR was used to confirm the absence of ether linkages (*19*). The simple dimers (nonhydroxymethylated) are also not normally detected in prepolymer systems prepared under alkaline conditions with a formaldehyde-phenol mole ratio greater than 1. The more complex dimers and polynuclear components have relative retention times greater than 6.0, or are not eluted at all under the described conditions.

Figure 1 shows a chromatogram of a resole acetate mixture, where the hemiformal groups were not cleaved before acetylation. Peak identifications were confirmed by freeze-drying dilute basic solutions of each hydroxymethylphenol model compound in formalin, acetylating each dehydrated product, and chromatographing the acetylated samples. Retention times of hemiformal derivatives derived from each parent molecule were assigned in this manner. In each case, PMR was used to confirm the presence of the hemiformal structures (*19*).

The ionization characteristics of the acetate model compounds were investigated by determining whether the observed component peak heights and areas were proportional to their concentration in synthetic mixtures. The compounds are resolvable only by temperature programming and hydrogen flame detector response varies as the temperature at which a component is eluted varies. However, if a reproducible temperature programming cycle is employed, the response of the detector to each component is reasonably linear.

The quantization was accomplished most effectively by relating the area under the curves to component concentration, using the internal standard technique. Area correction factor (ACF) values were determined relative to benzyl acetate. Statistically, good ACF values were obtained for synthetic blends of acetate model compounds in individual concentration ranges of 0.1 to 5 grams per 100 ml. of acetone solution, with the benzyl acetate level constant at 0.80 gram per 100 ml. (Table IV). If the component level was less than 0.1 gram per 100 ml., the precision suffered and the constancy of the ACF values varied significantly. The quantization can be further improved by the use of a second internal standard which is eluted just after the 2,4,6-THMP tetraacetate peak. The dimer bis(4-acetoxy-3,5-dimethylphenyl)methane has the proper retention time (Table III) and excellent thermal stability. Basing the ACF of the 2,4,6-THMP ester on the dimer, rather than on the benzyl acetate, significantly improves the precision (Table IV). There was no statistical advantage found, however, in basing the ACF of any of the other components on the dimer rather than on benzyl acetate. The dimer concentration, as a standard, was maintained constant at 1.00 gram per 100 ml. The improvement in both precision and accuracy obtainable by cleaving the hemiformal groups prior to acetylation is obvious, since only parent components then need to be analyzed. The removal of the hemiformal interference is necessary if the dimer is to be used as a second internal standard.

Table V shows quantitative data obtained for a synthetic blend of six esterified resole model compounds. The im-

Table III. Physical Properties of the Acetate Esters and Relative Retention Times

Acetylated component	Boiling or melting point, °C.[a]	R.I., $n_D^{25°}$	Relative retention times[b]
Phenol	45	1.5009	0.73
Benzyl acetate (std.-1)	61	1.5001	1.00
2-Hydroxymethylphenol (2-HMP)	121	1.4988	1.95
3-Hydroxymethylphenol (3-HMP)	131	1.5021	2.18
4-Hydroxymethylphenol (4-HMP)	134	1.5016	2.20
2,6-Dihydroxymethylphenol (2,6-DHMP)	166	1.4982	3.18
2,4-Dihydroxymethylphenol (2,4-DHMP)	173	1.5006	3.41
2,4,6-Trihydroxymethylphenol (2,4,6-THMP)	202	1.5007	4.50
Bis(4-acetoxy-3,5-dimethylphenyl)methane (std.-2)	146 (m.p.)	—	5.11
2,2′-Dihydroxydiphenylmethane	46 (m.p.)	—	3.75
2,4′-Dihydroxydiphenylmethane	73 (m.p.)	—	4.12
4,4′-Dihydroxydiphenylmethane	74 (m.p.)	—	4.46
2,2′-Dihydroxydibenzyl ether	—[c]	—	4.50
4,4′-Dihydroxydibenzyl ether	—[c]	—	5.20

[a] All boiling points at 1.5 mm.
[b] Retention times relative to benzyl acetate on SE-30 substrate.
[c] Boiling points not measured, structure confirmed by PMR(*19*).

Table IV. Area Correction Factors (ACF) and Accuracy Determination

(Internal standard technique)

Acetylated component	Av., ACF[a]	No. of detns., n	Std. dev., s	95% confidence limits for av. of n ACF detns., %
Phenol	0.866	7	0.027	±2.86
2-HMP	1.110	9	0.026	±1.79
4-HMP	1.185	7	0.015	±1.16
2,6-DHMP	1.314	7	0.025	±1.92
2,4-DHMP	1.446	8	0.052	±3.00
2,4,6-THMP	1.570	9	0.085	±4.16
2,4,6-THMP	1.652[b]	9	0.028	±1.67

[a] Values determined using benzyl acetate as standard, unless noted otherwise.
[b] Determined using bis(4-acetoxy-3,5-dimethylphenyl)methane standard.

Table V. Analysis of Resole Acetate Synthetic Blend

Acetylated component	Added, %	Found individual determinations[a]				Mean %	Mean error
Phenol	4.26	4.20	4.20	4.15	4.23	4.28	4.21	−1.13
2-HMP	11.15	11.46	11.30	11.20	11.22	11.31	11.31	+1.40
4-HMP	11.60	11.46	11.48	11.76	11.51	11.85	11.61	+0.10
2,6-DHMP	18.44	18.20	18.25	18.88	18.64	18.29	18.45	+0.06
2,4-DHMP	17.80	17.77	17.90	17.52	17.33	17.15	17.53	−1.49
2,4,6-THMP	36.76	37.97	36.44	35.55	34.11	36.49	36.11	−2.33
2,4,6-THMP[b]	36.76	37.05	36.76	36.16	36.32	36.98	36.65	−0.29

[a] Values calculated using ACF based on benzyl acetate, unless otherwise noted.
[b] Values calculated using ACF based on bis(4-acetoxy-3,5-dimethylphenyl)-methane.

provement in precision afforded by using the dimer reference for the 2,4,6-THMP ester evaluation can be seen from the data. When an accurate means of peak area measurement is used, one of the most significant sources of poor precision is nonduplication of GLC conditions for repetitive runs of the same sample. Some of the ACF values are susceptible to change with time, as the column ages, or as other conditions vary, resulting in poor accuracy. Consequently, ACF values should be periodically rechecked, using standard solutions kept on hand. Unknowns must be run under conditions identical to the ones used to evaluate the ACF values.

Applications. Table VI shows quantitative data obtained for the analysis of Resole B acetate, which contains only mononuclear components. The resin was acetylated after the hemiformal groups were cleaved. Nearly 100% of the resin is accounted for by the analysis. Specific structure values, calculated from the average of the data in Table VI, are compared with the values determined by a PMR analysis of the same sample (Table II, Ac-3). Agreement between the two methods is very good. By utilizing both methods one can determine both the mononuclear components and the number-average structure of any soluble resole prepolymer.

The described GLC method has been successfully applied to a large variety of resole systems. Mononuclear resole components have been quantitatively analyzed in systems where they are the main constituents, and in higher-molecular-weight systems, where they are present in lesser amounts. This method permits the measurement of resole components with greater speed and accuracy than were heretofore possible.

Table VI. Component Analysis of Resole Prepolymer

Acetylated component	Resole B acetate duplicates, weight %	
Phenol	1.55	1.51
2-HMP	5.95	6.09
4-HMP	11.40	11.58
2,6-DHMP	6.46	6.22
2,4-DHMP	25.53	25.03
2,4,6-THMP	49.06	49.21
Av. composite	99.90	

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