Journal of Chromatography, 396 (1987) 121–128
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 19 469

ANALYSIS OF CROSS-LINKED ALKYD AMINO FORMALDEHYDE RESIN SYSTEMS

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(First received December 22nd, 1986; revised manuscript received January 30th, 1987)

SUMMARY

The analysis of the alkyd components of a cross-linked resin system with butylated urea, butylated melamine or butylated benzoguanamine formaldehyde resins is reported. Chemical cleavage of the ether links between the two resins and hydrolytic cleavage of the alkyd is achieved by acid reaction with *p*-toluenesulphonic acid–acetic anhydride, orthophosphoric acid or acetic anhydride–acetic acid reagents with the products being identified by gas chromatography as appropriate derivatives.

INTRODUCTION

The analysis of simple orthophthalate alkyd products is well established[1] with a procedure being adopted as an American Society for Testing and Materials (ASTM) Specification in 1952[2]. The traditional solution hydrolysis with alcoholic alkali[2,3] is still employed, the original gravimetric assay being replaced by more rapid and selective chromatographic procedures[4,5].

Developments in alkyd and polyester resin technology have introduced other reactants which are much less readily hydrolysed and more vigourous hydrolysis conditions have been employed using higher reaction temperatures and greater concentrations.

Alkali fusion using molten potassium hydroxide hemihydrate and sodium acetate (5%) as flux has been extensively used with a variety of hydrolysis-resistant condensation polymers[6] and has found some use with polymeric esters. Haken and Rohanna[7] have reported the analysis of linear polyesters both in the uncured and cured form. The reaction was conducted for 30 min at 250°C and the resin was effectively cleaved into its original reactants or their derivatives. With cross-linked resins in the form of laminates the bonds produced by free radical polymerisation of the ethylenic double bonds in the monomeric styrene and in the maleate part of the polyester were not cleaved. Both alkali and acid fusion in association with gas chromatography (GC) have been recently used with conventional oil-modified silicone

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0021-9673/87/$03.50

alkyds by Haken *et al.*[8]. The alkali fusion was conducted essentially as in the earlier work[7] where acid fusion employed a mixed anhydride reagent prepared by refluxing equimolecular proportions of acetic anhydride and *p*-toluenesulphonic acid according to the procedure of Tsuji and Konishi[9,10]. The reaction was carried out for 2 h under reflux. Some preference has been shown for the use of acid catalysed hydrolysis with esters using polyfunctional alcohols as these are more readily separated and estimated as their tri- or tetracetate derivatives. The same reaction preference has also been reported with some complex polyurethane systems[11,12].

Few analyses of amine aldehyde resins have been reported due to their intractable nature. Chemical analysis has generally been restricted to the determination of pendant alkoxy groups. The resins are usually alkylated normally with *n*-butanol and this is readily recovered by cleavage of the ether link using a variety of acids including phosphoric[13,14], hydrobromic[15–18], hydrochloric[19], hydroiodic[20], *p*-toluenesulphonic[21] and mixed anhydrides of *p*-toluenesulphonic and acetic acids[9,10]. NMR has been used with some success[22,23] but the procedure has found little general acceptance.

The cross-linking of an alkyd with an amine formaldehyde resin has formed the basis of baking enamels in the coatings industry for several decades and currently the same reactive amine resins are also used to cross-link the newer coating resins.

The analysis of such cross-linked systems has been negligible due to their insolubility and low reactivity. The analysis of silicone polyesters including some cross-linked materials has been reported by McFadden and Scheung[24] using solution hydrolysis with tetramethyl ammonium hydroxide to liberate the constituent polyols. The application to cross-linked systems was stated to be poor.

The present work describes the analysis of the alkyd component of systems where conventional plasticising alkyds have been cross-linked with representative amine formaldehyde resins. The methodology involves chemical cleavage with either the mixed anhydride reagent of acetic anhydride and *p*-toluenesulphonic acid, orthophosphoric acid or acetic anhydride–acetic acid reagents. Acid catalysed hydrolysis of the polyester occurs with simultaneous cleavage of the ether groups linking the two polymer systems. The amine formaldehyde resin remains intact as a derivative and may be recovered as with any other saponifiable material.

EXPERIMENTAL

Samples

Commercially available alkyd resins of the plasticizing type based on coconut and soya bean oil, respectively and butylated amino formaldehyde resins based on urea, melamine and benzoguanamine were used. Details of the various resins are given below.

Coconut alkyd: 30% coconut oil, 25% glycerol, 45% phthalic anhydride; non-volatile, 60%; xylene–butanol, 1:9.

Short oil soya alkyd: 28% soya bean oil, 17% orthophthalic acid, 19% isophthalic acid, 7.0% adipic acid, 1.5% benzoic acid, 27.5% glycerol; non-volatile, 55%; solvesso 100–*n*-butanol, 80:20.

Butylated urea formaldehyde: urea–formaldehyde, 1: 2–4 (mol:mol; non-volatile, 60%; xylene–*n*-butanol, 1:9.

Butylated melamine formaldehyde: melamine–formaldehyde, 1:4–5 (mol:mol).

Butylated benzoguanamine formaldehyde (commercial product): benzoguanamine–formaldehyde ratio (not know); non-volatile, 60%; xylene–*n*-butanol, 65:35.

The cross-linked samples were prepared by heating thin sections of the mixed resins for 3 h at 150°C. The ratios of alkyd to amino resin vary greatly depending on the application. With low bake system the ratio may be 90:10 while with appliance and similar coating the aminoplast may form 30–40% of the vehicle. The degree of

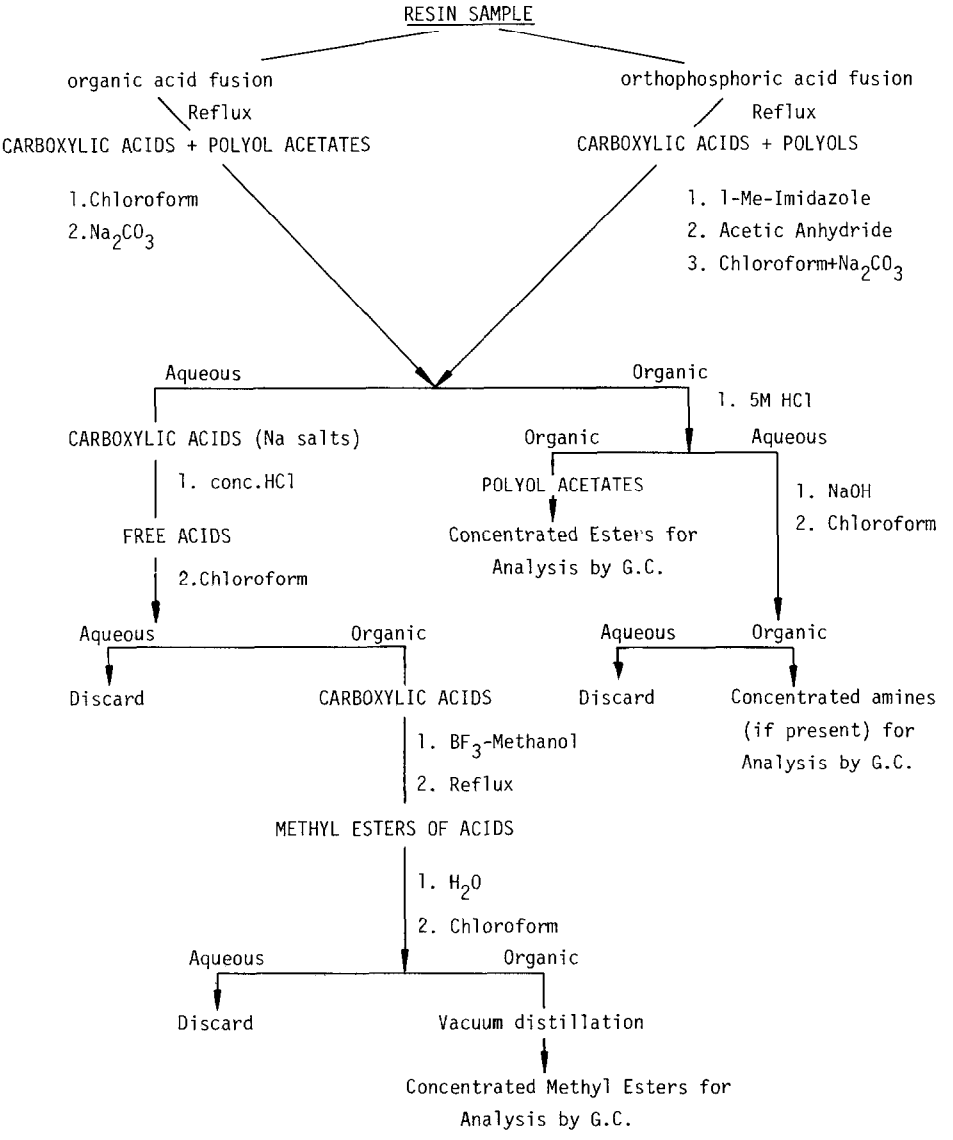

Fig. 1. Scheme for analysis of cross-linked alkyd systems.

cross-linking increases with the proportion of aminoplast and the possibility of cleavage is reduced. The proportion of aminoplast used in this work was 30%.

Acid fusion

The degradation of various polymers has recently been reported[6] and it has been shown that both acid catalysed hydrolysis and cleavage of ether linkages occurs. The acidic reagents used were: (i) *p*-toluenesulphonic acid–acetic anhydride; (ii) 85% orthophosphoric acid and; (iii) acetic anhydride–acetic acid.

(i) p-Toluenesulphonic acid and acetic anhydride reaction. The reagent was prepared by refluxing equimolar proportions of the reactants for $\frac{1}{2}$ h at 125°C[9,10]. The fusion was carried out by refluxing 100 mg of the resin and 5 ml of reagent in a microflask at 125°C for 2 h. After the reaction period the system was allowed to cool. The contents of the flask were dissolved in 10 ml chloroform and the residual acids were neutralised using satured sodium carbonate solution. The contents of the flask were transferred to a separating funnel for the separation and derivative steps as shown in Fig. 1.

(ii) 85% Orthophosphoric acid reaction. The acid (5 ml) was refluxed with 100 mg sample at 125°C for 4 h. After refluxing the flask was allowed to cool and 2.5 ml acetic anhydride was added. The mixture was refluxed for 1 h with 1 ml 1-methylimidazole as catalyst to effect complete acetylation of the polyhydric alcohols. On cooling the separation and derivatisation steps (Fig. 1) were carried out.

(iii) Acetic anhydride–acetic acid reaction. A 100-mg amount of resin, 2.5 ml acetic anhydride and 0.4 ml water were refluxed at 125°C for 3–4 h on cooling the separation and derivatisation steps were conducted

Derivatisation

After fusion with the *p*-toluenesulphonic acid–acetic anhydride or the acetic anhydride–acetic acid reagents the procedure as shown below was followed.

(1) After the acid fusion reaction and subsequent cooling, the contents of the flask/reactor were dissolved in 10 ml of chloroform, ensuring that solid material had dissolved.

(2) The organic solution was then transferred to a 50-ml conical flask, were it was neutralized with a saturated solution of sodium carbonate. The resultant aqueous and organic phases were transferred to a small separating funnel.

(3) The contents were then extracted three times with 7.5-ml portions of chloroform, ensuring that the organic layer was filtered through anhydrous sodium sulphate on phase separating filter paper.

(4) The aqueous sodium carbonate solution was then rendered slightly acidic using concentrated hydrochloric acid. The carboxylic acids liberated were extracted three times with 7.5-ml portions of chloroform, the organic layer being filtered as before.

(5) The organic layer containing the carboxylic acids was placed in a round-bottomed flask and 2.5 ml of 14% BF_3 in methanol were added. The flask with a water-cooled condenser was refluxed at 125°C for 1 h.

(6) After refluxing, and subsequent cooling, 7.5 ml of water was added to destroy the unreacted methylating reagent. The methyl esters formed were extracted using three 5-ml portions of chloroform, again ensuring filtration of the organic layer.

This layer was concentrated under reduced pressure to a small volume for GC analysis of the esters.

(7) The organic layer from step 3 was then extracted three times with 5-ml portions of 5 *M* hydrochloric acid. The combined aqueous extract was then rendered slightly basic by the addition of sodium hydroxide pellets. The basic aqueous solution, which would contain any amines, was extracted three times with 5-ml portions of chloroform, again ensuring adequate filtration, and then concentration for GC analysis.

(8) The resultant organic layer from step 7 containing the acetate esters of the polyols, was concentrated to a small volume for GC analysis.

Note: For alkyd resin analysis, step 7 was omitted and the acetate containing solution (organic) from step 3 was concentrated for GC analysis of the polyol acetate corresponding to the glycerol portion.

With the orthophosphoric acid reaction the acetylation step is required before the separation. The analytical scheme for degradation with organic and phosphoric acids is shown in Fig. 1.

Gas chromatography

GC was carried out using a Hewlett-Packard 5750 Research Model gas chromatograph with flame ionisation detection and with helium as carrier gas.

Methyl esters

The methyl esters were prepared using a proprietary (14%) reagent (No. 216800, Alltech, Deerfield, IL, U.S.A.) boron trifluoride$_3$–methanol as indicated in ASTM. Specification D2800-1975[25]. Separation of the coconut oil was conducted using a 6 ft × $\frac{1}{4}$ in. O.D. aluminium column packed with 5% neopentyl glycol succinate on Chromosorb WAW-DMCS. The coconut oil esters were separated with the column operated isothermally for 3 min at 95°C and then temperature programmed at 60°C/min to 185°C.

The soya oil esters were separated isothermally (185°C) on an 12 ft × $\frac{1}{4}$ in. O.D. aluminium column packed with 5% diethylene glycol succinate on Chromosorb W-HMDS.

Polyfunctional alcohol esters

These were separated on the neopentyl glycol succinate column and with the same conditions as the coconut methyl ester.

RESULTS AND DISCUSSION

Analysis of the butylated urea formaldehyde resin and its condensation products with the two alkyd resins was first conducted using the *p*-toluenesulphonic acid–acetic anhydride reagent. It was observed that when the fusion products were dissolved in the chloroform and after addition of sodium carbonate to neutralise the residual acids a black residue appeared at the interface of the organic and aqueous layers. This residue was removed, washed and dried for subsequent examination. As a synthesis of urea involves the indirect dehydration of ammonium carbamate prepared by the high pressure reaction of carbon dioxide and ammonia it was believed

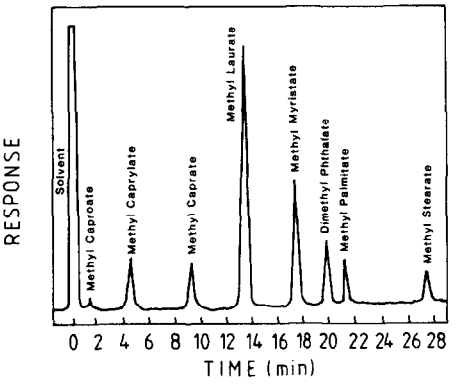

Fig. 2. Chromatogram shown separation of methyl esters from coconut oil alkyd resin.

that the reverse reaction may occur on acid fusion. For this reason the reactions were repeated in a steel-pressure tube fitted with an injection septum. Head space analysis were carried out using a Porapak Q column and a thermal conductivity detector. Peaks corresponding to ammonia and carbon dioxide were not observed although a preliminary experiment using solid urea showed rapid and complete reaction.

The chromatogram from the coconut oil alkyd product is shown in Fig. 2, the dimethyl orthophthalate being eluted between dimethyl myristate and dimethyl palmitate. Fig. 3 shows the chromatogram of the short oil soya product. The additional alkyd components being shown with the dimethyl isophthalate being eluted before the dimethyl orthophthalate. The separation of the three isomeric phthalate esters has been extensively studied. On a non-polar column (OV-1) the orthoester is eluted

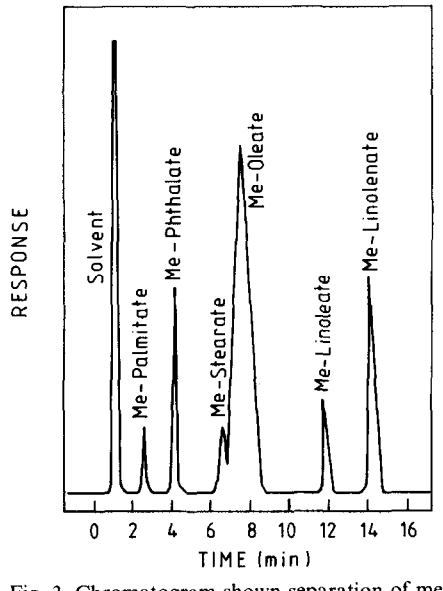

Fig. 3. Chromatogram shown separation of methyl esters from soya oil alkyd resin.

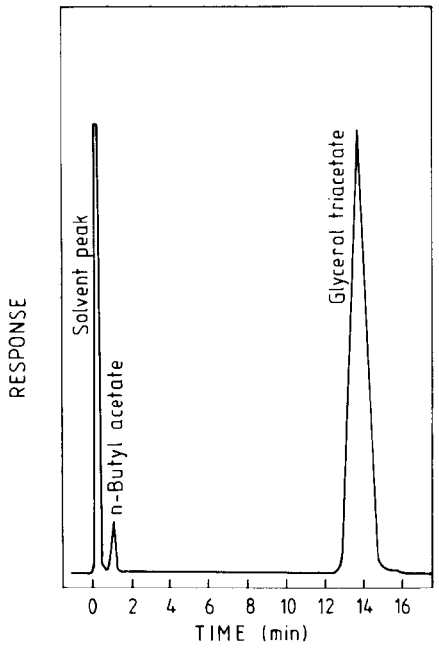

Fig. 4. Chromatogram showing separation of acetyl esters of butanol and glycerol.

before the isoester which is coeluted with the tereester[26]. With increasing polarity the isoester tends to be eluted first, the retention values depending on the particular polyester used[7]. Baseline separation of the three phthalate esters is achieved using a highly polar cyanoalkyl stationary phase *i.e.* SILAR 10 CP[7].

Separation of the glycerol from the alkyd as the triacetate and butyl acetate from the butoxy groups of the urea formaldehyde resin are shown in Fig. 4.

The experiments were repeated with the cross-linked resin products containing butylated melamine formaldehyde and butylated benzoguanamine formaldehyde resins with both alkyd resins and the aminoplasts cross-linked alone. In all cases a black residue was obtained while analysis showing cleavage of the alkyd from the aminoplast and of the alkyd itself was evident by the appearance of methyl esters and acetate derivatives.

Examination of the washed and dried black residues was carried out by infra-red examination as potassium bromide pellets. In all cases the residues showed obvious similarities to the parent aminoplasts but with only one aminoplast of each type being considered the method could not be used with any certainty as a method of identification and much further consideration of the residues is necessary. It is apparent that the alkoxy groups originally present are removed and the resulting hydroxyl groups are neutralised with the formation of a salt.

The analysis reported is qualitative but the cleavage of the alkyd from the aminoplast is essentially quantitative. This may be demonstrated by examination of infra-red spectrum of the residue where characteristic absorption bands of the alkyd system are completely absent. The cleavage of the alkyd has previously been demon-

strated to proceed to completion[7,8]. Spectral and chemical examination of the aminoplast resin shows that alkoxy groups originally present are completely removed.

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