Use of Gas-Liquid Chromatography in the Analysis of Rigid Polyurethane Foam Polyols

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Synopsis

Detailed characterization of the low molecular weight polyols used as intermediates in rigid polyurethane foam production has not been feasible to date. Gas-liquid chromatography of the trimethylsilyl ether derivatives of the polyols now offers a more complete picture of polyol composition, particularly with regard to the molecular weight distribution. The data may be interpreted on a semiquantitative basis. The study of processing variables in polyol manufacture, detection of impurities and analysis of unknown polyols or those based on mixed initiators may all be facilitated by use of this GLC technique.

INTRODUCTION

The polyols used at present for polyurethane foam manufacture are usually propylene oxide adducts of polyhydric alcohols. Current analytical methods, such as hydroxyl value determination, do not give any information beyond the average composition of the polyol. The processing and properties of the final foam must, however, depend to some extent on the detailed composition of the original polyol with respect to individual molecular species. Investigation of this has, until recently, been hampered by the lack of a suitable analytical method.

We now wish to report the analysis of polyols used in rigid polyurethane foam production. The method used was that of gas-liquid chromatographic separation of trimethylsilyl ether derivatives.[1-3]

EXPERIMENTAL

Preparation of Trimethylsilyl Ethers

The method used for the preparation of the trimethylsilyl ether derivatives was an adaptation of that employed by Sweeley, Bentley, Makita and Wells.[1]

A sample of polyol (0.2 g) was dissolved in acetone (1 ml), hexamethyldisilazane (0.6 ml) added and the mixture shaken. Trimethylchlorosilane (0.3 ml) was added and the mixture shaken again. The mixture was allowed to stand for five minutes before being reshaken and then centrifuged.
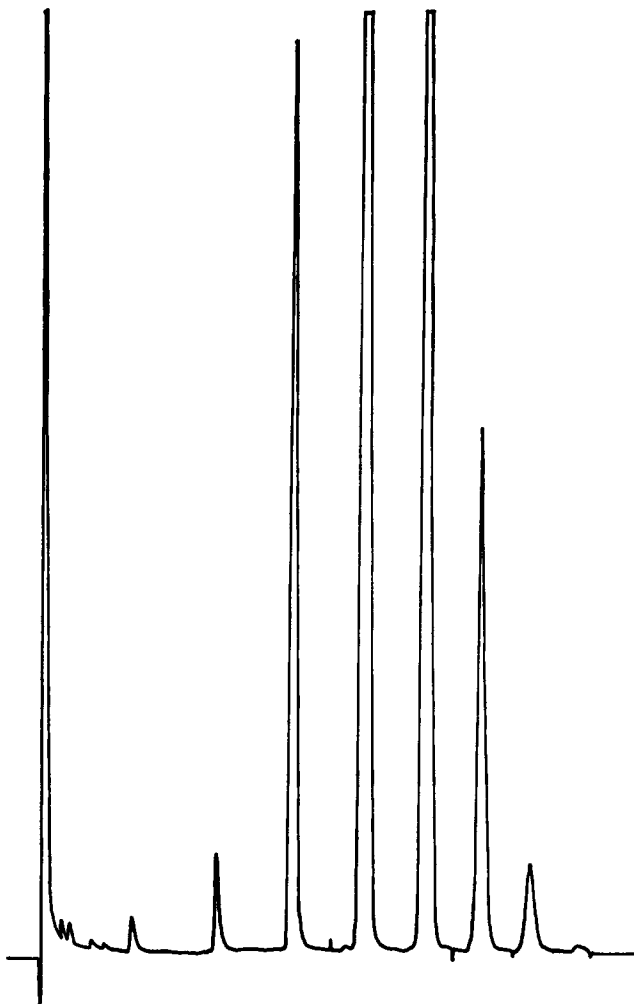
Fig. 1. Chromatogram of polyol *B*.

Samples for analysis were taken with a syringe directly from the super-natant liquid.

Gas Chromatographic Analysis

Separation of the polyol derivatives was carried out using an F & M 810 dual column chromatograph with flame ionisation detector. Both columns were 3 ft × ¹/₈ in. OD. stainless steel packed with 1.5% silicone SE-52 on 70/80 mesh "Chromosorb" G, which had been treated with dimethyl-chlorosilane and acid washed. Helium was used as carrier gas at a flow rate of 80 ml/min. The column temperature was programmed from 70 to 380°C at 8°/min, and then held at the higher temperature if necessary to
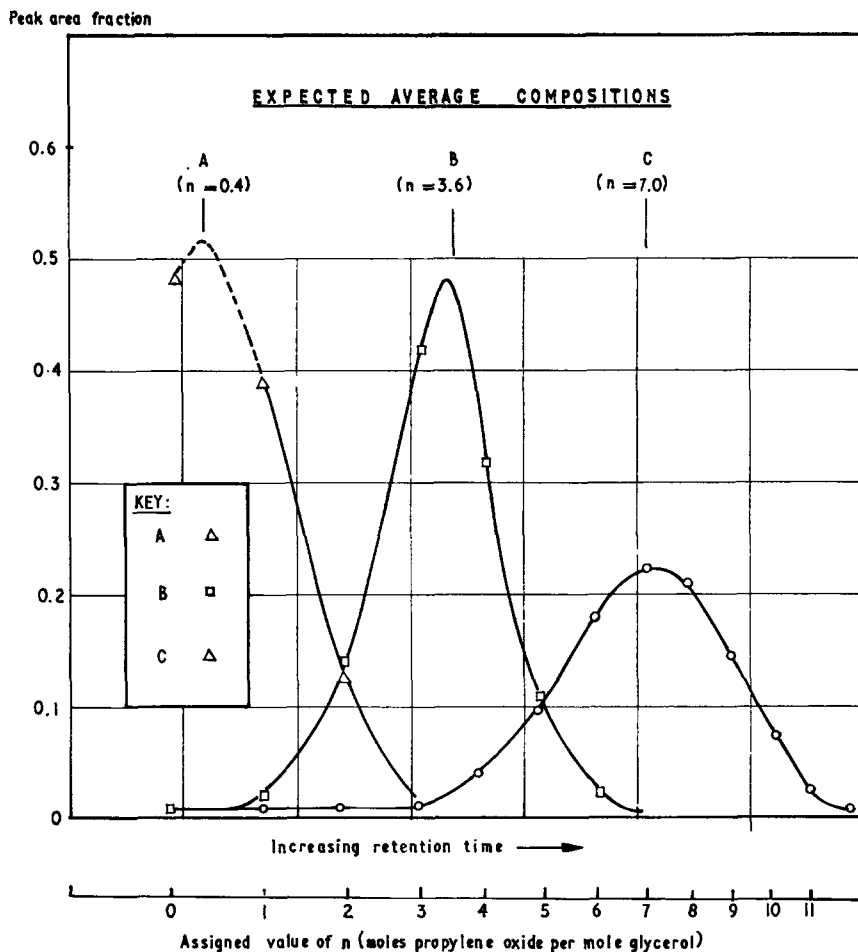
Peak area fraction

Fig. 2. Peak area distributions from chromatograms of polyols A, B, and C.

elute components with long retention times. The upper temperature was limited by the stability of the column packing. Because of this only polyols of molecular weight below 1000 could be analysed in a reasonable time. However, this limitation is of no great importance in the analysis of conventional, low molecular weight polyether polyols used to produce rigid foams.

Polyols

Polyols A, B, C, E, H, I, were made by base catalysed addition of propylene oxide to a polyhydric initiator such as glycerol, sorbitol, or sucrose.

Polyols D and F were made using boron trifluoride catalysis.

Polyols G, J, and K were of unknown composition.

RESULTS AND DISCUSSION

Interpretation of Chromatograms

Polyols A, B, and C are three glycerol/propylene oxide adducts with molecular weights of about 116, 300 and 500, respectively. The chromatogram of V is shown in Figure 1. The other polyols gave similar chromatograms. Figure 2 has been derived from the chromatograms of the three polyols. For each polyol, the area of an individual peak as a fraction of the total peak area, has been plotted against the peak retention time, and a smooth curve drawn through the points. All the peaks are seen to belong to a single series when plotted in this way. Also as expected, the maximum in the distribution curve occurs at a longer retention time for the higher molecular weight polyols.

Consideration of these features and comparison with chromatograms previously obtained from ethylene oxide adducts,[2] suggested that the individual peaks represented the different members of the homologous series of compounds formed by the addition of propylene oxide units to glycerol. The general composition of these compounds can be written "glycerol + n propylene oxide," where n is a positive integer. The first member of the series, glycerol itself, was found to have the same retention time as the first peak in the chromatogram of A. For that peak, therefore, n equals zero. For the next peak n was assumed equal to one, for the next n equals two and so on. These assignments are shown in Figure 2, giving a "calibration" of n against retention time. We have indicated on this scale the value of n corresponding to the average composition calculated from the hydroxyl value molecular weights of the polyols.

It is clear that the assignments given above lead to average compositions for the polyols which are close to those expected from their hydroxyl value molecular weights. (Number average and median molecular weights are very close for narrow distribution polymers.) The assumption that a chromatogram of the trimethylsilyl ether derivative of a polyol does represent the composition of the polyol itself would appear, therefore, to be justified. Having established this, we proceeded to make qualitative and semiquantitative comparisons between various polyols.

Effect of Polymerization Catalyst

The chromatograms of two glycerol-propylene oxide adducts of molecular weight about 300 are shown in Figures 1 and 3. One of the polyols, D, (Fig. 3) is made using a boron trifluoride catalyst, the other, B (Fig. 1), is made using potassium hydroxide. The chromatograms are quite similar but the acid catalyzed material apparently has a wider molecular weight distribution.

Chromatograms of two sorbitol-initiated polyols are shown in Figures 4 and 5. Polyol E (Fig. 4) was made using KOH catalysis, while Polyol F (Fig. 5) was made using BF_3 catalysis. The two polyols give quite different chromatograms, in contrast to the previous example. It has been sug-
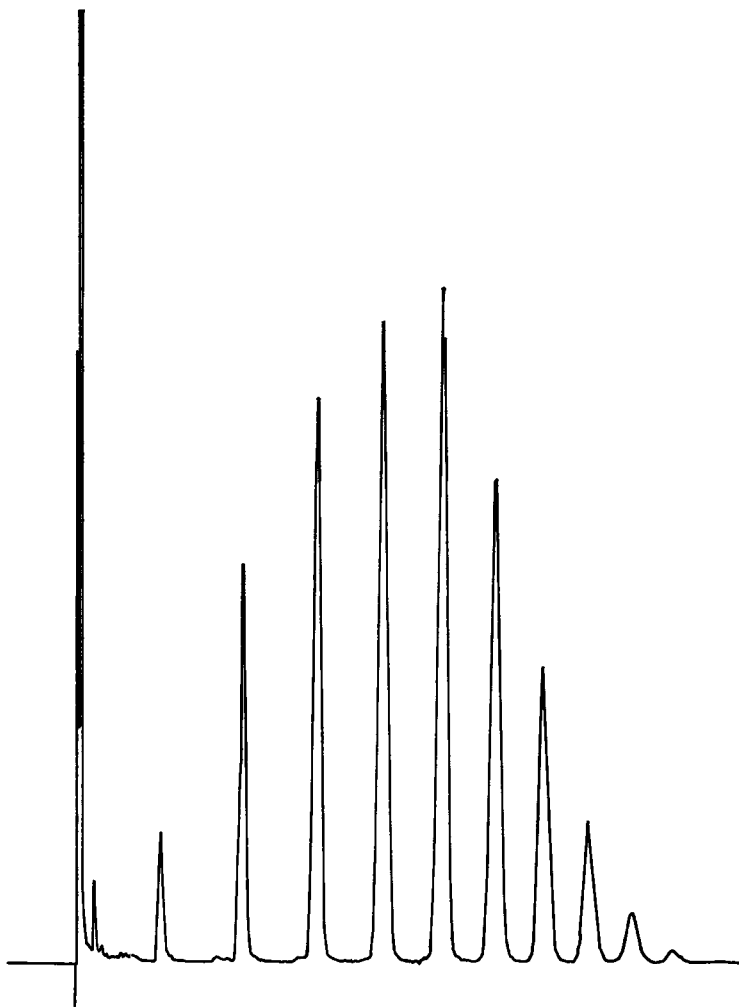
Fig. 3. Chromatogram of polyol D.

gested that the difference between the two sorbitol-based polyols is due to the occurrence of side reactions outside the sorbitol phase when BF_3 is used as catalyst;[4] such reactions are unlikely to occur in a glycerol-initiated polymerization.

In another experiment, it was found that a polyol made using potassium hydroxide and similar materials made by using amine catalysts gave virtually identical chromatograms. This does not mean that the polyols were identical however. Catalyst residues, for example, would not have been detected.

Comparison of Similar Polyols

Polyol E is based on anhydrous sorbitol, with a hydroxyl value of 610 mg KOH/g. Polyol G was thought to be a similar product, but its viss

cosity was appreciably lower than that of the laboratory material.   This difference was of considerable interest because lower viscosity materials are easier to handle during manufacture and foam production.

Chromatograms from the two polyols, shown in Figures 4 and 6, are seen to be very similar except for the presence in polyol G of some low
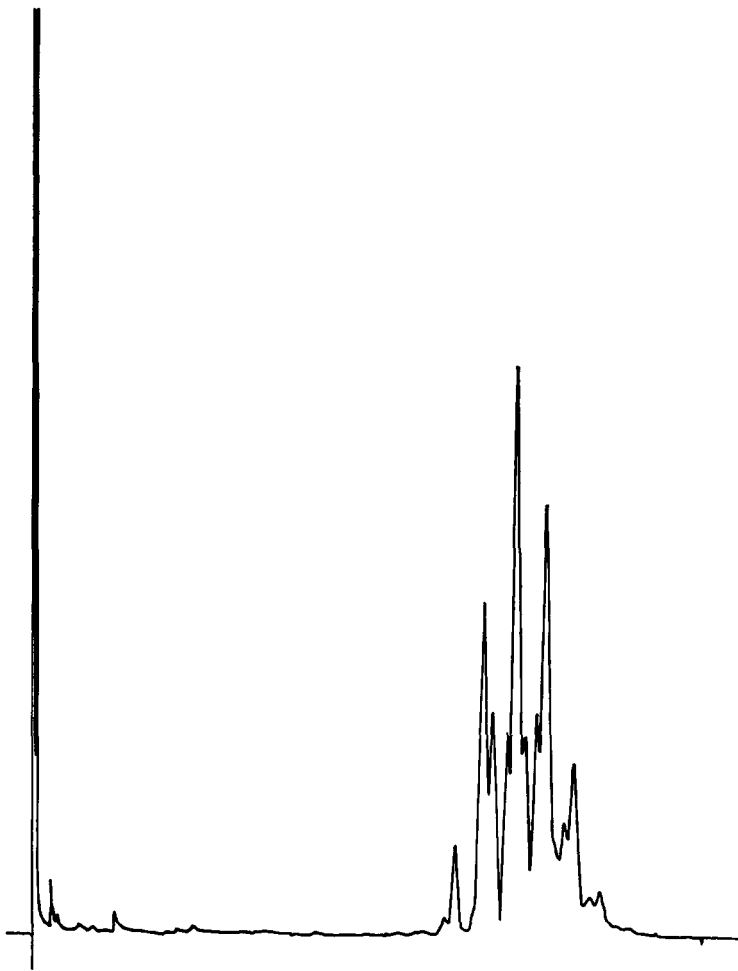

Fig. 4. Chromatogram of sorbitol adduct prepared using potassium hydroxide as catalyst; polyol E.

molecular weight compounds.   These are probably di- and tripropylene glycols and amount to about 3% of the total weight.   It was confirmed that blending polyol E with 2–3% wt of a mixture of the diols reduced its viscosity to about that of polyol G without any observable deleterious effects on the properties of resultant polyurethane foams.
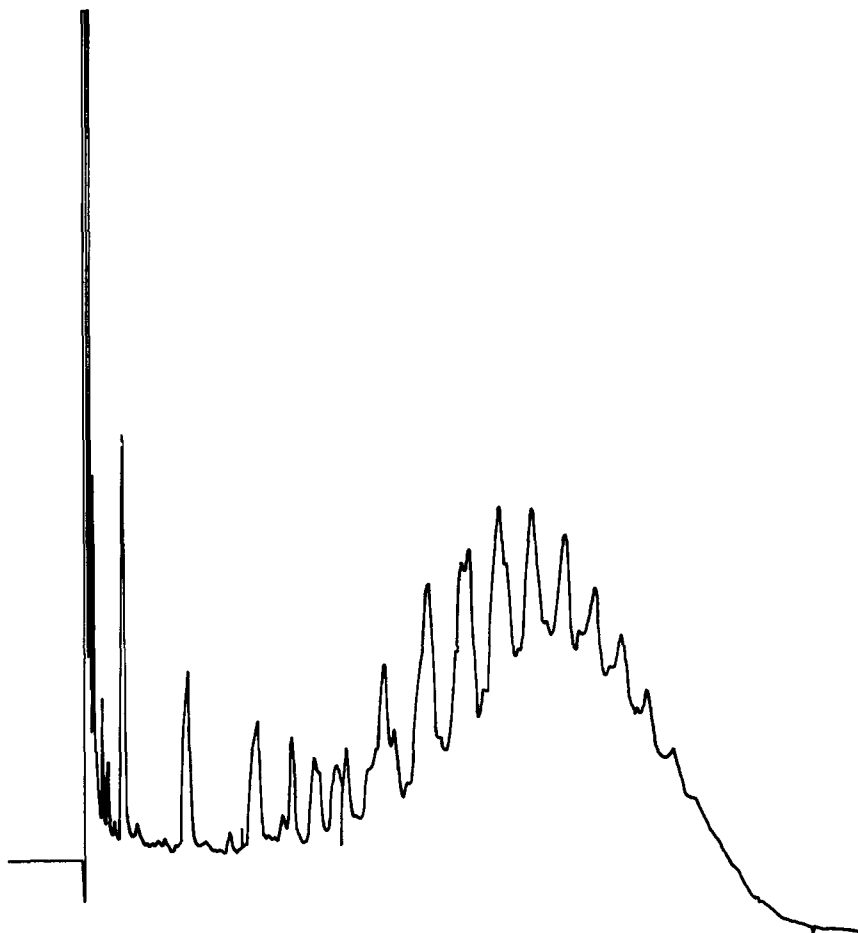
Fig. 5. Chromatogram of sorbitol adduct prepared using boron trifluoride as catalyst; polyol F.

Analysis of Polyols from Mixed Initiators

Polyol J was believed to be based on a mixture of glycerol and sucrose, propoxylated to a hydroxyl value of about 600 mg KOH/g. Two similar polyols were available in the laboratory, with glycerol-sucrose molar ratios of 3:1 (polyol I), and 4:1 (polyol H), and with hydroxyl values between 500 and 600 mg KOH/g. The chromatogram of polyol H is shown in Figure 7. The other polyols, I and J gave qualitatively similar chromatograms. The striking feature of these chromatograms is the presence of two main groups of peaks. The chromatograms were compared with those from polyols based on pure glycerol or pure sucrose with hydroxyl values of about 500. The retention times indicated that the first group of peaks (Fig. 7) was due to glycerol-based adducts and the second due to the sucrose adducts. A
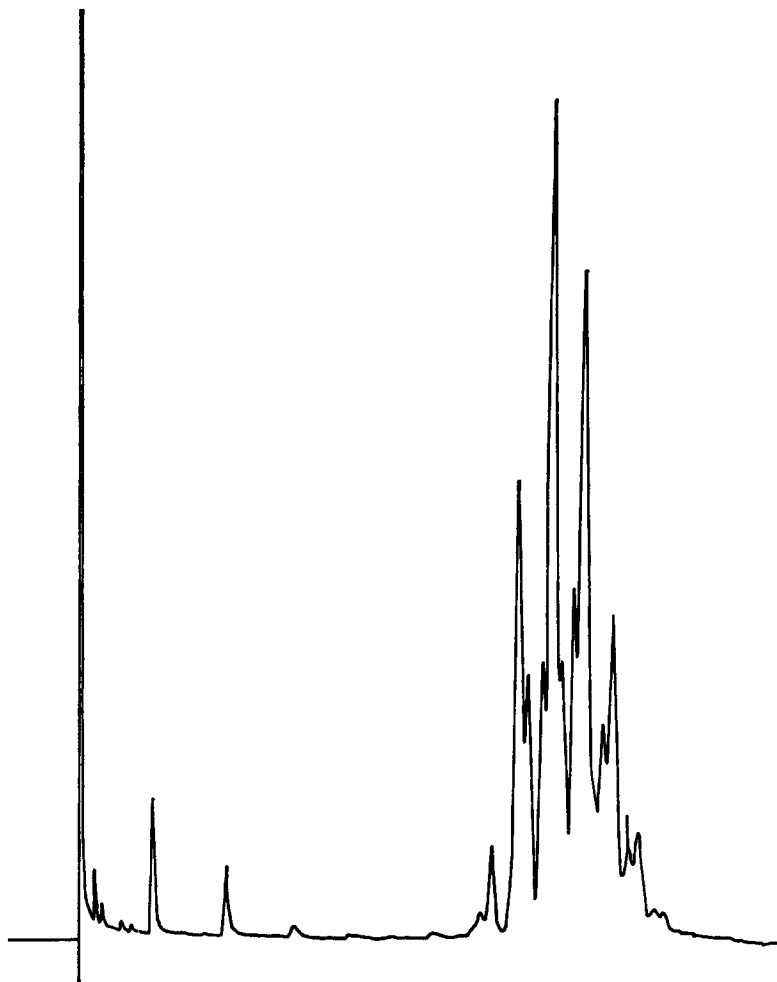
Fig. 6. Chromatogram of polyol *G*.

group of small peaks of short retention time which was present in the chromatogram of the polyol *J* was probably due to the presence of diols.

A measure of the ratio of glycerol to sucrose-based adducts in the polyol and hence of the initiator mixture used, can be obtained by measuring the

TABLE I
Peak Area Ratios from Polyol Chromatograms

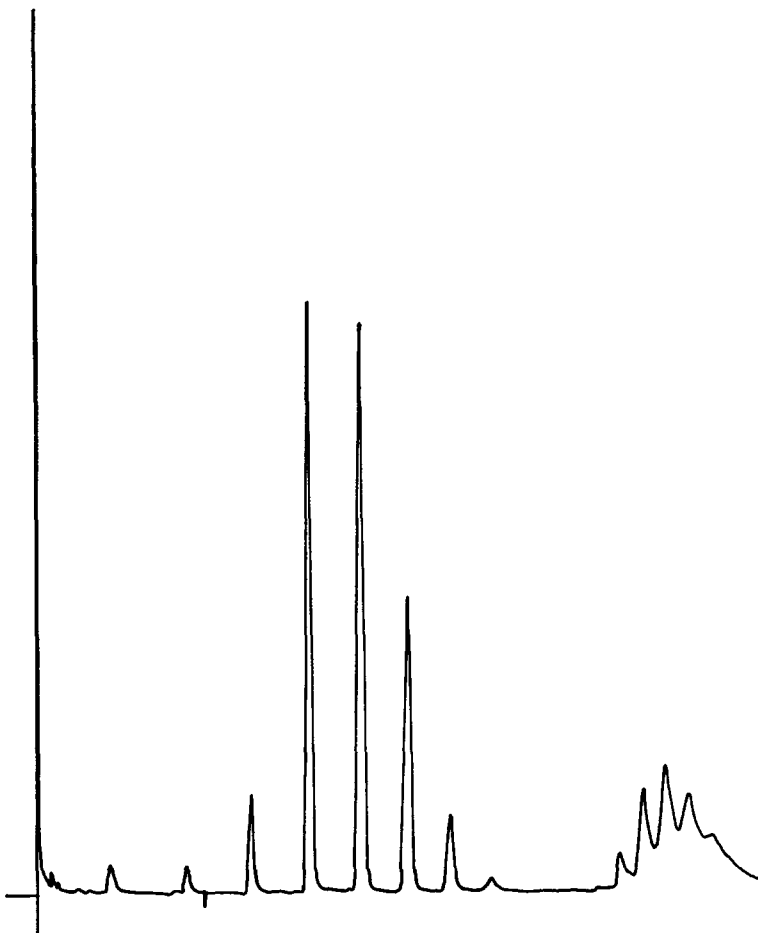| Polyol	Initiator ratio (moles) glycerol:sucrose	Peak area ratio
H	4:1	2:1
I	3:1	1.5:1
J	unknown	1:1

Fig. 7. Chromatogram of polyol H.

ratio of the areas of the two groups of peaks in the chromatogram. The area ratios found for the three polyols are shown in Table I.

The results suggest a glycerol-sucrose molar ratio of about 2:1 in the initiator of the commercial polyol J.

Examination of Polyols of Unknown Composition

In examples 3 and 4, information was available which suggested the possible compositions of the commercial materials and so enabled direct comparisons to be made with similar materials of known composition. If little or no information is available on the composition of the polyol, gas-liquid chromatography can still be a useful supplement to the standard methods of analysis.

Polyol K is a polyether triol, with a hydroxyl value of 380 mg KOH/g. The chromatogram of the polyol appeared to be similar to those of glycerol-
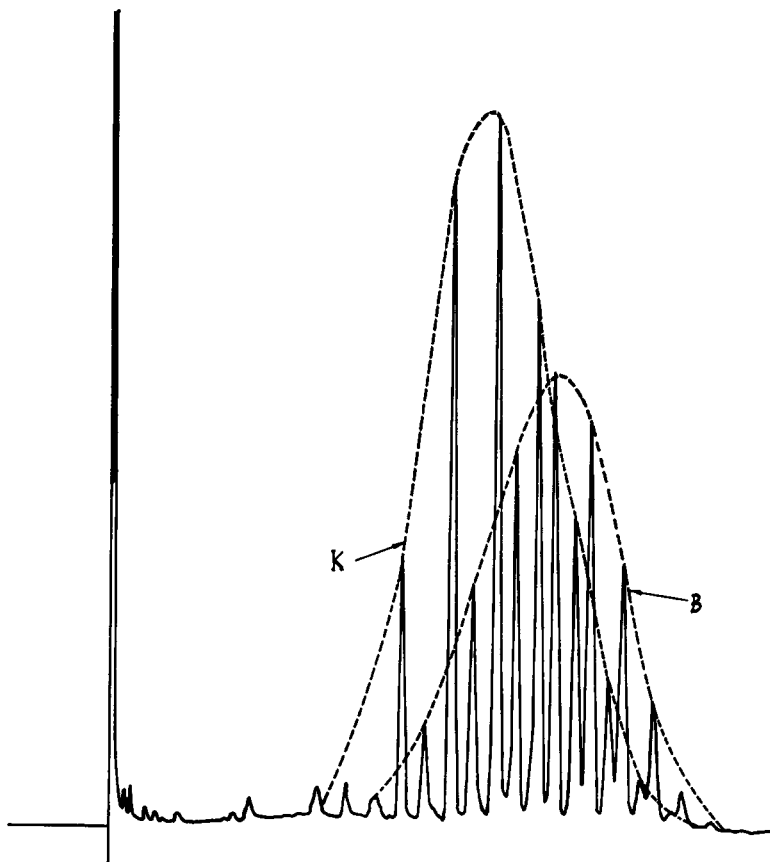
Fig. 8. Chromatogram of a mixture of polyols K and B.

based polyols, particularly polyol B (nominal hydroxyl value 336), with only one maximum in the distribution of regularly spaced peaks. The spacing and shapes of the individual peaks, and the width of the distribution were all similar to those found in the chromatogram of polyol B. The polyol would appear, therefore, to be a simple propylene oxide adduct of a triol. Figure 8 is a chromatogram of a mixture of polyols B and K. Obviously the two materials, while being similar in many respects, contain no major compounds in common. The peaks in the two chromatograms belong to different series. The simplest explanation of this is that different initiators are used in the manufacture of the two materials. It is probable that the material is based on trimethylolpropane. IR and NMR analyses also indicated that polyol K was a propylene oxide adduct, not based on glycerol, but could give no information on its molecular weight distribution.

References

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4. E. D. Garnet, unpublished work.