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CCL REPORT NO. 180

IDENTIFICATION AND DETERMINATION OF REACTIVE EPOXY DILUENTS BY GAS-LIQUID CHROMATOGRAPHY

FINAL REPORT

BY

GEORGE G. ESPOSITO

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U. S. ARMY COATING & CHEMICAL LABORATORY

Aberdeen Proving Ground

Maryland

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ABSTRACT

Programmed temperature gas chromatography (PTGC) is employed for the identification and determination of epoxy type reactive diluents in solventless epoxy compounds. The analysis can be applied directly to the product to be tested or, in the case of butyl glycidyl ether, to a sample separated from the resin.

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I. INTRODUCTION

Reactive diluents such as butyl glycidyl ether (BGE), allyl glycidyl ether (AGE), phenyl glycidyl ether (PGE), butanediol diglycidyl ether (BDE) and styrene oxide are used to modify epoxy resins used in coatings, adhesives, laminatates, castings and sealants. Handling problems are encountered when unmodified epoxies are employed and diluents must be added to reduce the viscosity. Organic solvents are not recommended for this purpose because solvents are retained in the polymer resulting in lower polymer strength.

When reactive diluents are incorporated into epoxy formulations, there is a great improvement in handling properties and only a minor sacrifice in the physical properties of the cured resin. The diluents contain epoxy groups which are capable of reacting in a manner similar to the epoxy resin and become an integral part of the polymer. These materials generaliy should not exceed 15 to 20 parts per hundred parts of resin.

Caulking compounds, based on a two component epoxy resin system, have been recommended for sealing weld joints in fuel tankers to prevent corrosion of the tank's interior and contamination of the fuel. It is essential that certain diluents be used in their proper proportion and analytical procedures are needed to insure conformity. The description of definitive analytical procedures for these materials could not be found in the literature. General tests such as epoxy equivalent, nonvolatile, etc. are inadequate and a more specific and accurate method is necessary. The objective of this investigation is to provide such a procedure.

PTGC has found broad utilization in the field of solvent analysis and this technique was also found suitable for the analysis of reactive epoxy diluents. The method can be applied directly to the epoxy component which has been weighed with an internal standard and thinned with acetone. Samples containing BGE are determined by thinning the sample with ethyl ether and immersing in an acetone-dry ice bath. After the resin precipitates, a portion of the liquid is reserved for the gas chromatographic analysis. The various reactive epoxy diluents are identified and determined by relating their retention times and peak areas to that of the internal standard.

II. DETAILS OF TEST

Chromatographic Unit

The instrument used to obtain the chromatograms was a Model 500 Linear Programmed Temperature Gas Chromatograph (F & M Scientific Co.) equipped with a Brown Electronik Recorder (Minneapolis-Honeywell Regulator Co.)

Operating Conditions

Detector cell temperature, °C.	300
Detector cell current, ma.	150
Injection port temperature, °C.	250
Helium flow at exit, cc. per minute	85
Initial column temperature, °C.	100
Terminal column temperature, °C.	200
Column heating rate, °C. per minute	7.9

Gas Chromatographic Column

A 10-ft. length of 1/4 inch copper tubing was packed with 20 parts silicone grease on 80 parts of acid washed 60-80 mesh chromosorb W.

Analysis

Accurately weigh about 2 grams of sample and 0.2 grams of methyl benzoate into a 25 ml. flask.

Direct. Thin with two milliliters of acetone and inject 3 microliters of thinned sample onto the column; follow the operating conditions described above.

Indirect. Dissolve or disperse the sample and methyl benzoate in 10 milliliters of ethyl ether and immerse in a dry ice-acetone bath. After the resin separates, isolate a few mls. by pouring the supernatent liquid into a small test tube. Allow the sample in the test tube to warm to room temperature and inject 10 microliters onto the column. Comply with the operating conditions described above.

Results

The separation of reactive diluents is shown in Figure 1. Figure 2 illustrates a separation obtained from a commercial product which was found to contain butyl glycidyl ether. A synthetic mixture of two reactive diluents with an epoxy resin produced the chromatogram shown in Figure 3.

Retention times, relative to methyl benzoate, are presented in Table I. Analytical results, obtained from mixtures of known composition, are shown in Table II. The analysis of a commercial product yielded 14.5% of butyl glycidyl ether which was in good agreement with the 15% indicated by the manufacturer.

III. DISCUSSION

The direct method works well, but epoxy resin is introduced into the injection port with every injection of sample, and the accumulation of carbonaceous material in the vaporization chamber is objectionable. In this investigation primary interest was centered on butyl glycidyl ether, since this was the reactive diluent used in the caulking compound being evaluated. Decomposition of resin in the injection port can be circumvented by using the indirect method in which the resin is separated prior to the introduction of the sample into the instrument. This method works well with BGE, but is not applicable to the other reactive diluents.

Butanediol diglycidyl ether was investigated along with the other reactive diluents and produced a peak which was not in proportion to the amount used. The procedure proposed can be used to identify BDE but is not recommended as a quantitative method for this compound.

The procedure described in this report enhances the capability of the laboratory in an area where little or no information was available. The procedure is relatively rapid and accurate.

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APPENDIX A

TABLE I

RELATIVE RETENTION TIME DATA FOR DILUENTS

	Relative Retention Time (methyl benzoate = 1)
Allyl glycidyl ether	0.51
Butyl glycidyl ether	0.73
Styrene oxide	0.90
Phenyl glycidyl ether	1.40
Butanediol diglycidyl ether	2.0

TABLE II

ANALYSIS OF KNOWN MIXTURES

Sample Type	Present, %	Found, %
1. Butyl glycidyl ether*	18.2	18.2; 18.3
2. Phenyl glycidyl ether**	9.8	9.5; 9.7
Allyl glycidyl ether	8.6	8.4; 8.6

*Blended with liquid epoxy resin, indirect method used.

**Blended with liquid epoxy resin, direct method used.

APPENDIX B

Figure 1
Separation of reactive epoxy diluents.

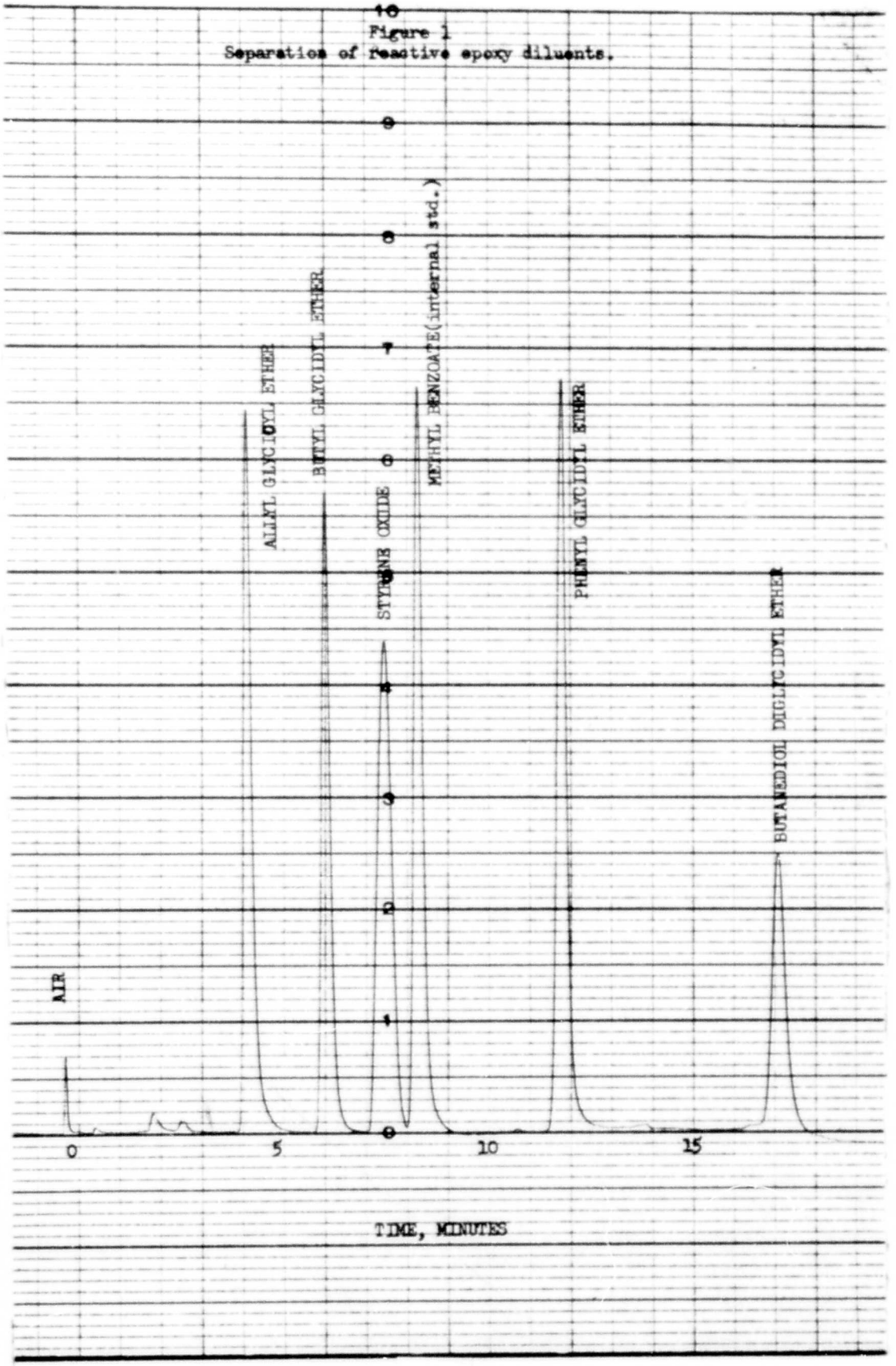

Figure 2
Analysis of commercial product.

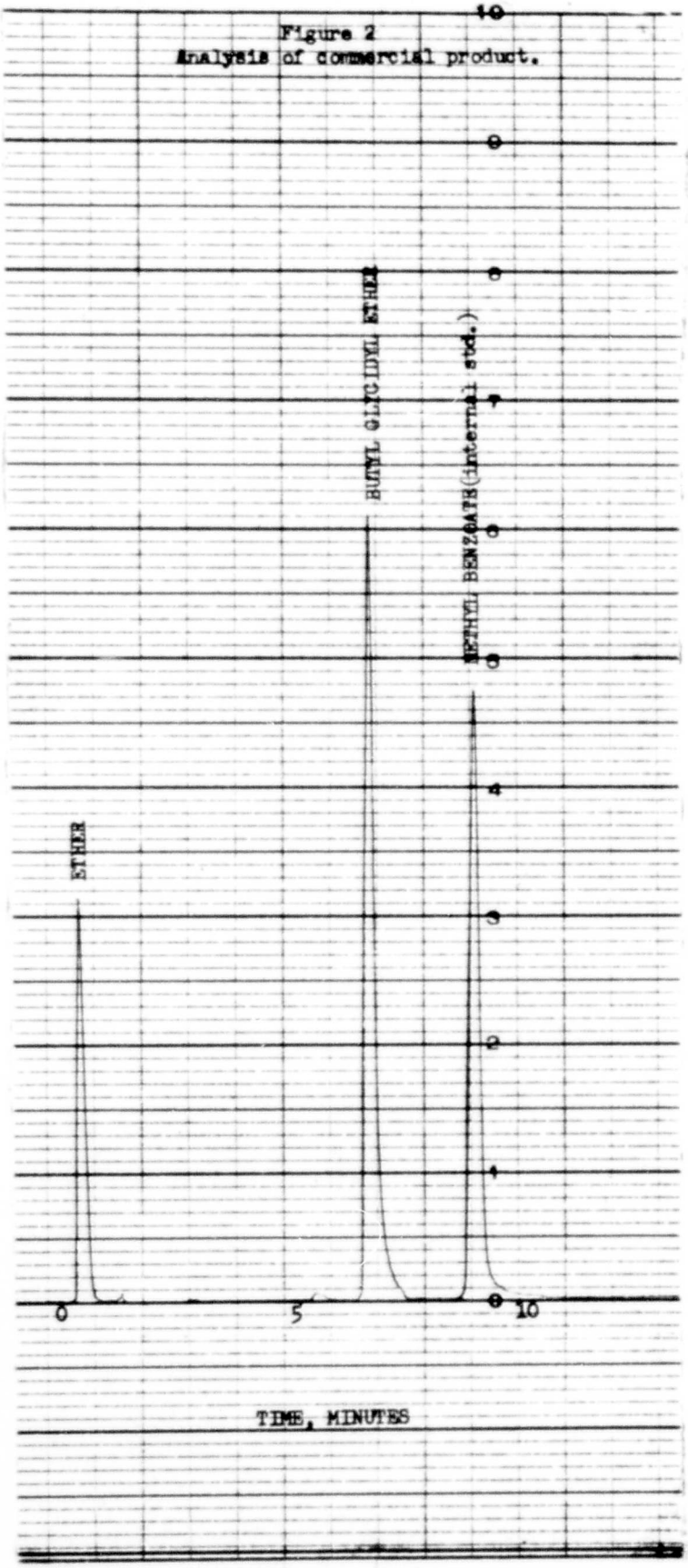

Figure 3
Analysis of synthetic mixture.