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COATINGS INTERMEDIATES

VINYL CHLORIDE AND VINYLIDENE CHLORIDE DETERMINATION IN VINYL TERPOLYMER LATEX

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R N WHEELER JR.

AUTHORS: A. E. Gabany, Jr. (2)

Work by: H. T. Bias
A. E. Gabany, Jr.

Supervisor: R. A. Bleidt (3)

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SUMMARY An existing gas chromatographic method of analysis for the determination of low levels of vinyl chloride monomer has been modified to include concurrently low levels of vinylidene chloride. The modification enabled the monom r analysis of QEX latex, vinyl chloride-vinylidene chlorid - glycidyl methacrylate terpolymer, which UCC is developing f r use as a coating resin for metal food containers.

Several QEX samples were analyzed with values determined ranging between 14 ppm to 0.13 percent vinyl chloride and 800 ppm to 0.18 percent vinylidene chloride. In addition two thin films, typical of can coatings, were analyzed for residual vinyl chloride monomer. The results indicated less than 1.5 ppm vinyl chloride present.

The results obtained for vinyl chloride and vinyliden chloride monomers are tablulated. The modified method of analysis is appended.

INTRODUCTION UCC is presently developing QEX latex, vinyl chloride-vinylidene chloride-glycidyl methacrylate terpolymer, for use as a coating resin for metal food contain rs. Sufficient progress has been made in the development work that FDA approval is being sought. However, in view of the rec nt activity relating to vinyl chloride, it became imperative that the residual monomer content be determined prior to expecting an approval by the FDA.

Messrs. H. T. Bias and R. A. Bleidt of the Res arch and Development Analytical Section recently reported a gas chromatographic method (1) which could determine low levels of vinyl chloride monomers in PVC resins. It was felt that this

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method, with some minor modifications, might be applicable for the QEX latex samples. There were, however, some possible drawbacks with the QEX latex. First, and probably most important, was the fact that the samples are approximately 65-70 percent water and secondly, the amenability of vinylidene chloride to the method had not been ascertained. In view of this, Dr. T. L. Dawson submitted samples of QEX latex for vinyl chloride and vinylidene chlorice analysis. He also submitted two thin film samples typical of can coatings which were cast from two of the latexes for residual vinyl chloride monomer analysis.

DISCUSSION The gas chromatographic method of analysis as reported (1) utilizes tetrahydrofuran (THF) as a solvent for the analysis. While this feature appeared attractive for QEX latexes, its use became the first necessary modification of the analysis. Our findings were that if THF is mixed with water, some unexplained reaction occurs which results in th formation of at least two unidentified compounds which dir ctly interfere in the ensuring GC analysis. Not only are the peaks only partially resolved from each other, but one has the same retention time as vinylidene chloride. Various operating parameters were experimented with in an attempt to resolv th problem but no satisfactory solution was found. Eventually it was determined that the best method was to analyze the latexes in their virgin form, i.e. without THF solvent.

After having determined to analyze the neat sample it was also decided to add an internal standard for quantitative purposes. Ethanol was chosen for the internal standard both for its solubility in the latex and the fact that its retention time was between those observed for vinyl chloride and vinylidene cnloride. Recorded in Table I are the results which were obtained on five QEX latex samples.

One of the samples, 7981-29-G102, was analyzed before and after a stripping experiment was performed which was designed to remove both vinyl chloride and vinylidene chloride. As can be seen from the data, 98.5 percent of the vinyl chloride was removed whereas 44.2 percent of the vinylidene chloride remained.

Two of the samples were used in the preparation of thin films typical of can coatings by baking for 4 minutes at 365°F. These films were then removed from the metal surface and submitted for monomer analysis. Recorded in Table II are the results obtained for these samples. It might be noted at this time that the method of analysis reported (1) for PVC resins was used to obtain these analyses.

The modified method of analysis is attached as App ndix A to this report.

BIBLIOGRAPHY

1) Bias, H. T. and Bleidt, R. A., Vinyl Resins, Gas Chromatographic Method for the Determination of Low Levels of Vinyl Chlorid Monomer, Project Report, R and D, South Charleston, W. Va. file No. 19072, January 2, 1974.

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A. E. Gabany, Jr.

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Attachment:
2 Tables
1 Appendix A

TABLE I

VINYL CHLORIDE AND VINYLIDENE CHLORIDE

CONTENT IN QEX LATEX[a]

	Results[b]	
Sample	Vinyl Chloride	Vinylidene Chlorid
QEX 2033-3	0.032	0.121
QEX 2033-10	0.130	0.100
QEX 2033-11	0.133	0.121
7981-29-G102 before stripping	0.093	0.181
7981-29-G102 after stripping[c]	0.0014	0.080

(a) All samples contain 30-35 percent solids

(b) Percent by weight

(c) Stripped 4-5 hours at 75°C

TABLE II

VINYL CHLORIDE CONTENT[(a)] IN THIN FILMS

CAST FROM QEX LATEX

Sample	Results
QEX 2033-10	<1.5 ppm
QEX 2033-11	<1.5 ppm

(a) Vinyl chloride analysis - Project Report fil No. 19072

APPENDIX A

DETERMINATION OF RESIDUAL VINYL CHLORIDE AND VINYLIDENE CHLORIDE MONOMERS IN VINYL TERPOLYMER LATEXES

1 PURPOSE A procedure for determining the amount of r sidual vinyl chloride and vinylidene chloride present in vinyl terpolymer latexes is described. The latex suspension to which an internal standard is added is analyzed using a gas chromatographic technique. The method is applicable for us with vinyl chloride-vinylidene chloride-glycidyl methacrylat terpolymers latexes and other vinyl chloride-vinylidene copolymer latexes in which there are no volatiles which int rf r in the determination.

2 EQUIPMENT AND REAGENTS

a) Gas Chromatograph, Hewlett-Packard (F and M) Model 5750 or equivalent, equipped with a hydrogen flame ionization detector.

b) Ethanol, reagent grade

3 INSTRUMENT PARAMETERS

Instrument	Hewlett-Packard F and M Model 5750 (or equivalent) equipped with hydrogen flame ionization detector
Column	6 feet x 1/8-inch stainless steel tubing packed with Chromosorb 102, 60/80 mesh
Temperatures	
Column	100°C isothermal for 8 minutes, manually increased to 250°C
Injection port	100°C (maximum)
Detector	300°C
Carrier gas	helium
Flows	
Helium carrier gas	25 cc/minute
Hydrogen	20 psi at cylinder head
Compressed air	40 psi at cylinder head
Sample size	2 microliters
Internal standard	ethanol
Approximate elution times	
Vinyl chloride	2 minutes
Ethanol	4 minutes
Vinylidene chloride	6 minutes

4 PROCEDURE Accurately weigh 10 to 15 milligrams of ethanol into a 6-dram vial containing 10 grams of the sample to be analyzed. Inject 2.0 µl of the solution into the gas chromatograph using the parameters listed in Section 3. Measure the areas of the vinyl chloride, ethanol, and vinylidene chloride peaks using an acceptable technique (e.g. planimeter, automatic integrator, etc.).

5 CALCULATION Calculate the weight percent of vinyl chlorid and vinylidene chloride using the formulae:

a) $\frac{A_1 \times S \times T_1}{A_2 \times T_2}$ = vinyl chloride, % by weight

b) $\frac{A_3 \times S \times T_3}{A_2 \times T_2}$ = vinylidene chloride, % by weight

A_1 = area of vinyl chloride

A_2 = area of ethanol

A_3 = area of vinylidene chloride

S = percent by weight of ethanol in sample

T_1 = recorder attenuation for vinyl chloride peak

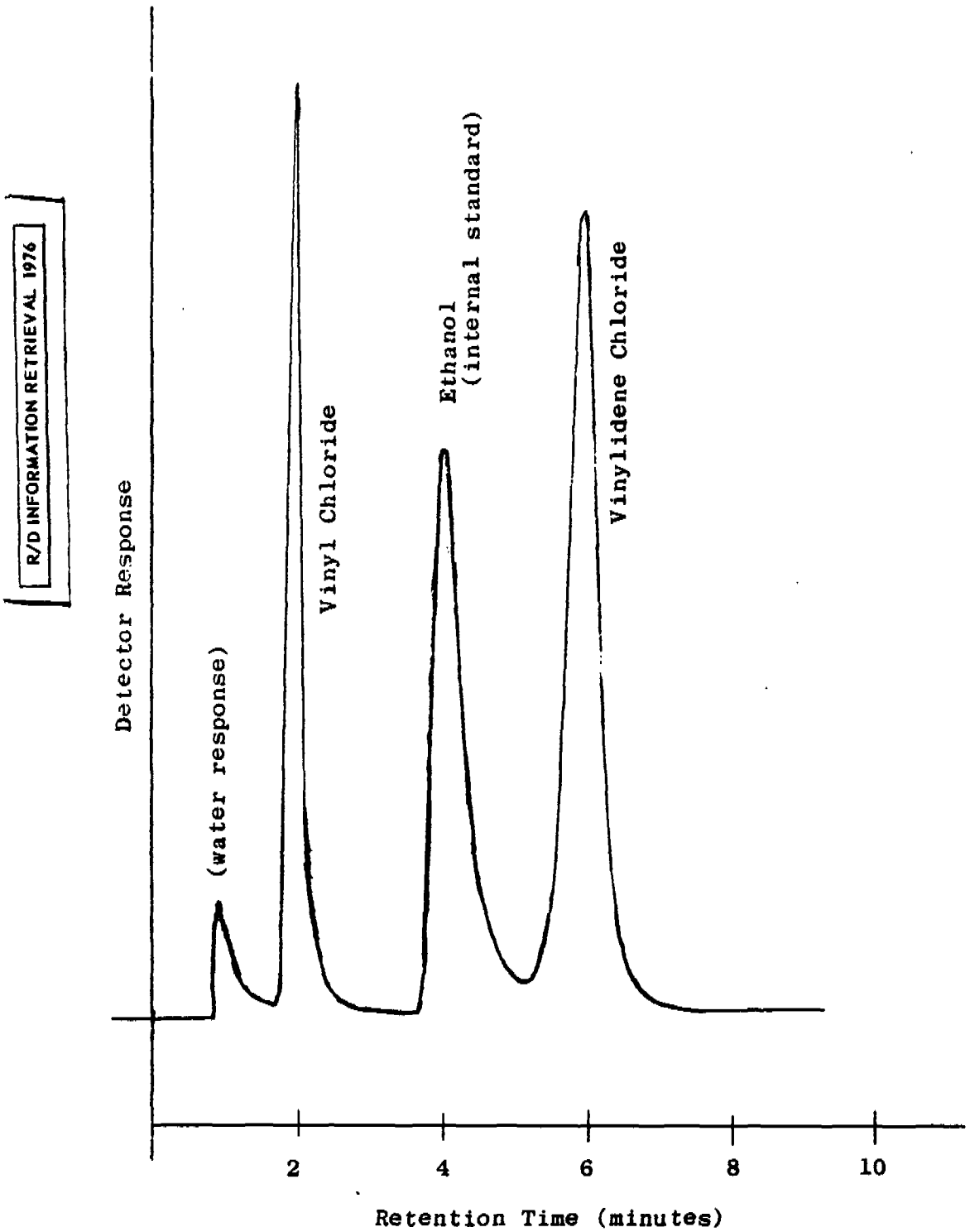
T_2 = recorder attenuation for ethanol peak

T_3 = recorder attenuation for vinylidene chloride p ak

6 TYPICAL CHROMATOGRAM A typical chromatogram is attached as Figure 1

FIGURE 1

TYPICAL GAS CHROMATOGRAM OF VINYL CHLORIDE-
VINYLIDENE CHLORIDE-GLYCIDYL METHACRYLATE TERPOLYMER
LATEX ANALYSIS FOR RESIDUAL MONOMERS



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