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UNION CARBIDE

INTERNAL CORRESPONDENCE

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CHEMICALS AND PLASTICS

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To (Name) Mr. R. N. Wheeler
Division Technical Center
Location South Charleston, WV

Date January 15, 1980

Originating Dept.

Answering letter date

Subject RVCM - OSHA
UCC - Solvent Vinyl Resins

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Attached is the draft of a proposed MEMO for OSHA describing work we have done measuring RVCM content of Union Carbide Solvent Vinyl Resins.

I understand this document is to be submitted to OSHA by February 10, 1980. I urge all who have comments, etc., to submit these to Nick Wheeler, Al Gregory and myself as soon as possible.

G. S. Peacock

GSP:ld
Attachment

UCC
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MEMO - RVCM CONTENT OF

UNION CARBIDE SOLVENT VINYL RESINS

Introduction

Union Carbide Corporation has been a manufacturer of solution polymerized vinyl chloride copolymer resins for more than 45 years. The solution polymerization process, used exclusively by Union Carbide, by its nature represents the most facile way, known technically, to remove residual vinyl chloride monomer. The manufacture, distribution and use of these products complies with all existing regulations and Union Carbide plans to demonstrate compliance with any future regulations.

The solution polymerized copolymers are listed by chemical identity in Regulation 175.300 for resinous and polymeric coatings and may lawfully be used as food contact surfaces applied to metallic substrates under this regulation.

On September 3, 1975, the FDA published a notice of two proposed rules relating to use of vinyl chloride polymers that come into contact with food. The first proposal called for amendment of existing FDA regulations by adding vinyl chloride monomer to the list of substances prohibited from use in, or in contact with human food. The second proposal contained a paragraph that specifically permits the continued use of vinyl chloride homopolymers and copolymers in coatings, gaskets, cap liners, flexible tubing and plasticized film. Neither of these proposals by the FDA were ever put into effect. The proposals did result in studies submitted to the FDA that demonstrate that rigid vinyl chloride homopolymers containing very low residual monomer levels can be

produced and that at these levels the monomer may not migrate to food. At this time, Union Carbide initiated an extensive testing program to demonstrate to ourselves, the appropriate government regulatory agencies and the industry that the solution polymerization process, used exclusively by Union Carbide, results in the lowest residual monomer level in the industry and that these products may be safely processed and used in industry and in food contact applications that will meet the criteria of any new regulations.

Analytical Testing

The initial objective of this work therefore was to develop the capability of measuring vinyl chloride monomer levels in the low ppb range using the headspace/GC method proposed by FDA analysts.[1]

It was early recognized there are many potential interferences when measuring RVCM in the ppb range. The peak attributed to vinyl chloride must be confirmed by a subsequent GC-MS analysis which is not always feasible when processing large numbers of samples. Vinyl chloride copolymers appear to contain many more interfering species than homopolymers. In addition, interferences are observed in most lots of helium sparged DMAC and more interfering species are introduced when the resins are dissolved in the solvents typically used during processing by the coatings industry.

The use of the Hall electrolytic detector to replace the FID detector in the FDA method appears to be an effective way to resolve non-chlorine containing interfering species. The results in Table I show the differences obtained using the FDA method with FID detection and the Hall detector. The interfering species in

the VAGH sample was subsequently identified by GC-MS as isobutylene.

TABLE I

RVCM - COMPARISON FID VS HECD

RVCM CONTENT - PPB FDA METHOD

	FID	HECD*
VYHH B-7661	110, 130	4, 4, <2, <2
VAGH A-4608	160	7, 7, <2
20% VYHH Solution in MEK	420	5
FDA Referee Sample	2, 1	4
FDA Results	6	-

*Hall Electrolytic Conductivity Detector.

Good agreement between FDA analyses and UCC analyses were obtained on FDA submitted referee samples. These plasticized PVC homopolymer samples were tested by UCC using the FDA method separately using FID detection or Hall electrolytic detection. Results are shown in Table II.

TABLE II

REFEREE SAMPLE TESTS

	RVCM Content - ppb		
Lab	FDA	UCC	
Detector	FID	FID	HECD
RVCM	6	1, 2	4

An evaluation of the precision of the FDA method using the HECD at very low monomer levels was completed. Five samples of an aged, well characterized blend of VYHH (vinyl chloride-vinyl acetate copolymer) were analyzed over a period of five days. Results are shown in Table III.

TABLE III

PRECISION-MODIFIED FDA METHOD

	RVCM - ppb
Individual Values Separate Analyses	1, 1, 2, 1, 1
Mean	1, 2
Standard Deviation	±0.45

F-45 Method

The F-45 method was used to test large numbers of production samples. This method was adapted and used because of the much lower analysis time required. Results, shown in Table IV, agree very well with data obtained using the FDA method with electrolytic conductivity detection.

The method is a headspace technique using an automatic analyzer (Perkin-Elmer F-45) coupled with an electrolytic conductivity (Hall) detector. The chromatographic column contains porous polymer (Tenax GC) and is backflushed to eliminate high boiling components. Polymers are dissolved in high boiling, interference-free solvent (dimethylacetamide) at concentrations of 7-29% depending on solubility considerations. Volatiles are freed from the resin solutions by heating at 80°C. Two types of standards are used:

commercially prepared VCM in nitrogen and monomer solutions in tetrahydrofuran prepared at this site.

VCM can be measured quantitatively in the 10 to 8000 ppb range by electronic integration routinely. A level of 4 ppb can be achieved using maximum sample size, an amplifying filter, and manual measurement. This procedure employs an automated headspace analyzer and a flame ionization detector. It had originally been developed by Dow Chemical. Similar methods have been described in the current literature; the most pertinent references are:

1) H. Hackenberg, A. P. Schmidt, "Gas Chromatographic Headspace Analysis", Heyden and Son, Ltd., London 1977, pp. 59-62.

2) "The Determination of Vinyl Chloride-A Plant Manual", Chemical Industries Association, Ltd., London 1977, Standard Methods #5 and #8.

Production Resin

An analysis of samples of production resins was made to determine:

1. Residual monomer content as produced.
2. Monomer content variability.
3. Residual monomer content as received by UCC customers.

The 'as produced' products were measured on Blend samples. Production variability data was determined from several Blend samples. The 'as received' monomer contents were determined on samples taken from bagged resin (50 lb. bags) stored in the laboratory from 2-4 weeks. We estimate the typical time from production through warehousing and the distribution system to the customer is six weeks.

The corresponding blend samples, taken before bagging, are shown. The results shown in Table IV are typical of UCC solvent vinyl resins. It should be noted that the data shown are results to date; testing on all products will be completed as the production schedule permits.

Particle Size

The rate of diffusion of a monomer from a polymer increases approximately as the square of the film thickness decreases. In the Union Carbide solution polymerization process, the dry resin is recovered from solution by precipitation with an alcohol-water mixture. The precipitate thus produced is subsequently dried in hot air. This leads to a porous particle that should result in rapid monomer loss. This theory seems to be confirmed by the observed decrease in monomer content as the products are stored in bags. Particle size and particle size distribution typical of the Union Carbide products is shown in Table V.

T. B. Gibb, G. S. Peacock

TABLE IV

UNION CARBIDE SOLVENT VINYL RESINS

Resin	Sample	Date 1979	Blend	RVCM - ppb Method F-45	FDA
VYHH	Blend	8-23	7920	38	
VYHH	Blend	8-23	7915	65	
VYHH	Bagged 4 weeks	9-24	7915	<16, 6	8
VMCA	Blend	8-9	140	<16, <16, 10	
"	"	8-13	138	6	
"	"	8-15	141	<16, <16	
"	"	8-23	142	39	32
"	Bagged 4 weeks	9-24	142	<16, <16, <16	
VAGH	Blend	-	4357	-	7, 7
"	Blend	-	4608	-	6
"	Bagged 2 weeks	-	4608	-	< 2
VAGD	Blend	-	4980	<10	
"	Blend	-	275	<10	
"	Bagged 4 weeks	-	275	<10	

TABLE V

TYPICAL UCC VINYL COPOLYMER

PARTICLE SIZE AND DISTRIBUTION

VYHH - Shift Composite - 12/2/79

Mesh	20	40	60	80	100	140	200	270	325	400	Median
Microns	841	420	250	177	149	105	74	53	44	37	80
Wt. % Through Screen	100	99	95	88	80	65	46	45	19	9	

References

(1) J. Lawrence Dennison, Charles V. Breder, Timothy McNeal, Roger C. Snyder, John A. Roach, and James A. Sphon; "Headspace Sampling and Gas-Solid Chromatographic Determination and Confirmation of < 1 ppb Vinyl Chloride Residues in Polyvinyl Chloride Food Packaging"; Journal of the Association of Official Analytical Chemists; Vol. 61, No. 4, 1978.

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