INTERIM REPORT

ANALYSIS OF DOW VINYL CHLORIDE

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SUMMARY Samples of vinyl chloride monomer representing typical Dow production have been analyzed using chemical and chromatographic techniques by both the Texas City and South Charleston plant laboratories. Disagreement as to impurity constituents, and level of impurities, is being resolved via a standard sample being prepared in Charleston.

Texas City and Dow data are in general agreement as to impurity and level of impurity in Dow's monomer. The only significant difference to be resolved is the level of vinyl acetylene.

DISCUSSION At the meeting in New York City on October 6, 1967, between representatives of UCC and Dow Chemical Company concerning the purchase of vinyl chloride, a monomer testing program was agreed upon in which duplicate samples representing Dow's current production would be provided to the UCC laboratories for internal evaluation. After completion of the analyses, a meeting would be held between UCC and Dow to compare results and resolve the differences which might have occurred. Results of the preliminary exchange of data between the UCC laboratories at Texas City and South Charleston are given in Table I.

It was evident from the initial comparison of data that an internal disagreement would have to be resolved prior to any exchange of data with Dow. Not only was the level of total impurities reported in disagreement, but the laboratories identified different constituents in the Dow monomer.

A comparison of the data indicated that both laboratories were observing essentially the same constituents, but that interpretation of the identity of these constituents was different. Further study of the Dow monomer was made at Texas City in an attempt to reconcile the differences of identification of the impurities. Primarily a distinction was involved in identification between acetylene and n-butane, butadiene and methyl acetylene, and vinyl acetylene and acetaldehyde. From this study, the Texas City Resins Laboratory observed that the separation of acetylene and n-butane, and the separation of butadiene and methyl acetylene, were impossible with the VPC column and method currently in use at Texas City. However, a separation was observed between vinyl acetyl ne and acetaldehyde, and the impurity in the Dow sample was determined to be vinyl acetylene. It might be noted that the South Charleston laboratory had not experienced vinyl acetylene in vinyl chloride prior to the analysis of the Dow

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monomer; thus their identification as acetaldehyde. Evaluation is currently in progress at South Charleston for determining the identification of this constituent.

From discussions with Rodney Webb of Dow Chemical, Freeport, Texas, it was determined that we should expect to find n-butane and butadiene in their monomer. Chemical analysis for acetylene (determined to be nil) substantiated the Texas City laboratory's identification of n-butane. Chemical analysis for aldehydes also was found to be nil. Although South Charleston and Dow laboratories are reporting additional impurities of less than 1 ppm, all laboratories essentially agree upon the identification of the main impurities (1ppm or more) in the Dow monomer supplied for the test program.

A meeting was held in South Charleston by M. E. Sutherland between interested parties of the UCC laboratories to discuss the differences in our chromatographic methods and the effects these differences might have upon the analysis of the Dow monomer. Solutions to reconcile our disagreement of analyses prior to a meeting with Dow were also discussed. J. F. Haskin and W. W. Fink of the Technical Center, co-authors of the chromatographic method(1) currently in use at Texas City, also attended the meeting to provide technical assistance during the discussions.

Although both methods in use by the UCC laboratories were determined to be similar, each instrument parameter was discussed to determine its possible effect on the analyses. Differences in column packing and mode of operation (temperature programming at Texas City vs a combination of isothermal and temperature programming at South Charleston) were not found to be critical, although possibly the combination technique will provide a better separation of the "lights." Liquid sampling versus gas sampling also could be quite critical if the condensed vinyl chloride is not handled with extreme care to prevent loss of the lighter components. The Texas City laboratory has not been successful in using a vapor technique of injection into the column. Sampling techniques should not cause the differences observed between the two laboratories.

The hydrogen flow rate was a parameter of concern since the flow rate is a critical aspect in gas chromatography. Sensitivity of the hydrogen flame detector is greatest at an optimum flow rate (different for every instrument), and as this optimum rate is exceeded, the sensitivity of the detector declines. The Texas City laboratory has been operating in excess of that recommended in the referenced chromatographic method of analysis.(1) Subsequent study of the optimum hydrogen flow rate used at Texas City indicates the need to decrease the hydrogen flow rate from 45 ml/min to 35 ml/min.

The South Charleston laboratory currently operates its Beckman GC-5 at a greater sensitivity (attenuation) than the Texas City laboratory's F and M 810. The desirability of operating at higher sensitivities is quite evident.

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(1) J. F. Haskin and W. W. Fink, 511, "Vinyl Chloride Analysis of Process Streams at Texas City," January 12, 1967.

The pr bability of detecting additional impurities is greater, although the total levels of impurities should not be affected by more than about 5%. The Texas City laboratory is currently evaluating the higher sensitivities to determine the optimum level of operation.

During the discussions it was determined that the greatest factor for the observed difference of analyses was the use of response factors to convert a volume percentage to a weight percentage. Texas City uses the conversion factors, but South Charleston currently reports volume percentages. Studies have revealed that each constituent has a certain sensitivity to the hydrogen flame detector. Only by reporting of concentrations based on a weight ratio can an accurate level of concentration be given. The Texas City laboratory currently uses response factors based on the referenced method. However, during the analysis of the Dow monomer by the Texas City laboratory, the methyl chloride response factor was redetermined. The response factor was found to be 2.34 (an increase from 0.810). Reporting of the level of methyl chloride in the Dow monomer was based on the new response factor. The Texas City laboratory has redetermined response factors for n-butane and isobutane since the meeting in South Charleston. However, the new factor did not influence the level of impurities previously evaluated. A continuation of this study in response factors is currently in progress at Texas City.

A decision was reached to utilize response factors in futur analysis of the Dow vinyl chloride. The Technical Center is preparing samples of known concentration of impurities most likely to be detected in the Dow monomer. These samples will be used to determine response factors so that future evaluations will be based on the same standard.

An informal meeting was held with Dow's Rodney Webb at Freeport, Texas, by F. L. Johnson and R. M. Arnold on December 7, 1967, to exchange data and to discuss any differences in analysis of the vinyl chloride. Results of the test program are given in Table II. It should be noted that Dow Chemical utilizes response factors in their evaluations of vinyl chloride. Dow has expressed an interest in participating in the use of the standard to determine response factors. The only disagreement in the vinyl chloride analyses was in the reported level of concentration of vinyl acetylene. Each laboratory will redetermine their vinyl acetylene response factor using a standard.

Additional evaluation of the Dow vinyl chloride was made at all participating laboratories to determine water content, iron, volatiles, and acid concentration. Results of this evaluation are also given in Table II. There appears to be no difficulty in agreeing upon suitable analytical methods for running the specification tests.

PROGRAM A reconciliation of results among the three laboratories will be accomplished by utilizing a standard to determine response factors. However, continued evaluation at both UCC laboratories of Dow vinyl chloride is necessary to further refine our internal methods of analysis, as well as to gather additional data on the quality of Dow's vinyl chloride. Dow test methods will be obtained and reviewed.

TABLE I

	TEXAS CITY				SOUTH CHARLESTON	
Dow Monomer	IA	IB	IIA	IIB	IA	IIB
Iso-Butane	3	3	3	3	12	13
Acetylene					21	6
n-Butane	6	7	1	2		
Allene					<1	<1
Butadiene					4	3
Methyl Acetylene	Trace	Trace	Trace	Trace		
Methyl Chloride	12	9	21	21	18	25
Vinyl Acetylene	4	4	10	10		
Acetaldehyde					17	31
3-Chloropropene				2		
1,1-Dichloroethane			Trace			
Total Impurities (Organic)	25	23	35	38	78	82

TABLE II

	TEXAS CITY				SOUTH CHARLESTON		DOW	
Dow Monomer	IA	IB	IIA	IIB	IB	IIB	IA-IB	IIA-IIB
Acid (HCl)	Nil	-	Nil	-	Nil	Nil	Nil	Nil
Iron	Nil	-	Nil	-	-	-	Nil	Nil
Volatiles	Nil	-	Nil	-	-	-	Nil	Nil
Water	70	-	70	-	Nil	Nil	30	30
Phenol	-	-	-	-	<2	<2	-	-
Iso-Butane	3	3	3	3	12	13	3.31	2.96
n-Butane	6	7	1	2	21	6	4.53	1.49
Butene-1							0.13	0.09
Allene					<1	<1	-	0.09
Trans-Butene-2							-	0.07
Butadiene	Trace	Trace	Trace	Trace	4	3	0.98	0.85
Methyl Acetylene					<1	<1		
Methyl Chloride	12	9	21	21	18	25	15.45	23.3
Vinyl Acetylene	4	4	10	10	17	31	1.78	4.82
3-Chloropropene				2				
1,1-Dichloroethane				Trace				
Total Impurities (Organic)	25	23	35	38	78	82	26.18	33.67

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