FINAL REPORT

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# ANALYSIS OF DOW VINYL CHLORIDE

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SUMMARY An exchange of standard samples containing known amounts of expected impurities in Dow vinyl chloride has been made between the UCC laboratories at South Charleston and Texas City and the Dow laboratory at Freeport, Texas. Future evaluations by the three laboratories will be based on these standards. Resolution of the disagreement between the Texas City and Dow laboratories has been accomplished through use of a standard. There still remains resolution of the disagreement as to reported levels of certain impurities between the Texas City and South Charleston laboratories.

The Texas City Resins Laboratory has evaluated the Dow analytical methods for vinyl chloride. Implementation of these methods into the monomer contract as referee methods has been found acceptable except for the acidity and phenol tests. UCC methods of analysis for these two specifications will be included in the contract as the acceptable referee method.

INTRODUCTION Preliminary investigation of Dow vinyl chloride in November, 1967, revealed that differences between chromatographic methods at the Texas City and South Charleston laboratories could be resolved only through the use of response factors to report weight percent impurities in vinyl chloride. A standard sample containing expected impurities in Dow vinyl chloride was to be prepared by the Charleston Technical Center and sent to respective laboratories for calculation of response factors.

A meeting in Freeport, Texas, in December, 1967, between representatives of UCC and Dow indicated general agreement in the reported impurities found in typical production samples of Dow vinyl chloride. Only the reported level of vinyl acetylene remained to be resolved. Chemical methods for analyzing vinyl chloride were exchanged. The Texas City Resins Laboratory was to implement a study of these methods to determine their acceptance as referee methods for vinyl chloride specifications.

DISCUSSION In October, 1967, representatives of UCC and Dow agreed on implementing a test program to define the vinyl chloride specifications to be incorporated into a monomer purchase contract. The initial phase of this program between the UCC and Dow laboratories indicated the need for not only

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reaching agreement in analytical methods between the UCC and Dow laboratories, but also between UCC laboratories at Texas City and South Charleston. Standardization of chromatographic methods of analysis for vinyl chloride was determined to be possible only through the use of common response factors used to convert volume percent impurities to weight percent impurities in vinyl chloride.

Three different standards of vinyl chloride containing known amounts of the expected impurities in the Dow monomer were sent to the UCC and Dow laboratories for implementation into their respective chromatographic test methods. One standard was prepared at the Technical Center, one by the Dow laboratory at Freeport, and one containing a known amount of vinyl acetylene was mutually prepared at Texas City and Freeport. Use of these standards permitted calculation of response factors for all expected vinyl chloride impurities.

So that an additional exchange of vinyl chloride samples could be eliminated, the "new" response factors were used on previous vinyl chloride data common to the three laboratories. Results of this phase of the monomer test program are found in Table I. Differences between the Texas City and Dow laboratories that were previously reported appear to be resolved. The only serious difference appears to be the level of vinyl acetylene reported between the South Charleston laboratory and the laboratories at Texas City and Freeport.

This observed difference in vinyl acetylene content should not be cause for extreme alarm in view of the initial differences between the UCC laboratories. Great progress has been made in a few short months. Resolution of the present differences can be accomplished in a short time by a concerted effort on the part of both laboratories.

The Texas City Resins Laboratory now has the capability of utilizing a vapor injection technique. Routine analyses of vinyl chloride are now being made at attenuation (sensitivity) levels compatible with the South Charleston laboratory. Utilization of these factors in future vinyl chloride analyses will add impetus to resolving the internal differences between the UCC laboratories.

Evaluation at Texas City has been made on the Dow chemical methods which were to be designated referee methods for the particular vinyl chloride specification unless serious differences were detected between the Dow and UCC methods. Results of this evaluation are as follows:

1. Acetylene - The current method in use at Texas City is almost identical to the Dow method. Modification of UCC-22-211-3 for acetylene was made several years ago to eliminate preparation of standards of known amounts of acetylene and the errors and hazards involved in weighing such a volatile and dangerous compound.

2. Aldehyde - The Dow method was found to be acceptable providing modification be made to indicate the use of a visible DU instrument measurement rather than a turbidimetric measurement. UCC does not have a turbidimeter at Texas City. Expense for its purchase is not necessary in view of the results obtained on the DU spectrophotometer.

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3. Acidity - Both UCC and Dow methods are similar. The only significant differences are in choice of indicators and UCC's use of a blank. Dow informally indicated preference to the UCC method.

4. Iron - The Dow method is much more sensitive at the 0.15 ppm level than the UCC method, which is simply a color comparison of the unknown to a standard. The color formation is very faint at this low concentration and is not sensitive to small changes in iron concentrations. The Texas City Resins Laboratory will implement an Atomic Absorption method for determining iron in vinyl chloride in the near future. However, the Dow laboratories do not have this capability.

5. Non-volatiles - Both UCC and Dow methods are the same.

6. Phenol - Both methods are similar. The Dow method scans the phenol sample from 220-320 mμ and determines the absorbance from a maximum and minimum reading obtained from a potentiometric recorder. The UCC method measures absorbance directly at 271 mμ . If the Dow method is to be used as a referee method, it should be modified to a measurement compatible with the UCC method.

7. $H_2O$ - The Dow method is less susceptible to interference by moisture in the air. The closed system is more desirable than the open environment inherent in the Carbide method. However, the Dow method specified in the contract should indicate exclusion of the instrumental technique involving use of an automatic titrator. The Texas City Resins Laboratory does not have this capability of analysis.

8. Peroxides - The Dow method is the more sensitive method of the two and should be the specified referee method. The UCC method is quite erratic at peroxide levels $< 0.1$ ppm.

9. Sulfur - UCC does not have a method for determining sulfur in vinyl chloride. The Dow method should be the indicated referee method.

Although the Dow method of analysis for determining oxygen was received, it was not evaluated by the Texas City Resins Laboratory. Evaluation would have necessitated preparation of oxygen standards and additional chromatographic columns. Several tank cars were analyzed for oxygen(before and after unloading) by the Texas City Chemicals Laboratory using a UCC chromatographic method. Results of this evaluation are found in Table II. Residual oxygen content would not appear to be a problem when the monomer purchase contract takes effect. Residual oxygen levels, in fact, should be significantly lower since vinyl chloride vapors instead of nitrogen will be used to pump liquid vinyl chloride from the tank cars.

## RECOMMENDATIONS

1. The Dow chemical methods of analysis should be accepted as the referee methods except for phenol and acidity. The Dow method for aldehyde should be modified as indicated in the previous section.

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2. Additional samples of vinyl chloride should be exchanged between the South Charleston and Texas City laboratories until mutual agreement as to concentration of reported impurities is reached. The South Charleston laboratory should undertake the responsibility of developing the capability to report the quality of vinyl chloride as defined by the Texas City and Dow laboratories.

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Attachments (2)

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TABLE II

ANALYSIS OF DOW VINYL CHLORIDE USING COMMON RESPONSE FACTORS

| | TEXAS CITY | | | SOUTH CHARLESTON | | | DOW | | |
|---|---|---|---|---|---|---|---|---|---|
| Impurities | IA-IB | IIA-IIB | 3351 | IB | IIB | 3351 | IA-IB | IIA-IIB | 3351 |
| Isobutane | 3 | 3 | 6 | 3.84 | 4.16 | 7.04 | 3.31 | 2.96 | 7.8 |
| n-Butane | 6.5 | 1.5 | 9 | 7.56 | 2.16 | 9 | 4.53 | 1.49 | 8.9 |
| Butene-1 | - | - | - | - | - | - | 0.13 | 0.09 | - |
| Allene | - | - | - | < 1 | < 1 | .55 | - | .09 | - |
| Trans-butene-2 | - | - | - | - | - | - | - | .07 | - |
| Methyl Acetylene | - | - | - | < 1 | < 1 | - | - | - | - |
| 1,3-Butadiene | Trace | Trace | Trace | 1.4 | 1.05 | .35 | .98 | .85 | .7 |
| Methyl Chloride | 14.6 | 25.6 | 17 | 19.8 | 27.5 | 14.3 | 15.45 | 23.3 | 17.1 |
| Vinyl Acetylene | 3 | 8 | 10 | 9.9 | 17.8 | 4.6 | 3.31 | 8.27 | 10.6 |
| 3-Chloropropene | - | 2 | - | - | - | - | - | - | - |
| 1,1-Dichloroethane | - | Trace | - | - | - | - | - | - | - |
| Total Impurities, ppm | 27.1 | 40.1 | 42 | 43.5 | 53.7 | 35.8 | 27.7 | 37.1 | 45.1 |

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TABLE II

OXYGEN ANALYSIS IN DOW SHIPMENTS OF VCl

| Car No. | Date | PPM Oxygen (by volume) | |
|---|---|---|---|
| | | Full | Empty |
| DOWX-3351 | 12-21-67 | 68 | 1141 |
| GATX-30771 | 12-31-67 | 94 | 580 |
| DOWX-3352 | 12-31-67 | 105 | 558 |
| DOWX-3351 | 1-2-68 | 210 | 178 |
| GATX-30762 | 1-2-68 | 220 | 520 |
| GATX-30771 | 1-11-68 | 10 | 600 |
| GATX-30762 | 1-12-68 | 79 | - |
| DOWX-3352 | 1-25-68 | - | 875 |
| GATX-30771 | 1-29-68 | - | 300 |

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