VINYL CHLORIDE

POSSIBLE SOURCES OF

POLYMERIZATION INHIBITORS IN NO. 1 SYSTEM

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SUMMARY Two possible sources of the inhibitor which is interfering with the polymerization of vinyl chloride from Vinyl Chloride Unit No. 1 were investigated.

A sample of the kettle residue from the vinyl chloride refining still at Building 154 was distilled through a column of 46 theoretical plates. The fractions were analyzed on the mass spectrometer. The major components found in the sample were ethylene dichloride, propylene dichloride, vinyl chloride, acetaldehyde, and trichlorethane. Small amounts of vinyl bromide, 1,1-dichlorethane, dichlorethene, allyl chloride, propyl chloride, acetone, methyl chloride, dichlormethane, chloroform, and water were also present. Seventy per cent of the charge was recovered as good ethylene dichloride which did not affect vinyl acetate polymerization. Inhibitory material present appeared to be concentrated in fractions 1, 2, and 3. These fractions boiling between 13° and 25°C. were the only ones to reduce appreciably th polymerization rate of vinyl acetate. The composite fraction contained approximately 76 per cent vinyl chloride, 15 per cent acetaldehyde, and small amounts of propyl chloride, dichlorethane, dichlorethene, and vinyl bromide.

A sample of low boiling fore-fraction from the refining of ethylene dichloride at Building 42 was distilled in the laboratory using a column of 46 theoretical plates. The various fractions were analyzed on the mass spectrometer. The material was found to contain large amounts of ethylene dichloride, ethyl chloride, chloroform, and dichlorethene. Acetaldehyde, carbon tetrachloride, dichlorethane, dichlormethane, acetone, allyl chloride, propyl chloride, methyl chloride, and formaldehyde were present in small amounts.

No unusual compound that would reduce the polymerization rate of vinyl chloride was found in either the fore-fraction or kettle residue samples.

INTRODUCTION A survey was made of possible sources of the inhibitor which has appeared in the vinyl chloride from Vinyl Chloride Unit No. 1 during the past several months. The process was traced with the assistance of all technical men concerned from ethylene through ethylene dichloride to vinyl chloride and its distillation in the No. 2610 still at Building 154. Two samples were selected for careful examination. The first of these was a portion of the residue which was obtained from No. 2610 still and which consisted largely of ethylene dichloride. The second sample was obtained from the fore-fraction isolated in the refining of ethylene dichloride, the raw material for the production of vinyl chloride. This fore-fraction is discharged to the sewer. The residue from No. 2610 still is also discharged to the sewer at present, but there is considerable interest in reworking this material to recover ethylene dichloride at Building 42.

DISCUSSION The procedure involved in handling the samples was the same in each case. Approximately 1,500 grams of sample was charged to a 2-liter flask equipped with a Glas-col heating mantle. Maintaining a 5:1 reflux ratio, the material was distilled through a vacuum-jacketed column of 46 theoretical plates. The column was packed with 1/16-inch nichrome helices. A brine-cooled condenser was used and the low boiling fractions were collected in a dry ice-acetone cold trap. Fractions collected at appropriate intervals were examined on the Consolidated mass spectrometer.

A. Kettle Residue from Still No. 2610 at Building 154

Vinyl chloride produced by the reaction of ethylene dichloride and aqueous sodium hydroxide at Vinyl Chloride Unit No. 1 is refined at Building 154. A sample of the kettle residue from refining still No. 2610 was fractionated in the laboratory through a column of 46 theoretical plates. About 4 per cent of the charge boiled below 25°C. and contained mostly vinyl chloride and acetaldehyde. The major portion (62 per cent) of the charge boiled between 82° and 83.5° centigrade. A specific gravity of 1.25 at 20°/15.6°C. indicated this material to be fairly pure ethylene dichloride. Details of the distillation are shown in Table I. The residue, comprising 22 per cent of the charge, had a boiling range of 96° to 127° centigrade. Results of a standard distillation of a 100-cc. sample of the residue are listed in Table II.

Samples of the various fractions were examined on the Consolidated mass spectrometer. In addition to ethylene dichloride, vinyl chloride, and acetaldehyde, the sample also contained methyl chloride, water, dichlorethene, 1,1-dichlorethane, dichlormethane, and chloroform.

Small amounts of vinyl bromide, allyl chloride, propyl chloride, and acetone were also found, and the standard distillation revealed the presence of propylene dichloride and trichlorethane in the residue. Results of the spectrometer analyses are shown in Table III. A summary of the quantitative data on the original sample based on the distillation and spectrometer analysis is given in Table IV.

The inhibitory effect of the various fractions was determined by means of a modified vinyl acetate activity test. One cc. of contaminant was added to 22 cc. of one-period vinyl acetate containing 0.40 gram dibenzoyl peroxide. The number of 15-second heating periods required to start polymerization is an indication of the activity of the vinyl acetate.

The contaminating material appeared to be concentrated in the lower boiling fractions. A composite of fraction 1, 2, and 3 boiling between 13°C. and 25°C. reduced the activity of vinyl acetate from one period to three periods. These fractions contained primarily vinyl chloride and acetaldehyde with small amounts of dichlorethane, dichlorethene, propyl chloride, and a trace of vinyl bromide. The ethylene dichloride fraction did not affect the activity of vinyl acetate at all. Results of these activity tests are shown in Table V. The slight effect noted in the fore-fraction, and fractions 4, 5, 6, and 7 may have been caused by acetaldehyde. No unusual and potent polymerization retarder was discovered by the analysis.

B. Fore-Fraction from Ethylene Dichloride Refining Still

The ethylene dichloride used for the synthesis of vinyl chloride at the No. 1 Unit is made and distilled in the vicinity of Building 42. A 2-gallon sample of low boiling fore-fraction from the refining of ethylene dichloride was received. Some of this material was distilled through the laboratory column of 46 theoretical plates. Twenty-nine per cent of the charge boiled below 26°C. and contained approximately 70 per cent ethyl chloride and 5 per cent acetaldehyde. A fraction containing ethylene dichloride and comprising 35 per cent of the charge boiled at 83°C. and had a gravity of 1.258 at 20°/15.6° centigrade. Fractions 3 and 4 boiling between 50° and 78°C. comprised over 7 per cent of the charge and contained mostly chloroform, carbon tetrachloride, and ethylene dichloride. Other components of the charge were identified as dichlorethenes, dichlormethane, 1,1-dichlorethane, acetone, allyl chloride, propyl chloride, methyl chloride, and formaldehyde. The residue, amounting to about 16 per cent of the charge, contained 90 per cent ethylene dichloride. Complete distillation data are shown in Table VI.

The fractions from the distillation were analyzed on the mass spectrometer. The analyses are shown in Table VII. The analytical data for the original sample obtained from the distillation and spectrometer studies are summarized in Table VIII. No inhibitor was found in the sample.

TABLE I

Sample:	Kettle residue from still No. 2610
Date:	8:00 a.m., June 9, 1945
Column:	Vacuum-jacketed, 30 by 1,560 mm.
Packing:	1/16-inch nichrome helices
Theoretical plates:	46
Reflux ratio:	5:1

Fraction No.	Temperature, °C.	Percentage of charge
Fore-fraction	Below 13.2	1.29
1	13.2 to 14.5	0.27
2	14.5 to 20.0	0.43
3	20.0 to 25.2	1.32
4	25.2 to 45.0	1.20
5	45.0 to 47.0	0.26
6	47.0 to 60.0	0.67
7	61.0 to 67.5	1.20
8	67.5 to 70.0(1)	3.76
9	70.0 to 71.5(1)	1.05
10	71.5 to 82.0(1)	1.98
11	82.0 to 82.8	4.60
12	82.8 to 83.5	57.95
Residue	Above 96	22.51

(1) These fractions were heterogeneous water and dichloride mixtures. Water was not evident in the sample as received, but during storage rain leaked into the container.

TABLE II

Standard Distillation of Residue from Table I

Cc.	Temp., °C.	Cc.	Temp., °C.	Cc.	Temp., °C.
I.b.p.	96.0	35	99.4	75	105.5
2	97.0	40	99.6	80	108.0
5	97.2	45	100.0	85	110.9
10	97.9	50	100.0	90	111.8
15	98.0	55	100.5	92	114.2
20	98.5	60	101.1	94	119.0
25	98.8	65	102.1	94.9	120.0
30	99.0	70	103.5	95.2	127.0

TABLE III

Mass Spectrometer Analysis of Fraction from Table I

Compound	Fore-fraction	Composite of fractions 1, 2, 3	Composite of fractions 4, 5, 6, 7
Vinyl chloride	96.7	76	-
Acetaldehyde	0.1	15	54
Methyl chloride	0.1	-	-
Carbon dioxide	3.0(1)	-	-
Propyl chloride	-	Some	Some
1,1-Dichlorethane	-	Some	10
Dichlorethene	-	Some	20
Vinyl bromide	-	Trace	Trace
Allyl chloride	-	-	Some
Acetone	-	-	Some
Chloroform	-	-	Some
Dichlormethane	-	-	Trace

(1) Probably absorbed from dry ice-acetone cold trap.

TABLE IV

Analysis of Kettle Residue from Still No. 2610

Sampled at 8 a.m., June 9, 1945

Compound	Concentration, %(1)	Boiling point, °C.
Methyl chloride	0.35	-24.0
Vinyl chloride	2.8	-13.0
Acetaldehyde	2.1	20.9
Vinyl bromide	Small amount	5.8
Dichlorethene	Small amount	37.0
1,1-Dichlorethane	Small amount	57.3
Dichlormethane	Trace	40.0
Allyl chloride	Small amount	44.6
Propyl chloride	Small amount	46.4
Acetone	Small amount	56.5
Ethylene dichloride	70.4	83.7
Propylene dichloride	8.0(2)	96.3
Water	8.0(2)	100.0
Trichlorethane	2.3(2)	113.0
Unidentified residue	4.7	Above 115
Chloroform	Small amount	61.0

(1) Based on material recovered from distillation.
(2) Estimated composition based on a standard distillation run on the residue from the fractionation.

TABLE V

Vinyl Acetate Activity Tests(1)

Contaminant(2)	Heating periods
None	1
Fore-fraction	2
Composite 1, 2, 3	3
Composite 4, 5	2
Fraction 6	2
Fraction 7	2
Fraction 8	1
Fraction 9	1
Fraction 10	1
Fraction 11	1
Fraction 12	1
Residue	2

(1) One cc. of contaminant is added to 22 cc. refined vinyl acetate containing 0.4 gm. dibenzoyl peroxide. The number of 15-second heating periods required to start polymerization is an indication of the activity of the vinyl acetate. Vinyl acetate containing no inhibitory material requires only 1 heating period.
(2) Fractions from laboratory distillation of kettle residue.

TABLE VI

Sample:	Fore-fraction from ethylene dichloride refining still
Date:	6:00 p.m., June 5, 1945
Column:	Vacuum-jacketed, 30 by 1,560 mm.
Packing:	1/16-inch nichrome helices
Theoretical plates:	46
Reflux ratio:	5:1

Fraction No.	Temp., °C.	Sp. gr., 20°/15.6°C.	Per cent of charge
Fore-fraction	Below 26	-	29.1
1	26 to 45	-	0.91
2	45 to 50	1.254	2.28
3	50 to 60	1.413	3.67
4	60 to 78	1.442	4.01
5	78 to 82	1.290	4.86
6	83	1.258	35.30
Residue	-	1.277	16.6

TABLE VII

Mass Spectrometer Analyses of Fractions from Laboratory Distillation of Fore-Fraction from Ethylene Dichloride Still

Compound	Fore-fraction	1	2	3	4	5	6	Resi-due
Ethyl chloride	70	10	Some	Some	-	Some	-	-
Acetaldehyde	5	Some	Some	-	-	-	-	-
Dichlorethene	Some	80	90	30	-	Some	Some	Some
Dichlormethane	Some	Some	Some	-	-	-	-	-
Acetone	-	-	-	Some	Some	Some	Some	Some
Allyl chloride	-	Some	Some	-	-	-	-	-
Propyl chloride	-	Some	-	-	-	-	-	-
Chloroform	Some	-	Some	60	80	10	Some	Some
Carbon tetra-chloride	Some	-	-	4	5	Some	-	-
Ethylene dichloride(1)	-	-	-	-	10	75	90	90
Formaldehyde	Some	-	-	-	-	-	-	-
Methyl chloride	-	Some	-	Some	-	-	-	-
1,1-Dichlor-ethane(1)	Some	Some	Some	Some	-	-	-	-

(1) No distinction was made between 1,1-dichlorethane and 1,2-dichlorethane in these analyses, but the boiling range of the various fractions serves to indicate the particular dichlorethane present.

TABLE VIII

Analysis of Fore-Fraction from Ethylene Dichloride Refining Still

Compound	Concentration, %(1)	Boiling point, °C.
Ethyl chloride	21.2	12
Ethylene dichloride(2)	52.5	83.7
Acetaldehyde	1.5	20.9
Chloroform	6.1	61
Dichlorethenes	4.0	37
Carbon tetrachloride	0.4	76.8
Dichloromethane	Some	40
1,1-Dichlorethane(2)	Some	57.3
Acetone	Some	56.0
Allyl chloride	Trace	44.6
Propyl chloride	Trace	46.4
Formaldehyde	Some	-21
Methyl chloride	Some	-24

(1) Analysis based on total weight of material recovered from distillation.

(2) Although no distinction was made in the mass spectrometric analyses between the two dichlorethanes, the boiling range of the fractions in which dichlorethanes were found indicated that ethylene dichloride was the principal component of the sample.

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