Conoco Chemicals Company
Conoco Inc.
P.O. Box 91, New Highway 25
Aberdeen, MS 39730

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November 13, 1981

Mr. Charles R. Jeter
Regional Administrator
Region IV
United States Environmental Protection Agency
345 Courtland St., N.E.
Atlanta, GA 30308

Dear Mr. Jeter:

At approximately 12:30 p.m. on November 5, 1981 our plant experienced a minor relief valve discharge. Pursuant to the National Emission Standard for vinyl chloride (40 CFR, Part 61, Subpart F, paragraph 61.65a) we are reporting this incident to your office. This discharge was reported to the National Response Center on November 5 under the Comprehensive Environmental Response, Compensation and Liability Act of 1980.

The vessel involved was the north fresh VCM charge filter in reactor module No. 1. The vessel relieved through a 3/4" x 1" relief valve which has a 1" rupture disk between it and the filter. The relief valve setting was 275 psig and the rupture disk was rated at 300 psig at 72°F.

The release occurred shortly after polymerization reactor D-600 was charged. An operator in the field noticed the discharge from the filter and notified the control room using the plant radio system. Another operator who was in the control room at the time immediately put on a self contained breathing air system and went to the filter. He blocked the filter in by closing 6" manual valves on the inlet and discharge of the filter, opened the valve on the filter to the recovery system and shut a manual valve under the relief valve which stopped the release. The time required to stop the release after it was detected was approximately two and one-half minutes. The release was stopped at 12:39 p.m.

The charging of D-600 reactor just prior to the release appeared to be normal. The reactors are charged automatically with a programable controller. This controller opens and closes valves and stops and starts pumps based on signals from flow meters which measure the amount of water and VCM charged to the reactors. Since there was no apparent cause for the relief valve discharge, charging of reactors was ceased until a reactor was test-charged with water to determine

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if the programable controller was working properly. The test charge revealed that the automatic on/off valve on the discharge side of the VCM charge pump did not close properly after the VCM charge was complete. After a built-in time delay in the sequencing operation, the programable controller restarted the VCM charge pump and then the automatic on/off valve closed properly. During this restarting of the pumps the VCM charge valves down stream of the filter prior to the reactor remained closed resulting in the pump momentarily discharging into the blocked-in filter. It is believed this is what happened on the previous charge to D-600 and the dead head pressure of the VCM charge pump was a sufficient hydraulic shock to burst the rupture disk and to open the relief valve at the filter.

Since the pump discharge valve closed almost immediately after the pump restarted, the relief valve should have reseated very quickly as soon as the pressure of the filter decreased to 175 psig. The relief valve was taken to the shop and inspected after the release and found to contain debris that kept the valve from reseating. Therefore, based on the testing of the charge system and the inspection of the relief valve, we believe there was a momentary (approximately 10 seconds) liquid VCM discharge from the relief valve until the VCM pump discharge valve closed and then a VCM vapor discharge until the manual valve under the relief valve was closed. The charge on D-600 was complete at 12:30 p.m. The vapor discharge lasted about nine minutes since the manual valve under the relief valve was closed at 12:39 p.m.

Using relief valve discharge calculational procedures provided by the relief valve manufacturer, Farris, the amount of liquid VCM released is estimated to be 18 pounds and the amount VCM vapor released is estimated to be 71 pounds; the total release is thus estimated to be 89 pounds of VCM. Copies of the discharge calculations are attached. The relief valve discharge stack is 10 feet above grade and no personnel were overexposed to vinyl chloride.

The weather conditions at the time of the release according to the plant weather station were as follows:

Barometric Pressure	-	29.94 inches of mercury
Temperature	-	74°F
Wind Direction	-	From Northeast
Wind Speed	-	Trace

To minimize the possibility of future discharges of this type a suitable relief valve which was previously used in another part of the plant was installed on the VCM filter. The discharge from the relief valve was piped to the VCM receiver before another reactor in the module was charged. Charging was delayed for 24 hours which resulted in one day of lost production. Thus if in the future the filter should become overpressured, it will releive into the VCM receiver and not to the atmosphere. Also the charge sequence was reprogrammed so that the VCM charge pump cannot

CONFIDENTIAL

start unless the VCM charge valves and the main reactor valve are open thus preventing the pump from discharging into the blocked in filter.

A balanced bellows relief valve for the VCM filter had been ordered prior to this release but delivery is not expected until early December 1981. Plans were to install the relief vlave on the filter and to pipe the discharge to a vessel in VCM service.

The reporting requirements of the Standard pertaining to relief valve discharges are summarized below:

Source: North Fresh VCM Charge Filter, Reactor Module No. 1

Nature: Discharge through relief system on North Fresh VCM Charge Filter, Reactor Module No. 1

Cause: Overpressure of the filter due to pump discharging into the blocked in filter and failure of the relief valve to reseat.

Date: November 5, 1981

Time: 12:30 p.m.

Approximate Discharge: 89 pounds VCM

Method of Determining Discharge: Relief Valve Calculation

Action Taken to Prevent Release:
1. Filter blocked in
2. Filter put under evacuation
3. Manual valve under relief valve closed

Measures Taken to Prevent Future Discharges:
1. Relief valve on filter replaced with another relief valve and the discharge from the relief valve is piped to the VCM receiver.
2. The charge sequence was reprogrammed such that the VCM charge pump cannot start unless the VCM charge valves and the main reactor valve are open.

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If there are any questions concerning this report, please contact me at (601) 369-8111, extension 2239.

Sincerely,

R. A. Frohreich

R. A. Frohreich

tap

c: Jerry Banks, Bureau of Pollution Control
JF, CRM, PEM, SJV, DLM, JJH

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RELIEF VALVE DISCHARGE CALCULATION
NORTH VCM CHARGE FILTER - REACTOR MODULE NO. 1
LIQUID DISCHARGE
12:30 P.M. - NOVEMBER 5, 1981

From: Teledyne Farris Safety Relief Valve Sizing Bulletin FE-336, page 3.1

$$A = \frac{V_L \sqrt{G}}{38.0 \quad Kd \sqrt{1.25 \; P_1 - P_2} \quad Kp \; Ku}$$

Where:

A = Effective Orifice area, in.^{2} = 0.098 in.^{2}
V_L = Relieving Rate, gallon per minute
G = Specific Gravity, = 0.9
Kd = Coefficient of Discharge = 0.64
Kp = Liquid Capacity Correction Factor, for 4% overpressure = 0.32
Ku = Viscosity Correction Factor = 1.0
P_1 = Set Pressure at Inlet, psig = 275 psig
P_2 = Back Pressure at Outlet, psig = 0 psig

Then: $$V_L = \frac{(0.098) \quad (38) \quad (0.64) \quad \sqrt{1.25 \times 275 - 0} \quad (0.32) \quad (1.0)}{\sqrt{0.9}}$$

= 14.9 gallons per minute

Vinyl chloride discharged in 10 seconds =

$$14.9 \frac{\text{gallon}}{\text{min.}} \times \frac{7.5 \text{ pound}}{\text{gallon}} \times \frac{1 \text{ min.}}{60 \text{ sec.}} \times 10 \text{ sec.} = 18 \text{ pounds VCM}$$

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RELIEF VALVE DISCHARGE CALCULATION
NORTH VCM CHARGE FILTER - REACTOR MODULE NO. 1
VAPOR DISCHARGE
12:30 P.M. - NOVEMBER 5, 1981

From: Teledyne Farris Safety Relief Valve Sizing Bulletin FE-336, page 31

$$A = \frac{W}{C\ Kd\ P} \frac{\sqrt{T}}{\sqrt{M}} \frac{\sqrt{Z}}{Kb}$$

Where:

A = Effective Orifice Area, in.^{2} = 0.081 in.^{2}
(Valve orifice area assumed to be one-half plugged)
W = Relieving Rate, pounds per hour
T = Inlet Temperature, ^oR = 460 + 74 = 534^oR
Z = Compressibility Factor = 0.92
C = Gas Flow Constant = ~~0.92~~ 315
Kd = Coefficinet of Discharge = 0.95
M = Molecular Weight = 62.5
Kb = Back Pressure Correction Factor = 1
P = Relieving Pressure, psia = 54.4 psia
(Vapor pressure of VCM @ 74^oF)

Then:

$$W = \frac{(0.081)\ (315)\ (0.95)\ (54.4)\ \sqrt{62.5}\ (1)}{\sqrt{534} \cdot \sqrt{0.92}}$$

= 475 pounds per hour

Vinyl chloride discharged in 9 minutes =
$475 \frac{\text{pound}}{\text{hr.}} \times \frac{1 \text{ hr.}}{60 \text{ min.}} \times 9 \text{ min.} = 71$ pounds VCM