MEETING REPORT

PART I: VINYL CHLORIDE REVIEW STUDY

I. Purpose

The purposes of the TRW/Conoco meeting were to:

a. Update TRW's Review Study acitivities.

b. Become familiar with Conoco PVC plant processes and control technology.

c. Discuss the current VC NESHAP and possible revisions of the standard.

d. Hear Conoco's presentation on emergency relief alternatives.

II. Place and Date

TRW Environmental Engineering Division Progress Center
3200 East Chapel Hill Road
Research Triangle Pack, North Carolina 27709

October 17, 1980

III. Attendees

Conoco

Walter Finch, Senior Process Engineer
Joseph C. Ledvina, Director Environmental Activities
John McCulley, Supervising Process Engineer
Curry L. Miller, Plant Manager, Aberdeen
J. Paul Warner, Senior Process Engineer, Oklahoma City

EPA

Leslie B. Evans, OAQPS VC Lead Engineer

TRW

James W. Bodamer, Jr., Project Engineer
Matthew Boss, Project Engineer
Margery A. Cassidy, Project Engineer
C. J. Chatlynne, Technical Manager
Charles Hester, Section Head

IV. Discussion

Mr. Bodamer presented an update on the status of the TRW/EPA Review Study and discussed the methodology used for data collection. An outline of the presentation is attached.

Mr. McCulley described the process used for polyvinyl chloride (PVC) production by Conoco at their Oklahoma City plant. The Aberdeen plant is similar. Polymerization is by suspension and is a batch process. Vinyl chloride monomer (VCM) is received by rail from the Conoco EDC/VCM plant in Lake Charles, transferred to storage vessels, and charged into the reactor where it is polymerized to a conversion of approximately 80 percent. Unreacted VCM is removed from the reactor and sent to recovery. The slurry is stripped and goes to the blend tanks and to the dryers where it is dried to 0.2 percent water content.

CONTROL TECHNOLOGY

Unreacted monomer is vented from the reactor to the recovery system where it is compressed, condensed, and stored for reuse. The PVC slurry is then steam stripped.

Inert gases removed from the reactor along with the unreacted VCM are concentrated in a refrigerated condenser and then combusted in a gas-fired incinerator. After stripping, the polymer slurry is drained to blend tanks. Air introduced into the reactor during the slurry transfer is removed by evacuation to the atmosphere before charging the reactor with VCM. The steam stripping operation is controlled to keep the combined emission of VCM from the polymer slurry and VCM in the evacuated air below the slurry residual VCM and reactor opening loss limits (420 pounds VCM per MM pounds PVC).

Waste water originating from equipment purging and pump and compressor seal flushing is stripped batchwise. Conoco use a continuous sequential area monitoring system to monitor fugitive emissions.

Double mechanical seals are used in the PVC process and tandem seals in the EDC/VCM process. Water leakage into the process (as can occur with double mechanical seals) is not a problem in the PVC system. However, water leakage in the EDC/VCM process can cause severe corrosion; therefore, vented, oil-filled tandem seals are used. VCM leakage into the tandem seal cavity is combusted in a plant incinerator.

The oxy vent stream at the EDC/VCM plant is not incinerated. VCM emissions from the oxy vent are controlled by controlling process operating conditions. All the other EDC/VCM vent streams do go to incinerators. Conoco have two 48×10^6 BTU incinerators at their Lake Charles EDC/VCM plant and on 1×10^6 BTU incinerator for each of their PVC plants.

EMERGENCY RELEASE PREVENTION AND ALTERNATIVES FOR CONTROL

Reactor relief vulnerability, means of prevention (other than containment), and options for add-on control devices were discussed. Conco listed four causes of emergency releases:

1. Operator error.
2. General equipment malfunction.
3. Events external to the system.
4. Specific failure of the kill system.

In order for any of the first three events to result in an emergency release, the fourth failure of the kill system must also occur. (An exception to this rule would be failure of the rupture disc, in which case the relief valve may open from the shock of the rupture disc failure. Conoco use BS&B's prescored, reverse-buckling discs.)

Examples of operator errors that could lead to a reactor relief are overfilling of the reactor, adding too much initiator, and manual errors in controlling the cooling system.

Equipment malfunction examples include cooling system failure (motor, motor-pump couplings, valves, etc), rupture disc failure, and false indication by process instrumentation.

Examples of external events are power failures, fires, etc.

Because the kill system is considered by Conoco to be their primary means of controlling relief valve (RV) discharges, several aspects of this technology were discussed at length. Early detection of an upset condition and redundance of control equipment are the most important requisites to preventing an emergency situation from reaching the kill system stage of control. This detection program includes:

1. Two sets of reactor temperature and pressure indicators on the control panel (on separate transmitters) are supplemented by pressure gauges on each reactor.

2. Use of temperature indicators represents a level of redundance in that an increase in pressure (for VCM) will be accompanied by a rise in temperature.

3. Operators are always in two-way radio contact with control panel personnel.

4. High pressure and high temperature alarms sound in the control room and, if acknowledged, turn off. If the pressure continues to rise, a second alarm, set at a higher pressure, sounds and cannot be shut off until the reactor pressure drops below its set point. This alarm also sets off a siren which can be heard throughout the plant.

5. A temperature control instrument on the control panel regulates the water flow to a reactor. If this flow is improperly regulated, a panel switch can be used to override the controller, sending maximum cooling water flow to the reactor.

6. The panel has reactor amperage indicators with alarms. A low amperage reading is used to confirm that the reactor has emptied after stripping to avoid overfilling the reactor on the next charge. Low amperage can result from a failure in the agitation system.

7. There is a backup power system for the control panel.

Two kill systems are maintained. The first kill system uses high pressure water injection. It is a completely manual system and is used to control reactor pressure increases during normal plant operation. It cannot be used in the event of a power failure.

The second kill system is used to stop the reaction in an emergency such as loss of cooling, agitation, or a power failure. This system uses high pressure nitrogen (precharged) to inject the killing agent. It is a remotely operated system backed up by a manual injection line. The injection valves are also nitrogen operated to insure that they will operate in a power failure or some other condition causing loss of instrument air supply. This short-stop is effective without mixing because of the refluxing action resulting from the reflux condensers on the reactors. The system has been tested in Conoco's pilot plant and has proven to be effective under worst case conditions including loss of cooling and agitation.

The kill systems for each reactor can be activated from the control board or locally at the reactor. The system from one reactor can be used on a different reactor, and each system contains enough for two complete kills in one reactor.

Other backup systems include:

1. Cooling water for reactors. Provisions are made to supply water to the reactor from cross-ties with city water or from the firewater pumps (diesel-driven). Each of these capabilities is checked once each week. Also, instrumentation prevents this backup cooling water flow from going to users other than the reactors.

2. Two separate racks of nitrogen bottles are available to back up the plant instrument air.

3. Two-way radio communication systems.

4. Severe weather radio.

5. Capability of venting to the recovery system (if there is no power failure) or to another vessel.

Installation of the rupture disc involves use of a pretorqued system. These discs can be tested up to 90 percent of burst pressure in a test stand in the shop. (Conoco do not use knife-head discs because of susceptibility of cracking at the welds.) Before the reactor is charged, approximately twenty pounds of pressure is applied and the pressure gauge above the rupture disc is checked to insure reliability of the rupture disc. A percentage of each lot of discs is checked (by random selection), and the lot is rejected or accepted by this means. Nickel discs are used, rather than stainless steel, to protect against corrosion. Discs are changed every six months. Relief valves are changed every twelve months. The reactor system is hydrostatically tested after installation of the relief valves. Emergency procedures involving relief valve discharges are updated once every year, and the rupture disc manufacturer's representative comes to the plant each year to retrain plant maintenance personnel in disc handling and installation procedures.

Fire, as a cause of relief valve discharge, was discussed. A fixed spray fire fighting system and movable fire water monitors are installed throughout the VCM containing portion of the plant. Hydrocarbon (HC) sensors detect explosive concentrations with an alarm set at 20 percent of the LEL and watering systems triggered at 40 percent of the LEL. These HC detectors are independent of the fugitive emission detection system. In addition, there are fire sensors throughout the VCM areas which activate the water systems if the sensor's temperature increases too quickly or reaches a set limit.

Backup cooling is used in lieu of a backup power system at Conoco. The rationale presented was that, if the problem is due to a broken agitator shaft, motor, pump, etc, backup power will not alleviate the situation. The emergency kill system will control the reactor pressure in these types of situations. Therefore, the kill system is of prime importance. Backup cooling can extend the time available for effective use of the kill system.

Both of Conoco's plants use an extensive interlock system to prevent mistakes that could release VCM to the atmosphere, damage equipment, or otherwise seriously effect the plant operation. For example, there is an interlock which prevents the reactor dump valve from opening if the reactor is under pressure, thereby avoiding the accidental dumping of a reactor containing a large amount of VCM. The Aberdeen plant uses programmable logic controllers for its interlock control system. The Oklahoma City plant uses a hard-wired relay logic system.

Containment and Alternatives

Mr. Finch discussed the results of Conoco's preliminary studies and evaluations of relief containment/control devices. Three systems considered were gasholders, flares, and pressurized containment. Venting to a taller stack was also considered but not regarded as containment. In addition to the safety-related aspects of these systems, the following points were considered:

1. All relief valves must be connected to the system for complete containment. Assuming a ten-reactor plant, is the system designed to accommodate one reactor or should the worst case (10) be considered?

2. Partial system venting was evaluated as was the problems associated with venting the vapors alone. Considering adiabatic cooling conditions, transfer at a rate that would allow only the vapor to be vented would result in a gain of only 0.1 to 1.5 minutes until the safety valve would discharge. The transfer is limited to this rate to avoid foaming slurry carryover. Thus, the venting of only vapor from the reactor has a minimal effect. (This was determined by a computer simulation using in-house kinetics.)

3. If whole reactor processes were vented, then consideration must be given to reactors containing PVC at various polymerization stages in order to size the containment system needed.

Examples of one manufacturer's rough budget prices for erected gasholders are as follows (April 1980 costs, without piping, paint, or foundation):

1×10^6 Cubic Feet	\$3.3 MM
0.5×10^6 Cubic Feet	\$2.0 MM

1. The piston velocity of a gasholder is of concern since the average piston velocity required (based on relief time, amount of VCM relieved, and gasholder diameter) can be about equal to the maximum recommended piston velocity. However, it may be possible to increase the gasholder diameter.

2. The life of the flexible gasholder seals is estimated at two years. Replacement cost is 5 percent to 10 percent of the original gasholder, and replacement time is four to six weeks with a 20- to 22-week delivery time possible. This information was provided by a gasholder manufacturer.

3. Seal failure is characterized by small leaks increasing in number until they become unmanageable. Again, this information came from a gasholder manufacturer.

4. Clearing the material in preparation for vessel entry could present a safety problem. The manufacturer recommends purging to the atmosphere. Sweep and shovel and/or spraying appear to be the only alternative for removing solids.

In addition to gasholders, knockout vessels were evaluated. This vessel would allow gravitational separation of the PVC slurry from the VCM vapor upstream of a gasholder or a flare. Preliminary sizing was done using maximum simulated relief rates, atmospheric pressure conditions, and conventional sizing techniques for a horizontal separator handling a foamy liquid. The calculated capacity required for a plant with four large reactors would be 300,000 to 500,000 cubic feet. Since the pressure drop in the vent line from the knockout drum cannot be controlled without compromising system reliability, the knockout vessel must operate near atmospheric pressure. The study was based on maximum simulated vapor and liquid flow rates of more than 1×10^6 and 5×10^6 pounds per hour, respectively. Also, because a multiphase situation exists, the very real problem of lines plugging with polymerizing slurry must be considered.

The potential for backpressure on the relief valve was evaluated. A conventional relief valve can take backpressure up to 10 percent of its set pressure before closing. Closing starts in a balanced-bellows relief valve at 40 to 50 percent of set pressure. The pilot-operated relief valve can be opened on a differential pressure basis; but because of the small pilot tube diameter, this type of relief valve is intended only for clean service. Therefore, in evaluating any type of relief valve, the backpressure effect must be considered. It would be very difficult to design a relief valve vent header for a group of reactors that would provide the required low backpressure for multiple reactor relief and still prevent slurry and vapor separation and solids plugging during low relief rates from just one reactor.

Design parameters for gasholders must also incorporate the following:

1. Interior construction material. The polymerization products can be acidic and corrosive to carbon steel. Also, the flexible seal must be compatible with organic vapors besides VCM which can be present.

2. Fill rates. The movable piston must be considered when designing the system for these rates. The air space above the piston must be designed to avoid pressure buildup and a venting system evaluated.

Failure of the gasholder would result in a gas cloud close to ground level due to the low pressure and velocity of the vapor. Overfilling of the gasholder is a definite possibility. This represents a serious safety problem. Personnel exposure during the removal of unstripped slurry is another safety factor.

Flares were evaluated by Conoco. Here there is also a need for a low pressure vapor/liquid separator. Required capacity for this would be the same as for the gasholder. Optimum height for the flare would be 250 to 300 feet but would probably be restricted by crane capabilities to 200 feet. The flare diameter would be 42 to 48 inches for maximum rate. To prevent burning personnel due to high radiation levels from the flare during a release, a clear area must be provided around the flare. A radius of 550 feet is required to limit radiation below 1,500 BTU per hour per square foot. Cost of the flare is estimated at $400,000 plus $1,900,000 for the separator. (These costs do not include piping and headers.) In addition to the concern about slurry separation, flaring as a means of VCM emissions control involves problems with the HCl formed when VCM is burned.

Venting the VCM vapor through a tall stack was also considered. The vapor/liquid separation and backpressure considerations are the same as for the other cases. An additional problem is that, at a low relief rate from one reactor, the vapor velocity at the top of the large diameter vent stack would be too low for adequate dispersion and a flammable vapor cloud may be formed and ignited.

Pressure vessels as receivers for containment would also be limited by backpressure problems. For relief valve discharges, very large receiving vessels are required. Polymerization may very well be in process at the time of discharge and relief valves would still be required on the receiving vessel.

Vapor cloud flammability modeling and information on vent flammability from small scale tests indicate that ground level clouds from direct relief of a reactor to the atmosphere do not contain a flammable mixture.

The conclusion reached by Conoco was that relief to the atmosphere from the ractor (with near sonic velocity) is safer than relief from the containment or venting alternatives when all factors, including vent flammability, are considered. Conoco regard their emergency kill system as the most effective means of controlling emissions (BACT).

Recommended Improvements of the Standard

The following suggestions were made by Conoco regarding possible changes in the standard:

1. Section 61.66 Equivalent Procedures. Time limit for submission is now 60 days (after construction) for a new source. Conoco suggest that sources should be able to submit an equivalency at anytime.

2. Analysis Method 107. Because the standard requires analysis of a sample within 24 hours, an instrument that is down for repair can cause a noncompliance situation. (For instance, sometimes it has been difficult to obtain parts for Perkin-Elmer instruments.) Conoco suggest (a) do not restrict analysis to a specific instrument and (b) allow an equivalency for analysis of refrigerated samples after 24 hours.

3. Method 106 for Reactor Opening Loss (ROL) Measurements.

   After stripping slurry, the reactor vapor space is essentially all steam. It is very difficult to avoid steam condensation when sampling the reactor vapor space. Assuming a good sample has been collected, the steam will condense in the sample bomb before laboratory analysis. Method 106 does not correct for steam condensation in the sample.

   Conoco's experience indicates that sampling at three points in the reactor (top, middle, and bottom) is not required to get a representative sample. A good sample can be collected at the top of the reactor immediately after stripping. Also, the size of the sampling bag called for in Method 106 is too large for ROL sampling. It was really intended for incinerator sampling where a much larger sample is collected.

In addition to the above sample problems, the ROL measurement itself costs plant productivity by lengthening the batch reactor's cycle time. The recommended solution to these problems is to allow plants to use calculation procedures based on stripping flows and conditions to demonstrate ROL compliance.

4. Reliability of portable leak detectors (Century Organic Vapor Analyzer, HNU, etc) has been a problem in the past. However, their reliability has improved somewhat as plant instrument personnel gain experience with them and strengthen weak points.

V. Conclusions

Information obtained from Conoco will be added to data gathered from other plants to be evaluated in the review study. If further or more detailed information is required, they will be contacted at a later date for additional material.