

CHEMICALS



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DATE January 11, 1972

FROM Don Metzger

SUBJECT **CONFIDENTIAL**

The report covering the Hazard Review of the Tri-Ethane and VDCM Plants is attached. The actual review of Tri-Ethane was conducted in the months prior to the explosion in the TCE Plant. This report, while written after the explosion, is strictly a compilation of the questions asked during the review. No additions or deletions have been made due to experience gained from the explosion and subsequent investigation.

One point should be made that is not evident in the report. All potential chemical reactions were reviewed, including the possibility of excess chlorine being present in the reactor. This was known to be a problem and was a prime consideration in the other sections of the review, particularly instrumentation.

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TO C. L. Payne

DATE January 11, 1972

FROM Don Metzger

SUBJECT Hazard Review of Tri-Ethane
and VDCM Plant

Hazard Review Team: Lynch, Bedenbaugh, J. M. Davis, Duhon, Gorton,
Metzger

Summary

This report summarizes the Hazard Review of the Tri-Ethane and VDCM Plants. The questions which were unresolved during the review are listed first. The more important resolved questions, with answers, are also listed. Very few major problems or potentials were found in the plant. The allowable levels of some highly reactive light organic components in the system, and the use of towmotors in flammable areas are examples. Most of the questions deal with relatively minor changes in equipment, instrumentation and procedures.

Discussion

The Hazard Review of the Tri-Ethane and VDCM Plants was conducted using the Hazard Review Manual. The areas of equipment design and condition, operating procedures and instructions, chemical and process safety, and personnel safety were reviewed with the appropriate members of the Hazard Review Team. A total of 113 manhours were spent on the review.

The questions which were unresolved during the review are listed below. Also listed are the more important resolved questions, with answers, to provide a readily accessible record of the review and to provide a list of jobs to be done.

Unresolved Questions

1. Drums of flammable materials are now handled with a towmotor which has numerous potential ignition sources. Permits are required in the operating area, but are not required at the NRE Storage Building northeast of IPP. A permit would not provide protection if a spill occurred while operating the towmotor. Are explosion proof towmotors needed, or is it adequate to implement a program of training and designating of people responsible?
2. The existing engineering specifications for utility drops allows the installation of utility drops around handrails in such a way as to cause an obstruction hazard when using the handrail. Is a change in the specification warranted?

3. The sprinkler system in the Stabilizer Storage Area, including the storage building, is actuated by the vapor detector system. Tripping of this system can cause appreciable damage. Commodities stored in cardboard drums are susceptible to water damage; also, all the steel drums must be unstacked and removed from the building and dried off to prevent corrosion of the drums. Is automatic tripping of the sprinkler system by the vapor detectors warranted in this area?
4. Dichloroacetylene (DCA) and Monochloroacetylene (MCA) are formed by the cracking of trichloroethylene and vinylidene chloride, respectively. Both DCA and MCA are highly reactive and unstable. What are the safe upper limits of concentration of these compounds in the liquid and vapor phases?
5. Can ethylene and chlorine be present in the vapor phase of the TCE Reactor in the necessary proportions to give an uncontrollable reaction?
6. A cooling tower water leak in the VDC Section condensers could go undetected because the VDC system is a wet system. Can contamination of the VDC by cooling water treatment chemicals create undesirable conditions?

Resolved Questions

1. Personnel Safety

- A. Question: Is adequate handling, toxicity and treatment information available on all chemicals used in the area?

Answer: Adequate information has not been provided for the cooling tower water treatment chemicals purchased from Betz. This information has been requested from the Betz sales representative. It is felt that normal handling procedures are adequate for other chemicals in the area which are not specifically described in the Operating Manual (such as laboratory chemicals).

- B. Q: Are storeroom personnel periodically instructed on the hazards of chemicals they handle for the Tri-Ethane Area?

A: Murry Davis will follow up to get the appropriate safety meetings scheduled.

C. Q: Are adequate safety showers and eye wash hoses provided?

A: Yes; however, the proper use of eye wash hoses, particularly the 15 minute time requirement, should be re-emphasized to all plant employees.

II. Chemical and Process Safety

A. Q: Are significant quantities of dichloroethylene (DCA) formed in the stills in the TCE Section?

A: DCA may be formed in the reboilers in the TCE Section, but should be quickly vented due to its high vapor pressure relative to the other components in the stills.

B. Q: Can significant quantities of DCA be concentrated in the VDC or MC Sections?

A: DCA is formed in abnormal amounts in the VDC Section when the heavies concentration in the TCE feed is high, such as when the Heavies Still is bypassed. DCA can concentrate in the MC Reactor and vent system. The MC vent condensate stream will be routinely analyzed to monitor DCA level. Further laboratory study will be conducted as needed to determine the DCA concentration profile in the plant.

C. Q: Can significant quantities of monochloroacetylene (MCA) be concentrated in the VDC Section?

A: A continuous nitrogen sweep is maintained on the VDC Drying Still vent system to keep MCA concentration down. MCA can be concentrated in the VDC Still overhead, particularly when on total reflux. This concentration is monitored by lab analysis and will be observed.

D. Q: Can VDC in storage or other vessel polymerize at an uncontrollable rate under foreseeable conditions?

A: Laboratory tests have shown that contamination of VDC with AIBN does not lead to rapid polymerization. Thermal polymerization is also slow enough to be controlled.

- E. Q: Is the concentration of peroxides in the VDC Section known and/or monitored?
- A: A profile of the peroxide level in the plant is needed.
- F. Q: The bottoms from the MC Dopp Kettle are not analyzed on a routine basis. Is a periodic analysis needed?
- A: Analysis of this stream is difficult due to its tarry nature. However, in light of past experience the analysis should be routinely conducted.
- G. Q: Live steam is injected into the VDC Reactor and Still. Can foreseeable contamination of the steam result in any hazardous conditions?
- A: Dissolved oxygen content should be within acceptable range due to low solubility at condensate temperature. The concentration of amines or other additives in condensate should also be acceptable.
- H. Q: Is nitrogen routinely checked for possible contaminants?
- A: Periodic checks of the oxygen content will be made.

III. Operator Training

- Q: Are operators retrained on a periodic schedule and is the level of training periodically reviewed?
- A: The operators are tested occasionally. This testing will continue and training given as needed.

IV. Fire Protection

- A. Q: Do any of the chemicals in the area present any unusual fire fighting problems?
- A: Nitromethane becomes shock sensitive at elevated temperatures, according to some sources. Personnel involved in fighting a fire in an area containing drums of nitromethane should concentrate on keeping the drums cool; however, the force of a full hose stream should not be directed on the drum. The emergency squad has been alerted to the problems with NRE.

B. Q: Is the position of the vapor detector automatic trip bypass switch checked and logged?

A: The switch position will be checked and the position recorded on the log sheets.

C. Q: Are all personnel in the area adequately trained in fire fighting techniques?

A: There is probably a long range need for operator and lead operator fire training.

V. Equipment

A. Agitators

Q: Are spare parts on hand for the Flasher and Dopp Kettle agitators?

A: No gear reducer parts are stocked, but a problem with the agitator should develop slowly enough to give time to order and receive parts.

B. Columns

1. Q: Should the pressure between rupture disc - safety relief valve combinations be routinely monitored? (This question applies to all equipment with RD-SRV combinations.)

A: This pressure should be routinely checked and logged.

2. Q: The pressure on the bottom part of the VDC Vaporizer is not continuously recorded or alarmed. The packing has plugged in the past by polymerization. Is the vessel adequately protected in view of the potential of the SRV for plugging?

A: The pressure in the vaporizer should not exceed about 150 psig, which corresponds to the maximum available condensing steam temperature. The vessel design pressure is 100 psig; thus, while the situation is undesirable, the vessel is well below the burst pressure.

3. Q: The VDC Reactor, VDC Still and VDC Drying Still are susceptible to plugging in the trays or packing, and could be overpressured at the bottom by the heat sources. Is the system adequately protected?

A: The pressure in the bottom of the VDC Still is recorded on the control board. Also, the trays in the VDC Still and Reactor would be displaced by high pressure in the still and relieve the pressure upward. The Drying Still has a reliable temperature recorder and alarm which should warn of excessive pressure buildup.

4. Q: Can damage occur in the VDC Reactor or Still in the event of malfunction of the steam desuperheater?

A: Damage could possibly occur in the Reactor with extended levels of high steam temperature, but operator rounds should catch this.

C. Dryers

1. Q: The TCE Vent Condensate Dryer, Heavies Still Bottoms Dryer, Stripper Feed Dryers, Specialty Carbon Bed and Dryer are all PPG fabricated vessels. Should formal calculations be made to determine their pressure ratings?

A: An engineering work order will be written to have these calculations made and filed.

2. Q: Are the glass bullseyes on the VDCM Dryers permissible?

A: These bullseyes are used during every dryer change. The probability of a major vapor cloud resulting from a broken glass is low due to the low pressure and relatively low volatility of the VDC.

D. Heat Exchangers

1. Q: Will one SRV on the chlorine vaporizer protect the vessel from overpressure due to being liquid full with steam chest pressure?

A: This point will be checked by operations personnel.

2. Q: Is the glass sight port needed on the MC Flasher?

A: The sight port is occasionally needed for inspection in the Flasher during operation. The Flasher has an MC-HCl-VDC mixture, which is non-flammable, under a pressure less than 5 psig. Thus, breakage of the glass would not result in a flammable vapor cloud.

3. Q: Is overpressure protection needed on the DH Still Reboilers, the VDCM Reactor heater or the VDCM Still Reboiler?

A: All of these exchangers have 150 psig design pressure, which is greater than the vapor pressure of VDC at the maximum steam temperature for the 30 psig steam feed.

4. Q: Is overpressure protection needed on the water side of the TCE Reactor Cooler?

A: No. The steam pressure which would be generated at the maximum reactor temperature of 250°F is 30 psig. The design pressure is 75 psig.

E. Instruments

1. Q: The steam to the chlorine vaporizer PCV is design d to fail closed on air failure. Is this the correct way?

A: Failure of the steam PCV closed would be sensed and alarmed by the vaporized chlorine temperature change, by loss of surge drum pressure and loss of flow to the reactor. This would be a controlled situation. Failure of th PCV in the open position could cause the SRV to blow on th vaporizer.

2. Q: Overpressurization of the Lights Still and Heavies Still Feed Drum and subsequent blowing of the rupture disc on the Feed Drum would result in dumping of the Lights Still contents to the atmosphere. Are existing controls adequate to prevent overpressurization?

A: This system could overpressure from several malfunctions, including low level in the HCl Separator, loss of feed or

reflux flows to the still, opening or closing of the Lights Still steam valve, opening of the N₂ pad PCV. Temperature alarms would warn of most of these problems; the alarm settings will be improved. The pressure rating of the Heavies Still Feed Drum will be checked to see if it is feasible to increase the bursting pressure of the rupture disc.

3. Q: Can the steam flow to the VDC Reactor or Still b large enough to substantially exceed the design vapor flow in the bottom of the Reactor?

A: The steam valve sizing can't be improved and still provide good operation. The maximum allowable flow will be re-emphasized to the operators.
4. Q: Drifting of the temperature on the VDC Reactor could cause dumping of the reactor to the sewer. Are the existing controls and alarms adequate to warn of dumping?

A: Vapor detectors at the reactor outlet line will warn of a spill if the process instrumentation does not warn of the condition.
5. Q: Drifting of the VDC Reactor level high could cause flooding of the bottom of the reactor and cause tray damage. Is adequate warning given?

A: The operator rounds are frequent enough to catch this condition if instrumentation failed.
6. Q: Drifting of the VDC Still bottom temperature could allow dumping of VDC to the Per-Tri acid pit. Plugging problems in the still do not allow the temperature alarm to be reliable. Can a significant vapor cloud develop?

A: The bottom stream is cooled before going to the acid pit and goes into the acid pit below the water level. This limits the possibility for vapor cloud formation. Also, operator rounds should catch this condition.

7. Q: Can the VDC Drying Still be overpressured by the nitrogen pad system?

A: A nitrogen sweep is maintained on the still overhead at all times, and could result in overpressuring the still. The nitrogen pressure reducing system will be evaluated and an SRV will be installed on the nitrogen line to the still if needed.

8. Q: Can the VDC Storage tanks be overpressurized by failure of the vent PCV's and/or nitrogen pad systems?

A: Failure of the vent PCV's in the closed position and subsequent filling of the tank would blow the rupture disc. A pressure switch and alarm will be installed. Also, the trim size in the vent PCV and nitrogen PCV will be checked to make sure the vent PCV can carry the full flow of the nitrogen PCV.

9. Q: The MC Reactor vent PCV fails open on air failure. Is this the correct failure position?

A: The failure position will be changed to allow failure in the closed position. *Done*

10. Q: The cooling water TCV to the MC Stripper Condenser fails closed on air failure. Is this the correct failure position?

A: Failure in the closed position could conceivably result in blowing the Stripper rupture disc. Consideration is being given to changing the failure position. *Done*

11. Q: The vent PCV's on the VDCM Reactor, VDCM Still, VDCM Day Tank and VDCM Storage Tanks all fail open on air failures. Are these the correct failure positions? *Done*

A: Failure in the open position could cause significant amounts of VDC vapor release, and possible oxygen contamination if the situation continued for some time. The failure positions will be changed. Also, a work order will be written to estimate the cost of additional vapor detector heads at potential points of concentration of VDC vapors.

12. Q: The 400/150 psig and 150/45 psig steam PCV's fail closed on air failure. In view of the plant shutdown this causes, is this the correct failure position?

A: It is felt that failure in the open position could cause major upsets which might be difficult to control, whereas shutdown is a controlled situation.

13. Q: Is the nitrogen pad system on the nitromethane drum header adequately protected to prevent overpressure of the drums?

A: The manometer has been used as the relieving device in the past. This will be re-evaluated to assure that it is adequate.

14. Q: Are adequate spare parts on hand for the instrument alarm system?

A: This has been a problem in the past. An RES has been written to either revamp the alarm system or make adequate spare parts readily available.

15. Q: Opening of the VDC Still vent PCV could cause a vapor cloud at the scrubber seal pot and also loss of VDC product. Are adequate warnings given when this PCV is open?

A: The high pressure alarm will be changed so that it alarms whenever the valve opens.

E. Reactors

Q: Can liquid free-fall occur in the VDCM Reactor under foreseeable circumstances?

A: Free-fall could occur during circulation of the reactor through the heater if the level were allowed to drop. The low level alarm will be reset to warn of a level below the heater discharge.

F. Tanks

1. Q: What means are required to solve plugging of the SRV on the VDC Retention Tank?

A: This vessel is not needed at the present production rates. A plan has been formulated to solve the plugging problem and will be implemented when the vessel is put into service.

2. Q: Is fire protection needed on the VDC Retention Tank?
- A: Yes. An engineering work order will be written by operations personnel.
3. Q: The design pressure of the TCE Vapor Separator is 50 psig, and the operating pressure is 45 psig. The vessel does not have a relief device. Does the probability of overpressure warrant changes?
- A: Overpressure can occur. The vessel is partially protected by other vessels in the system which have 75 psig rupture discs. The design calculations will be re-checked, and a maximum corrosion allowance established.
4. Q: The VDCM HQMME tanks have the potential for falling liquid from the VDC feed and recirculation lines. Are bottom inlets or standlegs needed to prevent static discharge? The large AIBN tank also has free-fall from the EDC feed line.
- A: These streams will be piped into the bottom of the tanks.
5. Q: Should the VDC Storage Tanks sight glasses have excess flow valves?
- A: Excess flow valves are not needed due to the low pressure in the tanks, and the vapor detectors in the area will warn of leaks.

VI. General

- A. Q: Nitromethane drums are water washed after use. The water-NRE mixture flows to the Parish Road ditch and into the Silica Pigments ditch. What happens to the NRE and can it create a hazardous condition?
- A: A study to determine what happens to the NRE will be initiated by operations personnel.

B. Q: Tricresyl phosphate (TCP) is used as a heat stabilizer in the TCE section stills. One isomer of TCP is highly toxic and is not the correct material for the job. Are we assured that we always will get the correct material?

A: Operations personnel will follow up with purchasing to point out the potential problems and assure correct TCP is purchased.