



To: Distribution

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Interoffice
Communication

Subject: Vinyl Chloride Safety Association - 1996

The Vinyl Chloride Safety Association (VCSA) held its annual meeting in Boston on October 3-4. The meeting was attended by 32 people. A copy of their business cards is attached. A copy of the agenda is also attached. Following are notes from the meeting:

1. **EDC Pipeline Failure** - Gene Pearce of Oxy reported on an incident that occurred in a VCM Plant direct chlorination section. Oxy has an on-line chlorine analyzer used to control trim ethylene flow to the reactor. The analyzer sample line plugged giving a false reading that cut back ethylene flow resulting in chlorine breakthrough from the direct chlorination reactor. The chlorine lowered the pH in down stream carbon steel equipment resulting in several leaks. Approximately 10,000 lbs. of EDC were spilled. To prevent future occurrence, Oxy took a slip stream of EDC, water washed it and installed a pH analyzer on the wash water.
2. **Pyrophoric Polyperoxide Incident At A PVC Plant** - Rudy Sandau of Esso - Sarnia reported that while cutting a recovery system VCM line with a torch, they heard a loud popping sound. They believe a polyperoxide (PVC peroxide) build up in the line was set off by the torch. A rusty dry powder residue was observed on the inside of the line after it was removed.
3. **Cracked Furnace Tube** - Ninni Heyerdahl of Norsk Hydro described various structural problems discovered in one of their EDC cracking furnaces. Convection section tubes were observed sagging. Upon investigation they found broken tube hangers, cracked tube sheets and bad welds. The convection section tubes are not inspected routinely. This furnace had been in service for 10 years. The recommendation was that there should be an inspection of older equipment.
4. **PVC Reactor Head Gasket Failure** - Sal Jantrania of Borden - Illiopolis, IL said that they had a gasket failure in the top head of a reactor. They use a glass impregnated Teflon gasket with adhesive to hold it in place. The gasket appeared to have extruded around the bolts. This was not a new gasket. SABIC (Saudi Arabia) said they use spiral wound gaskets in this service. Someone else said Viton O rings are best (which is what CVC uses).

5. **VCM Cooling Water Pump Failure** - Peter Guay of Borden - Geismar, LA reported on an incident where they had a resistor failure in the startup circuit that resulted in a fire in the main breaker and a shutdown of their cooling water pumps. The failed circuitry was manufactured by Westinghouse and was approximately 10 years old. Borden found two other similar systems in the Geismar plant. The recommendation was that electricians need to be included in Process Hazard Analysis teams.

6. **Fire in A Mass PVC Resin Reactor** - Herm Waltemate of Geon reported on a fire they had in a pre-poly reactor at their Scottsford, Alberta mass resin plant. Geon puts people in pre-poly reactors with a chain saw to cut lumps of resin from the reactor walls. The maintenance person apparently cut into a lump that contained liquid VCM resulting in a fire. He was not seriously burned. In the future, Geon will use high pressure water to remove the lumps.

7. **Dust Explosion At A PVC Compounding Plant** - Waltemate describes a dust explosion Geon had at their Niagara Fall, Ontario PVC Compounding plant. While using a cutting torch on some steel beams supporting the second floor (16 feet in the air) of their compounding building, a piece of the cut away beam dropped a few feet onto another beam raising a cloud of dust. The torch ignited the dust. Two workers were burned by the 20' fireball. They were not wearing fire protective clothing. Geon estimates it took only 8 joules of energy to ignite this particular dust. Ordinary PVC requires about a 1000 joules of energy to ignite. The energy required to cause ignition in this case was far less because of the very small particle size of the dust and the probability that it contained other materials besides PVC (e.g., plasticizer). Geon had hired a contractor to clean before doing the hot work, but, as it turned out, they didn't clean well enough. Geon is looking at requiring flame retardant clothing for all hot work regardless of where the work is.

8. **Emergency Response Plan** - Jim Kachtick of Oxy provided information on a butadiene release from the Oxy Corpus Christi plant that cost the company \$50MM to settle. No one in the nearby community of Robstown was injured. Everyone in Robstown was offered a physical which cost Oxy \$2MM. As a result of this incident, Oxy hired Radian Corporation to recommend emergency planning levels for several chemicals. A three level system equivalent to the ERPG-1, ERPG-2 and ERPG-3 was defined for VCM at levels of 50, 250 and 1000 PPM. Oxy is doing scenario modeling using the SAFER system to predict when fence line concentrations of selected chemicals exceed their guideline 2 (for VCM, 250 ppm) triggering evacuations, shelter in place and road closures. Oxy is attempting to get the Vinyl Institute member companies to implement a similar program.

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9. **EDC/VCM Process Tank Cleaning** - Ninni Heyerdahl of Norsk Hydro described the difficulties they had cleaning an EDC intermediate tank. The discussion from the floor confirmed that most other companies have similar problems. Techniques used to remove sludge from these tanks included slurring with EDC, slurring with weak caustic water, robots, steaming, filtration, sludge drying, and steam stripping of slurry water and/or condensate.
10. **Loss Prevention/Process Safety** - Doug McCutcheon of Dow - Ft. Saskatchewan presented a check list of items to consider in a good EDC/VCM unit design. Two specific items he mentioned are that Dow uses infrared detectors on compressor seals to sense eminent fires at seals. Secondly, Dow uses open trenches for surface drainage and to prevent spread of fires down the trench during spills and fires, limits the open area of the grating to less than 1/3 of the available area. This keeps the trench above the Upper Explosive Limit and inhibits fire spread down the trench.
11. **Dioxins/Furans In Oxy Catalyst** - Joachim Rettner of EVC described German requirements for clean enclosures around oxy catalyst maintenance activities because of the high dioxin/furan concentration on the catalyst. German regulations require asbestos-like controls for oxy catalyst changes. Germany has a worker exposure limit, in the form of a particulate level, for workers changing oxy catalyst. EVC has found that oxy catalyst typically contains 3,800 ug/kg (3.8 ppm) octachlorofuran. EVC has also found high levels of dioxins and furans in soil around oxychlorination units. They were required to remove 2,500 m³ of soil contaminated above the German soil standard of 1,000 ng/kg (1 ppt).
12. **US Dioxin Update** - Ron McReady of Dow provided an update on the Vinyl Institute Dioxin Characterization Study. Based on this work to date, the VCM/PVC industry contributes 10 g of dioxin to the environment out of an estimated 9,000 g. emitted annually in the US. This number may go up as data comes in on the dioxin content of biosludge from VCM plants.
- ✓ 13. **Angiosarcoma Update** - Joachim Rettner of EVC provided an update of the Angiosarcoma Registry. Last calendar year there were three new cases added to the Registry making the total number of cases to date 192; 109 in Europe, 52 in North America, 18 in Eastern Europe, and 6 elsewhere. Dr. Patterson of ICI/EVC is maintaining the Registry. Of the 52 North American cases, 46 were in the US. All cases are in workers who were employed prior to strict VCM employee exposure standards. All but one or two cases are in PVC workers. However, there is a possible case still under investigation for a Solvay employee in Italy who started work in 1980. Dr. Maltoni has been asked to look into this

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case and determine if it should be considered a case attributable to occupational exposure to VCM.

14. **VCM Exposure At Pilot Plants** - V. Venugopal of SABIC described possible employee exposure to VCM from venting PVC pilot plants. The amount vented was very small and in compliance with EPA NESHAPs, but SABIC was still concerned. They were advised to make their batches as small as possible and to completely react the VCM to minimize emissions.
15. **PVC Reaction Temperature Divergence** - Mark Woolston of Esso Canada showed PVC reaction temperature profiles that periodically (recently) kick up drastically, along with a corresponding pressure spike. He wanted suggestions on what was happening. V. Venugopal of SABIC suggested it might be poor agitation in the bottom of the reactor. Others suggested transient fouling of the temperature probe giving a false low temperature and cutting back cooling water flow.
16. **EDC Furnace Tube Failure** - Larry Samson of Dow described a failure in the convection section of a furnace tube that was suspected of being a manufacturing defect in attaching the fins to the tubes
17. **Oxychlorination Feed Control Problem** - Larry Samson discussed a deflagration they had during an oxy startup due to a glitch in their oxygen control system.
18. **Cracking Tube Failures** - Joachim Rettner of EVC showed tables describing analysis at 7 EVC EDC/VCM plants on furnace tube failures. The charts were difficult to read and there was not a handout, but as a result of this analysis, EVC is switching from Alloy 800 (Inconel?) to thicker Alloy 600 in the radiant section of their furnaces. They found less than expected life for Alloy 800 tubes; 80,000 hours versus 100,000 expected.
19. **PVC Peroxides** - Dr. Hans Westmijze of Akzo presented work they are doing to better understand PVC peroxides (polyperoxides). They are basing this work on a paper done after an incident at Huels in 1978. The paper published by B. Terwiesch, Sci. Chem. A17 pp. 1081-1092 (1982) titled Accident At Chemische Werke Huels (1978) describes how to formulate peroxides. It is believed that polyperoxides are alternating C-C and O-O groups with 10-12 units of each which are primarily deposited in the VCM recovery system. Dilute caustic solutions hydrolyze the peroxides.
20. **VCM Unloading Survey** - Sal Jantrania of Borden presented the results of a survey he did on VCM unloading. Borden had an unloading incident and was

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looking for some ideas on how to improve their unloading procedure. They believe that a vapor line and a liquid line off a rail car were hooked up incorrectly resulting in a release from their unloading compressor. From the survey, it appeared that companies were relying on proper labeling of tank car outlet lines to avoid mix ups. The Europeans have different size vapor and liquid connections on their VCM rail cars.

21. **Cracking Tube Survey** - Ninni Heyerdahl of Norsk Hydro presented the results of a survey on the use of steam snuffing systems on cracking furnaces. They had a system but it was removed because they didn't think it was of much value and the system required significant maintenance. Eight companies having a total of 21 furnaces responded to her survey. Seven of these companies had tube failures, one did not. Six company had steam snuffing systems; 3 of those had to use the system. One of those said the system was not effective.

✓ 22. **VCM/PVC Plant Operator Experience Level Survey** - Tom Morris of Dow presented the results of a survey comparing the experience level of technical people and operators today and 5 years ago. The survey results showed that experience levels in both VCM and PVC plants was increasing slightly despite re-engineering during the past year.

The group voted to hold the **1997 meeting in New Orleans during the first week of October.**



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