Reactive Chemicals review held on July 11, 1991

Polyethylene C Plant --2 year process review

Project rep: Michael Olsen

Attendees: Mark Mitchell, John Monroe, Frank Travis, Robert Moore, Brian Witt, Michael Myers, Mike Sticklen, Mike Newsom, Dave Mihalik, Buck Bailey, Scott Williams, D.V Leblanc, George Shofoluwe, Gerald Wagener

The Reactive Chemicals Committee is very appreciative of the effort you and the entire Poly C staff put into this reactive chemicals review. Obviously there was a tremendous amount of work which went into the preparation. The presentation was very well organized.

Concerns:

1. Update compatibility chart for Poly C Plant (some suggestions below)
   Chlorine: Yellow--Dowtherm A, Ethylene, Fuel gas, Heptane, hydrogen, Is par
   Octene -1, hexane,
   Green--Erucyamide, Irganox 10,10, 2-octanol,
   Note: Perhaps these should all be red

   Trethylaluminum--some alcohols are explosive with TEA--methanol, ethanol
   2-popanol
   -carbon tet mixtures are explosive--you use chlorothene in your plant and also freon--do these react also?
   -some amides are explosive such as diethylforamide--may suspect reaction with oleamide or possibly Erucamide

   Titanium tetrachloride and activated aluminum may be a problem

Answer: All of the MSDS sheets have been compiled and plans are to work with the Poly C R&D and plant support personnel to develop a new chart using the Texas developed reactivity chart program.

2. The reactive chemicals consequences of using non-compatible absorbent materials for cleaning up spills was mentioned. Special problems have been encountered within Dow with activated carbon and with cellulose base absorbents. Before using absorbents make sure adequate reactive chemicals test data exists to assure compatibility. The problem is a fire resulting from spontaneous oxidation.

Answer:

POLY C is presently using only one type of absorbent material, 3M Brand Oil Sorbent. No problems have been experienced. There are no plans to change to any other. The only testing found was RCT-86-0306, Oil Absorbent Pad vs Dowtherm A. Change would require a Management Change Approval.

3. A review of lab chemicals storage and handling should be conducted to identify reactive chemicals hazards. For example, are th re any old chemicals stored by Poly C which may be shock sensitive due to peroxide formation? With regards to proper labeling and chain of custody, a suggestion was made to contact Steve Caldwell in the R&D Analytical labs for for information on EPA Good Lab Practices.

Answer:

A review of the stored chemicals revealed none that were old. The proper labelling of all chemicals has been accomplished.

4. ARC test should be performed on the Vanadium oxytrichloride/Titanium tetrachloride mixture to identify reactive chemical hazard potential which may result from long term storage.

Answer:

Sandra Lange/Lee Spencer checking rx chem files for any testing that has been performed with VTi mix. Can also check with Akzo to see if they have info on long term storage of VTi that is exposed to heat from sunlight.

The MLT to HEC-3 conversion has happened. Therefore, no longer will use VTi and will not store. Therefore, N/A.

5. Mike Myers mentioned that Aluminum Alkyls have a tendency to precipitate from solution in cold weather and not re-dissolve. The precipitate tends to be chemical active and could pose a reactive chemicals hazard. Texas Aklyls should be contacted for their input to this potential problem.

Answer:

Barney Daigle of Texas Alkyls had tests conducted on BEM 2346 15 wt% in heptane and BEM 15 wt% in heptane for stability at low temperature. The tests were carried out by Ms. Minnie Christal at their TAI laboratory in Deer Park, Texas. Samples were stored at -10 Deg C for 3 days. No precipitation, discoloration, or any noticeable change was observed at the end of the test.

6. Consider expediting the installation of different size unloading nozzles for BEM and EADC tank trucks.

Answer:

Different mating flanges have been installed on the BEM tank trucks and off-loading plant flanged connnections. The BEM flanges have one male dowel and one female insert at 180 degrees from one another. The EADC flanges are normal raised face flanges. The male dowel would have to be broken off of the BEM flange to mate it to the EADC flange. This should be sufficient to alleviate this potential operating error of off-loading the wrong raw material to the wrong tank.

7. Review depad procedures for unloading alkyls. Specifically, what would be the reactive chemical consequences of not closing the manual nitrogen valve after offloading?

Answer:

Regulator on depad line is bypassed during unloading of Mg alkyl truck. Concern is that drum could go flat and flare header could back into the drum causing rx chem incident with BEM. Will look at available options to prevent this such as a regulator set above flare header pressure on the depad bypass line.

8. All pertinent reactive chemicals test data generated for the Poly C process should be kept on file at Poly C.

Answer:

The block reactive chemicals contact, Mike Olsen, attended training on accessing the "Dow Reactive Chemicals System", a part of the Dow Camps Menu System. A listing of all of the pertinent testing has been downloaded to the Poly C Group Vax Account, PYCPROJ. The management at Poly C agreed that access to the listings and electronic database were the most effective and efficient method of compliance.

9. Review the PSV sizing calculations for D301 and D303 and make sure that inadvertent mixing of EADC and BEM were considered. Are gaseous products generated during the exotherm?

Answer:

This scenario is not credible based on the following reasoning and compliance with the Corporate Relief Design Manual guidelines for sequential events to constitute a credible scenario. The following are the things that would have to go wrong to crosstie BEM and EADC.

ASSUME: EADC truck is here -- Try to unload into BEM header

1. The operator has to hook up to wrong unloading hose.

   The BEM hose has a male dowel pin and a female hole at 180 deg to each other on the flanged connection. The operator would have to break off the male pin to fit the hose onto an EADC truck.

2. The material is incorrectly identified.

   When the ID is run, the results come as a weight % of Al or Mg in the solution. This analysis is run by a lab operator before the truck is unloaded. The lab operator has to confirm that the material is within specifications before it can be unloaded.

3. The MOD has to be informed to load the material into the wrong vessel.

   Once the material has been identified as EADC, the inside operator would select the EADC vessel to be filled. The automatic valves in the EADC header would then open up to allow the vessel to be filled. If the EADC truck was hooked up to the BEM header, no flow would occur because those valves would not open. Since you would have no flow in either header, the operator would get an alarm telling him that he had a low pressure in the EADC vessel during the fill.

This scenario requires the occurence of more than two events in sequence, three to be exact. Based on Corporate Guidelines, the scenario is considered incredible and therefore, not valid. The existing design basis for the PSV's is fire sizing and is considered worst case.

10. Document D305A/D305 relief device design scenarios. Make sure that the credible worse case scenarios such as water addition from a leaking exchanger and overaddition of HCL were considered.

Answer:

The limiting reagent for the reaction is the HCl. Therefore, the sizing on the jacket should be based on worst case HCl flow, independent on the amount of BEM in the vessel. The reaction of the HCl is approx. 3800/lb. HCl exothermic. If the HCl control valve fails open [Eqn 3-3-3, Corporate Relief Design Manual], the maximum flowrate of HCl is 206 lb./hr. This assumption gives a total heat of reaction of 783,560 BTU/hr. Making the assumption of a 5.5 delta C across the cooling jacket, the required chilled water flowrate is 79,150 lb./hr. Using Eqn 3-3-3 for chilled water, the maximum flow through those valves is 111,410 lb./hr. However, this flow must be checked to see if the piping can pass that much flow. Using the table on p B-14 from CRANE, the maximum flow of chilled water through the 3" header is 163,042 lb./hr and the maximum total flow through the two-2" headers is 175,584 lb./hr. Therefore, the jacket design is capable of handling the heat input. In addition, the PSV calculations on D-305A were checked to insure that the vessel was protected. The PSVs were originally fire-sized using a fire heat input of 1.7 MMBTU/hr. Since the fire-size heat input is greater than the heat of reaction input, the fire-sizing takes precedence and the PSVs are sized correctly.

The following is in response to the water leak reaction:

TOTAL HYDROLYSIS REACTION -- TOTALLY HYDROLYZE BEM

[701 cal/gm BEM] * [1000gm/2.2046lb] * [9.4781x10^(-4) BTU/.2388 cal] * [481.25 lb BEM/batch] = 607,359.6 BTU that could be released from total hydrolysis.

Since .607MM < 1.7MM (fire size), they should be ok. HOWEVER, notice that the .607MM DOES NOT HAVE A TIME INTERVAL ON IT. Theoretically, you need 157.5 lb of water to totally hydrolyze the BEM. In addition, to exceed the 1.7 MM btu/hr fire input rate, the water leak would have to be greater than a 441 lb/hr rate. This is almost 1 GPM. An engineering assumption is required and the fire case is a quantitative, accepted method. Based on this, the assumption that the leak will not exceed ~1 GPM is the basis. If somehow the leak is large, once the reactants are expended the water will act as a cooling diluent. The normal tube side vs shell side differential pressure is less than 30 psi.

In addition, in the last "two-year" Reactive Chemical Review a concern was expressed over the potential for excessive HCL addition to D305A. The concern was that if HCL addition rate exceeded the cooling capacity of the system that a potentially dangerous temperature rise could result. Checks of the MOD V coding found the system to be protected against such an occurance. The MOD V will automatically block HCL if the temperature in D305A exceeds the setpoint by 10 degrees. This emergency block valve will not reopen until the temperature is within 5 degrees of setpoint. Given that the CSTR will approximate a first order system, no futher temperature rise should occur once the HCL addition is stopped.

11. Evaluate the reactive chemicals consequences of a tube leak on E-801 and E-305A.

Answer:

See the answer to number 10 above. In addition, E-801 and E-305A are hydrotested for leaks annually.

12. Determine if a rate of temperature rise alarm would be beneficial for detecting over addition of HCL in D305/D305A.

Answer:

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13. Concerning the Kaltaco and Mole Sieve beds:

--reevaluate pre-load shut off logic
--document the decisions for setting the high temperature alarm set points 120 deg C and 100 deg c respectively.
--develop procedures for deactivating, handling and shipping spent beds which are aimed at minimizing potential for spontaneous oxidation.

Answer:

The ethylene bed setpoints and automated shutoffs are set in compliance with the recommendations of the Linear Polyethylene Tech Center in LPETC STANDARD 204. The 120 deg C for the Katalco beds are set there because the normal operationg range for those beds are 80 - 105 Deg C. All valving on the Katalco bed systems is manual.

14. Review D-212, D-222, D232 water level control--determine the need for redundant level indicators.

Answer:

Current level indication is by a dip tube and bubbler set-up. A small water level is kept in the drums for catalyst kill. Reactor PSV's, dump lines, catalyst and CaSt PSV's discharge to these drums. The only time that problems arise in measuring the drum levels is when polymer has been discharged to the drum from the reactor, plugging the dip tube. Polymer discharges are detected by flow sensors on the lines to the drums. These instruments are on the critical instrument list. Response to getting polymer into the drums is to clean out the drums at earliest possible time. In the interim, the dip tube length is adjusted if needed to measure level. Alternate level instruments were investigated, but none found to be adequate. A redundant level indicator, such as hi hi level probe, are not necessary due to the use of the flow sensors on the RX PSV and dump lines.

15. Review ethylene/premix runaway potential when padding reactor out. What are the reactive chemical consequences of mixing ethylene and catalyst without solvent present? Perhaps Tech Center needs to look at this.

Answer:

Reactive chemicals testing on Ziegler catalyst residues and Ziegler catalyst starting materials in the presence of ethylene were generated via ARC in 1982. No runaway reaction was detected. The reaction of the ethylene to polyethylene creates heat, and as the temperature rises the active catalyst begans to deactivate, thus slowing the reaction.

16. Make sure that the nitrogen pad flow switch (a permissive for unloading calcium stereate) is on the critical instrument list. In situations where direct loading of calcium stearate into the top of D401 and D402 are mandated make sure procedures are adequate for assuring a nitrogen purge during loading. This is all aimed at reducing the dust explosion potential.

Answer:

The flow switch is on the critical instrument list. The procedures have been reviewed and are adequate.

17. A comment was made that the tube temperature in E511 approaches 280 deg C when the system is pressured to 400-500 psig. Reevaluate the potential for a ethylene decomposition.

Answer:

A plot of Pressure vs. Temperature for the decomposition limits for ethylene (obtained from high pressure LDPE process) indicates that at the range of pressures and temperatures experienced for the LLDPE process, we are well within the safe region. No problems associated with reaching 280 deg C at 400-500 psig in E-511 as far as ethylene decomposition.

18. Make sure that the proper insulation is being used in the Dowtherm area. Some insulation materials can cause spontaneous oxidation problems and even fires if hot Dowtherm from a leak is dispersed throughout.

Answer:

Foam glass insulation is the material of choice and is employed.

19. Investigate the reactive chemicals potential of the portable waste trailer that is routinely used for waste containment within Poly C.

Answer:

The potential is there. There is a procedure, SOL/OCT-P8, in place to minimize the hazard. In addition, a project is being investigated to eliminate the use of the waste trailer.

20. Develop a reactive chemicals compatibility chart for lab chemicals.

Answer:

This will require some long term prioritizing. Currently, the compatibility chart update for the process is the first priority.

21. In the calcium stearate area, investigate the reactive chemicals potential for loss of calcium stearate to the process with low reactor efficiencies and high ATE usage.

Answer:

Addressed during side-arm only trial. Some ATE carried over from devos made it to bottom of tower...from 80 ppb to 1 ppm after 4 days. Some is thermally decomposed in 2nd rx and exchangers, some could go with polymer and be killed by the pelletizer water. ATE does decompose to a non-pyrophoric species.

Possibly, after weeks could build up in column bottoms and be hazardous if sampling at this point. There are purges of column bottoms to D-809 once per shift (twice a day). At these purge rates, there has been no known experience of problems. The only two incidents in the CAMPS database are fires due to improper disposal.

All of the above answers were supplied by Poly C staff and operations personnel. This list of questions and answers has been continually updated as information became available and priorities dictate. This is the status as of this date.

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