Reactive Chemicals Book

POLY C REACTIVE CHEMICALS REVIEW

The two-year Poly C Reactive Chemicals Review has been scheduled for May 18, 1989, at 8:30 a.m. in the Poly C conference room. The purpose of the review is to force us, the owners of a process, to evaluate potential reactive chemicals incidents in our plant. Members of the LAD Reactive Chemicals Committee, as wells as research, tech center, and safety personnel, will attend to help us do this more thoroughly and objectively.

The plant has been divided into areas for discussion purposes. Listed below are the topics and the person responsible for each:

Process Introduction and Flow Diagram	KES
Raw Materials and Supplies	AH
Unloading and Storage	FT
Catalyst Mixing System	KES
Ethylene Purification and Compression	KFA
Reaction	BEM
Catalyst Kill	KES
Devolatilization	GOS
Solvent Recovery and Purification	KFA
Pelletizing	GOS
Material Handling	JS
Additive System	KFA
Dowtherm System	KES
Flare	FT
Utilities	FT

The discussion of each of these areas should include the following:

(1) Process flow, equipment, and reaction
(2) Reactive chemicals concerns
(3) Measures to monitor and control these situations (e.g. instrumentation and procedures).

Use "worst case" thinking to evaluate each area. Limit the discussion to chemical reactivity. Give special attention to any process modifications which have taken place since the last review.

Listed below are several resources which may be helpful in preparing for the review and their locations:

(1) LAD Reactive Chemicals Manual [red notebook; on my bookshelf]

(2) Previous Poly C Reactive Chemicals Review [included in front of Reactive Chemicals Manual]

(3) Raw material data sheets and reaction information [my bookshelf; one green and one black notebook]

(4) List of questions typically asked at RCR [attached]

To provide review materials to the committee members prior to the review, a dry run has been scheduled for May 8, 1989, at 1:00 p.m. in the Poly C conference room. Final copies of all review materials will be needed by "closing time" on May 11, 1989.

If you have any questions or suggestions, please let me know.

Switzer
3/29/89

REACTIVE CHEMICALS COMMITTEE'S
FAVORITE TYPES OF QUESTIONS AT PROCESS REVIEWS

REVIEWS, TESTS, & DATA

1. Has the process or project been reviewed in detail with your line supervision? with Thermal Lab, with any members of the Review Committee, with your Technology Center?
2. Have you talked to knowledgeable people about the possible side reactions in your process which might become uncontrolled?
3. What reactive chemicals incidents have occurred in your plant and other plants with this or similar processes and have you reviewed them with each new employee?
4. Have you completed the operating discipline and control logic diagrams for your plant or miniplant?
5. In a computer controlled process, have you checked to make sure that the computer program is consistent with the reactive chemicals technology? Does the computer fail safe?
6. Do you know and understand the reactive chemicals tests?
7. Has reactive chemicals testing been done on all materials and possible mixtures in your plant or miniplant including waste streams? Have you summarized results?
8. What is the most likely reactive chemical incident in your operation and how do you make certain that it doesn't occur?
9. Is ARC data available on unstable materials which may be subjected to friction or exposed to high temperatures for unusually long periods of time? Has the data been interpreted?
10. Is ARC data available on raw materials, intermediates, wastes, by-products, and products where needed?
11. What is the worst condition that can develop at each step in your process?
12. Do you secure data, evaluate, and review process changes before making them?
13. Have you recently updated your fire and explosion index calculations including actual maximum probable property damage?
14. Are there predetermined senarios that predict the magnitude of a chemical release? (Reasonable release)
15. Have you prepared a "reactivity matrix" for the process?

PERSONNEL

1. Have all of your personnel received reactive chemical training? Is it reviewed on a routine basis and documented?
2. Does your operating manual include emergency shutdown procedures? Evacuation procedures?

REACTION

1. Do you check the inhibitor content of raw materials that require inhibitors?
2. How do you check your raw materials to be sure you are using what the label specifies? Do you have a procedure to ensure that the wrong raw material or additive does not get into your process? Do you check impurity levels?
3. How do you check "heels" in tanks, reactors, and tank trucks before loading?
4. Are there any potential build-up problems with reactive chemicals by recycling, concentrating, etc?
5. Do you have redundancy in your raw material feed systems to prevent one from backfeeding into the other?
6. Is your reaction system designed and controlled such, that large amounts of reactants are not allowed the opportunity to react at the same time?

PRESENCE OR ABSENCE OF AIR

1. Some monomer inhibitors need O_2 present to be effective. Do you have any of these currently blanketed with N_2? Are there any monomers which will separate from the inhibitor upon freezing?
2. Do procedures preclude the presence of air at all times in systems containing flammable hydrocarbons?
3. Do you use a N_2 pad on storage tanks containing flammable or combustible materials? How do you prevent air from being sucked into a reactor during vacuum drum loading?
4. Is there a part of your process or storage that can experience hydrogen evolution?

DISTILLATION

1. What precautions are taken to protect against flammable/explosive conditions in distillation columns under vacuum?
2. Do you plan to use N_2 to break vacuum in a distillation column when handling flammable materials?

REACTION ENERGY

1. Is the heat exchange media reactive with the process stream?
2. What is the temperature of the heating medium in the exchanger, jacket, or line tracing, in relation to decomposition temperature of the process material? Have you made sure that the temperature of the medium can not exceed a safe maximum in case of a malfunction in the heating system?
3. Are you operating in the flammable range for any of your materials? Do you know the effects of temperature, pressure, change of oxidizer on the flammability limits? Are you operating above the flashpoint of the materials in your system?
4. Do you have procedures to prevent diesel effect or heat of compression hazards?
5. What are your procedures for initial start up of a reactor or molecular sieve beds to prevent excessive heat up of the beds?
6. What could happen in a "worst case" of energy release due to cooling failure, too much catalyst, agitator failure, reaction failure with feed flow continuing, etc.?
7. Do you know the maximum amount of energy (heat) available in your reaction? Based on this heat, have you calculated the maximum attainable temperature? Would this temperature create problems due to thermal fatigue, high pressure, etc.?
8. What do you know about the kinetics of your reaction? Is it fast, slow, mass transfer limited, surface limited? What possible impurities might function as a catalyst and drastically alter this rate?
9. How fast can you remove heat and how does that relate to the two items above?
10. What equipment or procedures do you apply to assure adequate mixing of reactants or inhibitors?
11. Have you determined the most severe conditions that can develop at each step of your process and do you have operating and/or emergency procedures covering these severe conditions?
12. Have you determined what could happen in a "worst case" energy release due to cooling failure, excessive catalyst, agitator failure, etc.?
13. Have you considered the effect of scale-up on your system? (i.e. heat exchange, agitation, frangible size, waste disposal, etc.)
14. If quenching agents are part of an emergency plan for runaway polymerizations, do you know whether or not the quenching agent is effective?

INSTRUMENTATION

1. For all potential sources of reactive chemicals incidents, do you have adequate instrumentation that can detect and control unwanted operating conditions?

CHECK OF CRITICAL INSTRUMENTS

2. Is there a positive program to ensure operability of critical instrument systems such as a high temperature shutdown system?
3. Do you have a critical instrument testing program and schedule for it in your plant? Are these instruments on a regular maintenance program for calibration and reliability? Do they fail safe?
4. How do you know a key instrument still holds its calibration?

MANUAL CONTROL

5. In a cubicle controlled process, can the operator control the system manually if a critical instrument is malfunctioning?
6. Can the operator override the alarm system of the computer controlled reaction?

EQUIPMENT

1. How do you know that the agitator is running before starting a sequence?
2. How do you prevent the contents of vessels under pressure from backing up into utilities or vent systems?
3. Can your system become hydraulically full? Will this cause damage to the vessel?
4. Has your process been adequately researched? Do you know all the insitu reactions going on in the system?
5. What was the last reaction run in this piece of equipment?
   - — How well was it cleaned?
   - — Was it inspected? Was it taken apart?
   - — What will be the effect of trace amounts of residues?
   - — Will the residues have a catalytic affect?
6. Have you considered the possibility of inadvertently creating flammable mixtures in auxillary equipment (scrubber, cooling towers).

FEEDING GASES

7. When using O_2: all lines, regulators, gages, valves, and other equipment must be cleaned. Has your equipment been cleaned (that will possibly come in contact with oxygen)?
8. When using hydrogen or other highly flammable gases in your system, do you use auto-shutoff valves to prevent leaks of this material? What kind?

PUMPS

9. Should the feed-pumps be interlocked with the agitator?
10. What have you done to prevent a pump from running deadheaded?
11. Would a deadheaded pump lead to an explosive reaction or pressure build-up? How is this avoided?
12. Can excessive temperatures occur at your pumps? Are you using temperature alarms and cut-offs?
13. What effects will low flow, start up, or shut down conditions have on the safety of your process?

LUBES, GASKETS, AND LININGS

14. Are you knowledgeable about the reactivity of the materials you handle, the inter-reactivity of the materials, and the materials of construction?
15. Can materials of construction cause an unwanted chemical reaction? What if a lining failure occurred?
16. Will gearcase oil, hydraulic oil, or the heat transfer media react with the contents of the reactor? The gas phase in the headspace?
17. Are the gaskets inert at the conditions found in the system? Are they constructed of the proper material and with the proper rating for the service they will experience?

FRANGIBLES AND RELIEF DEVICES

1. Have you calculated your frangible reliefs? Has the pressure relief device been sized for the type of reaction you are carrying out in your vessel?
2. Will your relief system handle your worst case or should the process be isolated or barricaded? Can you add inhibitors to stop or slow reactions?
3. In sizing the frangibles or relief valves:
   a. Have you calculated the adiabatic reaction rate and pressure rise?
   b. Was two phase relief flow considered?
   c. How many feet of pipe (and how many restrictions) are down stream of the frangible or relief valve?
   d. Where do the contents discharge? Is there a safety hazard to personnel? If to a vent tank, is this adequately vented and can it take the pressure which will build up in it?
      I. Is the Relief System large enough to vent this equipment if:
         a. Runaway reaction?
         b. Fire/Explosion?
         c. Runaway polymerization
      II. Have the following calculation been made:
         a. Worst case (everything goes to CO_2 & H_2O)?
         b. Exothermic runaway?
         c. Maximum volume/time the vent piping can handle?

DUST AND MIST EXPLOSIONS

1. Are you handling or is there a possibility of generating finely divided powders or dusts? If so, has the explosion hazard associated with your dust been tested? What is the effect of moisture content, particle size, and ignition energy on the dust explosion potential?
2. What is the particle size and distribution? Any contaminants?
3. Are there any *hot spots* in the system from internal or external sources?

DRYING AND HANDLING

4. In drying solids which are dusty, do you know the explosive range? Do you need a nitrogen blanket? How about relief panels? Containment? Flame suppression?

MIST AND FINE PARTICLES

5. Will the current operating conditions produce mist or fine particles in the head space of the equipment?
   A. If a mist or fine particles are created, what will be the impact on the system?
   B. Have flammability studies been done on the mist or small particles?
6. Have you considered static charge as an ignition source for flammables and dust?

STORAGE AND HANDLING OF RAW MATERIALS AND PRODUCTS

1. Do you positively identify all raw materials and do you audit your identification procedures to assure they are being correctly performed?
2. What precautions are taken to prevent uncontrolled temperature rises in storage tanks or in vessels not intended as reactors? Are there warning alarms? Is this Reactive Chemicals Review a part of new employee indoctrination program? What precautions are taken to prevent backup of materials into utility (N_2, water) lines?
3. Is the disposal of chemicals handled to avoid reactive chemical problems?
4. Do you store any peroxide forming materials? If so, how? Are there any materials such as some peroxides, which may ignite if spilled on a rubbish pile?
5. Do you know the condition of "unstable" materials in storage tanks, drum-sheds, warehouses, etc.? How do you store catalysts? Is the time and temperature relation known?
6. Are any of the materials you handle sensitive to exposure to air or water?

7. Have you reviewed your storage procedures for materials that react with water and for reactiv monomers, waste, etc.?
8. Are you absolutely sure you are storing and handling catalysts properly? (such as peroxides, metal alkyls, etc.).
9. Is there a possibility that a shipping container could be mislabeled, resulting in the wrong material being sent to a customer? Or to us?
10. Are oxidizing and reducing agents properly separated in storage?

SPILLS, LEAKS, EXPOSURE, FIRES, OR OTHER PERILS

1. Will your dikes (trays) hold spills of flammables that may occur? Do you have proper drainage so flammables are directed to a remote location?
2. Do you have data to determine the safety of absorbent materials to clean up spills?
3. Is there any way that a scrubber or heat transfer fluid could back into the reaction system to cause a high energy release reaction?
4. How do you assure that the catalyst does not go downstream with the product and become a hazard?
5. What happens to your process in the case of a total power failure, loss of cooling water, or loss of other critical services? What happens when these utilities are restored?
6. Do you know the reactive chemicals consequences of a high-energy input to your process such as:
   a. external fire?
   b. stuck valve on fluid to jacket (hot)?
   c. uncontrolled electrical input (dead-headed pump)?
   d. loss of coolant or refrigeration?
   e. excessive catalyst addition?
7. If the operator fails to take a **planned emergency corrective action**, what will happen next?
8. If there is residual catalyst in a reaction system, can this lead to a hazardous situation? If yes, what are you doing to prevent this?
9. Are the potential effects of pH, water, light, promoters, or other possible contaminants on reactivity known?
10. Have you discussed disposal of waste products with the proper people?