# 1995 Consolidated Audit
# Reactive Chemicals

## II. 1995 Reactive Chemical Audit Questionnaire

REVIEW OF REACTIVE CHEMICALS CONCERNS

This section provides a detailed format within which to conduct a self-audit of the process(es) under review. There are 23 sections that cover various aspects of plant operations that have Reactive Chemicals concerns and/or issues. With each section there are one or more places for you to add notes that are pertinent to your process. Previous Reactive Chemicals incidents have been included for most of the 23 sections.

A. EVALUATION OF REACTIVE CHEMICALS DATA

The objective of these questions is to determine if the appropriate test data have been obtained and appropriate safeguards provided. Refer to the Process Flow Sheet and Test Summary Data.

a. Have Reactive Chemicals test data been gathered and evaluated for the following:

| Yes | No | |
|---|---|---|
| [X] | [ ] | Process materials and mixtures that are normal to the operation; |
| [X] | [ ] | Mixtures that may result from abnormal conditions; |
| [X] | [ ] | Materials of construction throughout the process; |
| [X] | [ ] | Potential sources of flammable dusts tested/explosive range known; rate of pressure rise data; |
| [X] | [ ] | Accelerating Rate Calorimetry (ARC) test on reactive mixtures and formulations that are handled in drums or larger volumes; |
| [X] | [ ] | Auxiliary materials, e.g., cooling tower chemicals that are normal to the operation; |
| | | Are changes in the following entities tested: |
| [X] | [ ] | Chemical components |
| [X] | [ ] | Significant changes in concentrations, in formulations |
| [X] | [ ] | Materials of construction? |
| [X] | [ ] | Vent Sizing Package (VSP) run on reactors/tanks containing reactive materials. |

Additional Comments: CMP Chemistry is well defined and well known. The concentrations of the plant's main products vary throughout the process. None of the plant's products react with each other. Materials of construction are handled via PMMS piping specifications. No CMP compounds decompose or polymerize under storage conditions. Reactor pressure relief documentation is up to date and has been reviewed by Engineering. Both reactors are automatically shutdown by supervisory computer control systems.

b. Do all individuals involved with reactive chemicals evaluation understand the information on the data sheets and know the limitations for extrapolating operating parameters from the data? What kind of training have they had?

Response(s): CMP personnel are trained annually on reactive chemical scenarios. Reactive chemical reviews are held when abnormal chemistries or compounds are handled by the plant. This ensures we correctly interpret data.

c. Have existing reactive chemicals data been reviewed to ensure that they are still appropriate to the process under consideration. In particular, consider the following:

Does it thoroughly define hazardous bounds?
**Yes. Scenarios have been defined for all sections of the plant.**
Has the process been checked out with a material balance flow diagram?
**Yes.**
Do data include total potential energy available in case a runaway reaction occurs?
**Yes**
Have test data been reviewed with Reactive Chemicals Testing and updated?
When? **11/94** Who? **Rx. Chem Committee, plant staff for new superintendant review.**
Does your system have the capability to adequately remove heat in a worst case situation?

Response(s): The CMP Thermal Chlorinator (R-1300) and hydrochlorinators (R-250A/B) are automatically shutdown in a "run away" situation. Heat evoluation will not continues after high temperature trip occurs

B. CONFIRMING ANALYSIS OF RAW MATERIALS

a. Is there a program in place for chemically confirming all raw materials; are you comfortable with a Certificate of Analysis being required and received for those raw materials difficult to test? Do your suppliers manufacture look-alike chemicals that are different and could possibly be put in a mislabeled container by mistake?

Response(s): All materials used at CMP are positively verified by one of several methods.

b. Are inhibitor levels tested on in-coming raw materials that require an inhibitor? Have you worked with your suppliers of raw materials on specifications and potential contaminants?

Response(s): Raw materials (Chlorine, methanol, HCl) do not have inhibitors. We have specifications on accepted levels of contamination.

c. What level of training do analysts receive; are the analytical data for raw materials unambiguous; are there materials that could give similar analytical data?

Response(s): Operations personnel are trained in the lab and re-trained as per plant training plans. In all cases possible, very specific test methods (i.e., GC) are used for identification.

C. MATERIALS OF CONSTRUCTION

a. Has the process been reviewed for appropriate materials of construction with respect to operating conditions? Does the Tech Center provide information and/or recommendations for materials of construction? Is information sought from suppliers of raw materials?

Response(s): Materials of construction have been thouroughly reviewed and implemented. Integrity of the materials of construction is maintained through utilization of management of change and piping specification. The tech center is involved during analysis of new materials of construction.

b. Is testing required just prior to installing parts to assure the correct material of construction? Are materials used such as lubricants, thread compound, instrument filling fluids, etc., compatible with the process?

Response(s): CMP maintenance personnel are trained on the fact that no aluminum or titanium is used on mechanical equipment in the plant. Lubricants and instrument diaphragm fillers are compatible with the process.

c. Are undesirable materials of construction identified, controlled (by whom? _____), and communicated (to whom?_____)?

Response(s): Materials of construction are identified by CMP personnel and communicated through the Chlor-Alkali and Derivatives Maintenance group and the Inventory Management group.

d. Are materials monitored for corrosion in the process? Are conditions that can cause corrosion in the system well known?

Response(s): Corrosion is monitored on line for some CMP processes. CMP has a very good knowledge of streams that present corrosion problems. Nearly all CMP compounds can be corrosive in the presence of water.

D. SIDE REACTIONS

Have side reactions in your process been adequately researched and identified? Have conditions for unwanted reactions been identified such as pH, water, contaminants, H2 evolution, unusually lengthy temperature excursions? Is any part of your process or storage subject to peroxide, acetylide or azide formation? If so, are the sources known and a program in place to keep this under control?

Response(s): Side reactions include carbon formation in the thermalchlorination and hydrochlorination reactors if run at high temperatures for long periods. Other documented side reactions include the formation of phosgene via chlorination of oxygenated compounds in the thermalchlorination reactor. CMP is not subject to pH excursions. Peroxides are not formed in the process.

E. SCRUBBERS [] NA

a. Is backflow of the scrubber into the process possible? Is it possible to create an unwanted vacuum on the process from the operation of the scrubber? Are two or more process vessels relieved to a common scrubber?

**Scrubber backflow isn't possible. The THROX scrubbers run under a slight vacuum and scrub the effluent directly out of the THROX.**

b. Can flammable or reactive materials accumulate in the scrubber medium or vapor space? Can the vent stream overcome the scrubber on very high flow?

Response(s): The scrubbers continuously vent and are not succeptible to accumulation of flammable mixtures in the vapor space.

c. How is the scrubber medium monitored to assure its effectiveness?

Response(s): The vapor at the effluent drain is monitored for free chlorine by a chlorine monitor.

F. CATALYSTS ☐ NA

a. Where does the catalyst in the process end up? Can it become a hazard? Is it in the Material Balance? Can catalytic activity be lost, poisoned or inhibited such that reactants could be charged without reacting. Are all potential reactions known for improper flows or conditions across the catalyst bed?

Response(s): CMP utilizes a stationary alumina catalyst bed for hydrochlorination. This catalyst is poisoned by propylene oxide and results in decreased methanol throughput. When poisoned, the methanol concentrations in the reactor effluent increases as the catalyst activity degrades. This is identified by routine sampling and through research evaluation of reactor life expectancies. P.O. can come to CMP as a trace impurity from the DME returned by Cellulose to CMP. Samples are anaylzed to determine PO levels (normally non-detectable <5 ppm) prior to sending materials to CMP.
The catalyst is supported internally, and migration prevented by stratified layers of inert (ceramic) denstone balls. Vapor passes through a mechanical support that allows vapor to pass, but will not allow the balls through.

In addition to the hydrochlorination catalyst, CMP utilizes a molecular sieve bed for drying within the distillation train. Trace amounts of water (100ppm) is absorbed in the AW-300 moleculars sieve. Migration is prevented by the use of mechanical screens and strainers in the inlet and outlet piping. When initially put on line, the sieve from this bed did migrate downstream through all 3 major distillation columns (C-1510, C-1520, C-1540). Deposited molecular sieve caused localized severe corrosion to the reboiler on C-1540, the heaviest section of the distillation train where heavies and carbon collect. The reboiler had to be re-tubed in 1994 due to the damage sustained by the severe under-deposit corrosion.
Temperatures and pressure of the molecular sieve bed is monitored. Start up procedures cover the possibilities of exotherm upon initial line up.

b. Is the catalyst checked before loading a new batch? Does a new or fresh catalyst bed require a special procedure?

Response(s): Catalyst is analyzed by research. COA's are analyzed to ensure proper composition and surface area has been supplied. New catalyst beds are conditioned by very specific start up procedures in order to minimize exotherms upon initial start-up.

c. What are the procedures for starting up a catalyst bed or molecular sieve bed? Do they prevent a plug-flow type temperature front?

Response(s): Procedures are very specific and focus on slow introduction of feeds to the beds. Temperature profiles are closely monitored during start ups.

d. Can the material of construction cause a catalytic effect with the product? Are there any components in the product that can react with the material of construction and cause catalytic problems? Can iron enter the process causing a hazardous catalytic effect or stop the reaction; can FeCl3 be made by an acid condition? Can rust from carbon steel vessels become a potential source of unwanted catalyst?

Response(s): Materials of construction used at CMP are not catalytic. However, ferric chloride is present at CMP in low levels in some streams. When water enters the process, ferric chloride will be made. Product samples quickly show the presence of water in the CMP process. Corrosion probes are located in the process are locations where water would be detected.

G. INHIBITORS [] NA

a. Are inhibitor levels monitored? How are they monitored? Is the inhibitor affected by materials of construction or vice versa?

Response(s): Inhibitors are added as products are leaving distillation and entering storage. Flows are measured and alarmed on the TDC (M2) and Mod5 (M3). Samples of check tanks are analyzed to ensure that inhibitor targets are met. There are no major effects, other than product quality, if products are over-inhibited.
Inhibitors minimize trace amounts of HCl in the product to ensure that HCl levels don't rise after transfer to the customer.

b. Is inhibitor effectiveness temperature dependent or can cold temperatures cause separation of the inhibitor from the product? Does the inhibitor require a small amount of oxygen to be effective? If so, is it monitored so as to avoid being eliminated by nitrogen padding?

Response(s): Inhibitors effectiveness is not variable based on oxygen supply or temperature dependency.

H. ENVIRONMENTAL CONTROLS

a. How are the mixing of waste streams monitored for unwanted reactivity?

Response(s): Waste streams from CMP do not react with one another. Organic levels are closely monitored in CMP outfalls to ensure no BOD , TOC, or TPH problems arise.

b. How are carbon adsorption beds, pressure swing absorption units (PSA's), etc. monitored for correct operation?

Response(s): The raffinate from the beds is analyzed by an on stream GC analyzer. In addition bed temperatures are monitored and alarmed to identify overloading or oxygen presence. An on stream $O_2$ analyzer is used on PSA-1770 to ensure free oxygen is not present with methanol in the carbon beds.

I. LAB CHEMICAL STORAGE

a. Is there a policy governing ownership responsibility, and date of receipt, for chemicals being stored; is a log or chemical inventory kept; is disposal or transfer of ownership of chemicals and samples required when the current owner is transferred?

Response(s): The CMP lab is maintained and audited by a staff Laboratory Technician. This person is primarily responsible for all lab ownership and housekeeping. The lab is subject to consolidated audit review in which lab issues such as these are addressed.

b. Are unstable chemicals given special storage provisions; is moisture a problem with some chemicals you store? Are your chemicals stored by compatibility or alphabetically?

Response(s): Yes. Unstable chemicals are given special storage provisions. Moisture is a concern. Chemicals are stored by compatibility.

J. HAZARDOUS MATERIAL HANDLING - POTENTIAL CONSEQUENCES

a. Is the material you handle subject to heat of compression hazard? If so, what procedures are in place to prevent explosions when opening valves/starting pipeline flows?

Response(s): CMP compounds are not subject to heat of compression situations.

b. Can material be concentrated or built up in a recycle stream to the point of instability? Can polymer or other materials in the process build up and become pyrophoric when exposed to air; is oxygen monitored in process systems where a component can be easily oxidized; are any peroxide-forming materials and conditions present in your process? If so, how is this controlled?

Response(s): No recycle/instability problems exist. No polymers. Oxygen is not monitored in the CMP process, but M2 is sampled for phosgene. Oxygen in any form will become phosgene in the thermal chlorinator.

c. Can any of the materials, when contacted with a high surface area substrate, result in a lowering of the auto ignition temperature to a hazardous range?

Response(s): Hot oil within mineral wool insulation has a depressed auto-ignition temperature. This system is trained on, closely monitored on rounds, and protected by a foam system in case of fire.

d. Can prolonged storage of any material lead to a hazardous situation?

Response(s): CMP materials do not decompose or create hazardous situations.

K. WASTE HANDLING

a. Are the absorbents used in your area selected on the basis of test data? Are procedures in place to prevent spontaneous ignition with absorbents and filters? Any prohibited absorbents? Has everyone been trained on this?

Response(s): CMP has tested and approved an oil-sorb compound that is utilized for waste solidification purposes. This is the only material used at CMP. Due to a past incident in which fly ash was used to solidify a sulfuric acid containing stream, CMP limits the absorption compounds to only oil sorb.

b. Are different waste chemicals collected in a common container? If so, what are the controls over what is put into the container? Does control of waste include materials of construction; time limit of storage; written procedure for disposal.

Response(s): Excess product from operations organic process sampling is collected in a common waste container in the lab. The materials are not reactive with each other. This waste is collected and emptied to the THROX. Waste aqueous acid samples are disposed of in the process area during the next round of samples.

L. HEELS IN TANK CARS, TRAILERS, LINES, VESSELS, AND BARGES

Are heels, resulting from cleaning, a hazard with your products? Are procedures in place to analytically test all heels before making transfers? Are vapors in pressurized vessels/trailers analyzed if no liquid sample can be obtained? Are dedicated transport vessels used without confirming heel identity? If so, how do customer and vessel handling procedures ensure the contents of the returned vessel?

Response(s): All heels are analyzed by GC (liquid heels, M1 vapor heels) or IR (M2, M3 vapor heels). Loading procedures focus on management notification if heels are not within specifications.

M. EXCHANGERS [] NA

Yes No

a. [x] [ ] Does the failure of any heat transfer system result in an uncontrollable condition? Have you evaluated the effects of recirculation or cooling failure?

Failure of quench or hot oil heat transfer systems in the hydrochlorination area result in an unquench reaction. If this happens, reactors are tripped by operations according to emergency procedures. Failure of the K-1100 system would result in a complete plant shutdown.

b. Is the exchanger medium compatible with the process material? Will cross-contamination with the process be hazardous; is monitoring provided to detect a leak?

Response(s): Exchanger mediums are compatible. Cross contamination scenarios have been analyzed and are adequately protected against. No major reaction occurs if an exchanger fails.

c. Is temperature monitoring provided around the exchanger? Has the reboiler's maximum temperature been evaluated with respect to time/temperature exposure to the material being vaporized?

Response(s): Exchanger temperatures are monitored. Reboilers at maximum temperature will produce a small amount of HCl in finished products. This HCl is distilled out by lites strippers. The HCl is a result of cracking of C2 compounds in reboilers at temperatures greater than about 125 C. Only two reboilers (C-1510, C-1540) run near this range in the distillation train.

N. AGITATORS [X] NA

a. Has agitator failure (power failure) been evaluated during the step with the most available energy to determine if a runaway can occur? Is monitoring provided to detect agitator failure? Are reactive feed flows interlocked to stop on agitator failure?

Response(s):_____

_____

0. STATIC MIXERS [] NA

Can overheating occur within the static mixer if flow of reactants is suddenly stopped without purge-out? Are temperatures before and after the mixer monitored?

Response(s): Static mixers are utilized at the inlet of the hydrochlorination reactors to improve reactant mixing. There is no overheat if a purge is not completed upon emergency shutdown. A static mixer is also used for mixing sulfuric acid and water in the sulfuric treatment system. Again, no overheating is experienced in this system.

P. PUMPS

a. How are all pumps protected from deadheading? Does the monitoring scheme assure detection and alarm/SD on pump cavitation? If not, how is this detected and controlled? Are feed pumps interlocked with shutdown trips?

Response(s): Mag-drive pumps are protected by automatic recirculation valves (ARC valves) and temperature alarms. Other pumps are protected via flow monitoring and alarming and operator rounds.

b. Have recycle streams been evaluated for loss of recycle? Can extended time agitation lead to an unacceptable temperature rise? Is a reaction controlled by pumping through a heat exchanger?

Response(s): The major recycle stream for the thermal chlorination area comes from the distillation area. 50-80% of the reactor feed is from this stream. In the event this stream is lost, the Mod5 controller will make appropriate control moves, up to and including shutdown of R-1300 and distillation.

c. Are pump seals monitored for flow of seal fluid and seal loss; would a seal fluid leak into the process be a reactive chemicals hazard?

Response(s): Pump seal flush rates are monitored by operator rounds. Tandem seal oil pots run at much lower than process pressure (process leaks to oil pot). The oil is not reactive with CMP materials. Seal pot levels and pressures are also monitored on operator rounds to ensure internal seal failures are identified as soon as possible

d. Are there installations in the process where pumps are used for mixing? If so, has there been an evaluation of the effectiveness of mixing? Can unreacted materials be forwarded to undesirable places due to poor mixing?

Response(s): Propylene oxide and methylene chloride are mixed for various M2 product blends. Recirculating tank pumps are used for mixing. Undesirable pockets of poor mixing are not a problem and only cause minor product quality concerns.

Q. BACKFLOW

Have potential backflow scenarios been evaluated; has process backflow been effectively prevented in feed lines, nitrogen connections, condensate, gas cylinders? Is redundancy of protection provided?

Response(s): Backflow scenarios have been analyzed. Scenarios include:
1. Thermalchlorination (organics into chlorine header): Protected heavily by Mod5 alarms and trips on differential pressure (3 ways to measure and trip).
2. THROX combustion and vent headers: Check valves on vents. Vents from vent recovery to THROX based off of differential pressure.
3. PSA units. Back flow protected by N2 pads on tanks to ensure positive pressures are maintained when not breathing

Describe your backflow protection: See above.

R. FLOW RATE, DISTILLATION

a. Have low and high flow rates been evaluated for their effects on reaction stability and heat removal? If the control valve is fully open will this flow rate result in a hazardous situation?

Response(s): The thermalchlorination process stability is greatly affected by changes in the chlorine flow. If loss of control of feed control valves caused an unstable reactor, the Mod5 would trip the reactor prior to reaching flammability, temperature, or pressure limitations.

b. Has total reflux of your distillation columns or reactor systems been evaluated for loss of overheads through leaking overhead valves? Concentration of unstable components in certain trays?

Response(s): CMP distillation columns can be safely run on total reflux. There are no components that would become unstable at higher concentrations on any particular tray.

S. RELIEF DEVICES AND VENT SYSTEMS

Have relief devices been calculated for worst case reactive chemicals runaway; two-phase flow? Are relief device vent systems common to more than one system? If so, has the system been sized for back pressure when one or more than one reactor overpressures?

Response(s):
Relief devices have been properly sized for reactive chemical run away scenarios. Relief devices are vented to atmosphere for 95+% of CMP safety valves. A common PSV header exists on the load rack filters. These liquid relief PSVs are for products that are not reactive with one another. The amount of liquid relieved doesn't appreciably affect the pressure on the relief collection system.

T. COMPATIBILITY CHART

Has a current cross-compatibility chart been developed for chemicals used in the block that may be mixed unintentionally; are self-reactive materials and materials of construction, included in the data? Is the compatibility chart posted where all block employees can use it? Are employees trained in its use? Is there a policy for keeping the cross-compatibility chart up to date?

Response(s): The compatibility chart is up to date. It is posted in the control room and is reviewed during annual training.

U. REACTIVE CHEMICALS TRAINING AND SCENARIOS

a. Is a training module developed for Reactive Chemicals in the department? Is reactive chemicals training conducted/tested/documented? Is attendance checked for those needing training?

Response(s): A specific reactive chemicals training module has not been developed. Training is held annually on core reactive chemicals issues and issues.

Describe your training program and provide the most recent documentation: Training at CMP is IPT based. An operations interface is provided to a network of the most up-to-date procedures and IPT modules for reference. New issues are communicated to appropriate plant personnel by a Communique' book that is stored in the control room. Employees review all postings in the Communique' periodically.

b. Does reactive chemicals training include materials specific to the block; have hazard envelopes of chemical mixtures that are reactive/flammable/explosive been developed and included in the training program; are case histories of past incidents in your unit, the Dow world, and the chemical industry, related to your process, included in the training program; have potentially wrong mixtures or procedures been emphasized.

Response(s): Specific operations procedures refer to reactive chemical scenarios. Past incidents are filed in the plant reactive chemical files. The CMP/Per-tet Technology Center and Reactive chemical group communicate relevent reactive chemical events to CMP.

c. Are important parameters, such as pH, water, contaminants, similar analyzer peaks, assurance of exotherm onset, side reactions, etc. included in periodic training; are employees trained on the ways instruments and control devices are prone to fail?

Response(s): Specific reactive chemicals scenarios and potentials are included in periodic training. Control valve failure mode is noted on plant P&ID's which have been thoroughly updated as of 3/95.

d. Are employees drilled on scenarios covering reactive chemicals concerns with written corrective procedures and/or responses for process upsets? If so, how often and which shifts?

Response(s): CMP safety teams exercise quarterly emergency drills. The topic of these drills cover various emergency situations for CMP. In addition, CMP procedures are reviewed annually for updates and addition of learning value to the plant procedure system.

V. CUSTOMER INFORMATION/PRODUCT STEWARDSHIP

a. Are customers informed of potential reactive chemicals hazards of products/formulations? Is the customer information current; are changes in formulations or concentrations communicated to the customers?

Response(s): Dow TS&D representatives are responsible for communicating hazards of CMP products used. In addition, new customers are visited and audited to ensure they meet product handling requirements (piping requirements, mtls of construction, etc.). Product brochures are distributed throught TS&D and marketing factions.

b. Is assistance offered to the customer to pursue reactive chemicals concerns; do you assure yourself that the customers understand the data provided; are materials of construction concerns communicated to the customer?

Response(s): Yes. CMP's largest concerns are avoiding use of aluminum parts and piping in any transportation or pumping equipment for distributors and customers.

W. REACTIVE CHEMICALS REVIEWS

a. Are all processes reviewed by line supervision and engineers, technology center, Safety Director and the LAD Reactive Chemicals Committee within approximately 90 days of a new superintendent or at scheduled Consolidated Audits, not to exceed two years?

Response(s): Yes. Last new superintendent review was 11/94.

b. Are appropriate process changes reviewed by the Reactive Chemicals Committee before they are installed; are pre-startup reviews held for process changes and recommissioning equipment; are pre-startup reviews held for appropriate processes that are infrequently operated (> 6 mos.)?

Response(s): Yes. CMP heavily utilizes management of change discipline. Reactive chemical concerns are identified prior to process or equipment changes.

c. Are formulation changes reviewed by the Reactive Chemicals Committee before they are established?

Response(s): CMP is not subject to formulation changes.

NOT INCLUDED IN CONSOLIDATED AUDIT, BUT
MANDATORY FOR THE OTHER AUDITS:

CRITICAL INSTRUMENTS REVIEW
OPERATING DISCIPLINE REVIEW