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cc: Gretchen LeBlanc, 3601
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CAUSTIC 1/CHLOR-ALKALI 2 REACTIVE CHEMICALS PRE-REVIEW FOR CONSOLIDATED AUDIT & NEW SUPERINTENDENT REVIEW - OCTOBER 6, 1994

Project representative: Edie Myer

Committee members present: John Monroe, Buck Bailey, Joe Schell, Beatriz Cisneros, Seb Corbino, Brian Witt, Dean Grigsby for John Gross, Mark Mitchell, Gerald Wagener

Recommendations:

1. Develop a single up-to-date chemical compatibility chart that can be shared by both plants. Consider obtaining compatibility charts from sister plants within Dow and modify accordingly.

2. Review E-205/D-227 reactive chemical issues to insure that effective safeguards are in place for avoiding a worst case chlorination of chloroform. Review John Monroe's Aspen simulation for the carbon tet elimination project. Obtain updated complete taffy analysis and document the worst case scenario and lines of defense.

3. A follow-up response letter is needed for the concerns raised with the chlorine expansion pot project of 1992.

4. Concerning the new Booster Compressor:

   a. Were the materials of construction checked with the X-ray alloy instrument?

   b. Was the equipment blacklighted for the presence of organic residues.

14. Add a comment to the Reactive Chemical Packet that the EBV's on the chlorine pumps also serve as a line of defense for minimizing chlorine losses if a pump leaks.

15. Cell Area: Add the reactions of sodium bisulfite + acid and sodium thiosulfate + acid (which release SO2) to the chemistry section. Also include this as a worst case scenario and list lines of defense.

16. Cell Area: Determine the best line of defense for a hydrogen fire in a cell effluent trap. Should the rectifier be tripped? The practice of having someone put a water hose in the trap may be unsafe due to hydrogen re-igniting.

17. Power Area: Review potential for hot oil leaking onto porous insulations, especially calcium silicate. This can result in spontaneous ignition.

18. Hydrogen Collection Area:

    a. Calculate total backflow in the event the ABV does not close to determine venting capacity of T-206. Consider installing a check valve downstream of C-601 discharge valve (AO-114). Need clarification of CATC guideline 4.1.5.3.

    b. Review the potential for carbonate buildup and determine if this is a reactive chemicals concern.

    c. There is a reactive chemicals concern with T-603 bone char exposure to air during disposal. Develop disposal procedures to avoid spontaneous ignition problems.

19. Determine if reactive chemicals testing data exists for absorbents being used. Compatibility testing should be performed if data does not exist.

20. Concerning leak repair sealants: Update CA2's and Caustic's list of approved leak repair sealants.

21. Concerning lubricants/cleaning agents: Review procedures to insure that improper materials are not used for chlorine service items.

22. Review maintenance procedures in the Power area to insure that Chlorothene and copper containing anti-seize compounds are not used together when assembling equipment. Reactive chemicals incidents have resulted in the past with this combination.

NEW SUPERINTENDENT RE
OCT. '94
DUE 9-29-94
JM HARRISON

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		
☒	[ ]		Process materials and mixtures that are normal to the operation;
☒	[ ]		Mixtures that may result from abnormal conditions;
☒	[ ]		Materials of construction throughout the process;
[ ]	☒	N/A	Potential sources of flammable dusts tested/explosive range known; rate of pressure rise data;
☒	[ ]		Accelerating Rate Calorimetry (ARC) test on reactive mixtures and formulations that are handled in drums or larger volumes;
[ ]	☒	N/A	Auxiliary materials, e.g., cooling tower chemicals that are normal to the operation;
			Are changes in the following entities tested:
[ ]	☒	N/A	Chemical components
[ ]	☒	N/A	Significant changes in concentrations, in formulations
☒	[ ]		Materials of construction?
☒	[ ]		Vent Sizing Package (VSP) run on reactors/tanks containing reactive materials.

Additional Comments:_____

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): YES. BASIC TRAINING PERTAINING TO PROCESS, CHEMPAT - COMPATIBILITY CHARTS, INCIDENT REVIEWS AND REACTIVE CHEMICAL AUDITS

* 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:

YES. REACTIVE CHEMICAL AUDIT FEB. '94
NEW SUPERINTENDENT REVIEW OCT. '94 (IN CONJUNCTION W/ CH 24 CAUSTIC I)

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Does it thoroughly define hazardous bounds? YES
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? N/A
Have test data been reviewed with Reactive Chemicals Testing and updated? YES
When? _____ Who? _____
Does your system have the capability to adequately remove heat in a worst case situation?

Response(s): YES - STEAM CUT, COOLING/CHILLING

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): NO - DOW SUPPLIED ARE TESTED, VENDOR SUPPLIED ARE NOT (ie. OILS, SOLVENTS, LAB CHEMICALS, ETC.) / YES - (LAB CHEMICALS, OILS)

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): N/A - DO NOT USE INHIBITORS ON IN-COMING RAW MATERIALS/ YES - Cl_2 & POWER I.

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): RAW MATERIALS ARE RECEIVED VIA DEDICATED PIPELINE-NO IDENTIFICATION TESTING IS DONE. SODIUM BOROHYDRIDE IS NO LONGER USED (NICKEL EROSION EXPERIMENT)

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): YES - (MOC/ROOT CAUSE INVESTIGATIONS/REACTIVE CHEM REVIEWS/PIPE SPECS UPDATE)/ YES/YES US AREA CAUSTIC TEAM

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): NO/ YES - THROUGH PIPE SPECS - GASKETS, MATERIAL OF CONSTRUCTION ETC...

c. Are undesirable materials of construction identified, controlled (by whom? YES MATERIALS GROUP), and communicated (to whom? PLANT / PIPE SPECS)?

Response(s):

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

Response(s): YES - PRESSURE VESSEL PROGRAM, THICKNESS TESTS / YES - PIPE SPECS CAUSTIC SODA SERVICE GRAPH.

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): N/A

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?

Response(s): IRON CELLS 'OUT-OF-SERVICE' SINCE 4-'93.

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): N/A

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

Response(s): N/A

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): N/A

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

Response(s): N/A

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): N/A

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): NO / NO / NO / NO

G. INHIBITORS [X] NA

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

Response(s): N/A

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): N/A

H. ENVIRONMENTAL CONTROLS

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

Response(s): pH CONTROL SYSTEM ON OUTFALLS/DITCH.

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

Response(s): N/A

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): YES - PROCEDURES IN PLACE (DOCUMENT MANAGER & LAB MANUAL) TO DEFINE OWNERSHIP/RECEIPT OF CHEMICAL INVENTORY - MAINTAINED BY LANL (VENDOR) AND AUDITED BY CONSOLIDATED LABS. / TRANSFER OF OWNERSHIP NOT DOCUMENTED - CONSOLIDATED LABS.

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): NO UNSTABLE LAB CHEMICALS USED. CHEMICALS ARE SEGREGATED BY REACTIVE HAZARDS, ie., SEPARATION OF ORGANICS AND STRONG OXIDIZERS.

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): NO.

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/NO/

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): NO.

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

Response(s): NO - HAZARDOUS MATERIALS IN STORAGE ARE PICKED UP - DISPOSED/HANDLED BEFORE 90 DAYS.

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): YES / N/A / NO / NO. CAUSTIC I USES OIL SOAK PADS FOR OIL LEAKS. R&D RAN TEST ON CASTIC OIL PADS - TESTS NEGATIVE.

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): NO - RCRA TRAINING IN PLACE TO PREVENT / YES - WASTE CHARACTERIZATION FORMS COVER ALL OF THESE.

Describe your procedures: EACH DIFFERENT WASTE IS PLACED IN ITS OWN CONTAINER; LABELED W/ WASTE TYPE NOS., ENTERED INTO ENVT PROGRAM TO BE PICKED UP.

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): YES - HAVE A PRE-LOAD CHECK FOR PREVIOUS MATERIAL / NO / NO / NO / ANALYZE HEEL.

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? N/A

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): YES/NO/YES - TESTING IS PERFORMED DAILY PER ROUTINE SAMPLING AND TESTING SCHEDULE.

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): YES / N/A

N. AGITATORS ☒ 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): N/A

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): N/A

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): OPERATING DISCIPLINE / NO / AGITATOR PUMPS - BOARD MAN FLOW DATA / SOME - COOLING BOOSTER PUMPS.

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): YES/NO/ND.

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): YES - OPERATOR ROUNDS/NO.

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): NO/N/A/NO.

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): YES - GAS CYLINDERS N/A, N_2 N/A, NO.

Describe your backflow protection: USE OF CHECK VALVES, DOUBLE BLOCK & BLEEDS + INTERMEDIATE TANKS.

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): YES - OPERATING DISCIPLINE 150M LBS STEAM FOR BOILING H_2O 620 MLBS FOR BOILING NaOH/NO.

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): N/A.

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): YES / YES / NO / N/A.

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): YES - CHEMPAT CHART, NO SELF REACTIVE MATERIALS IN BLOCK / YES, CONTROL ROOM - REACTIVE CHEMICAL BOOK IN SUPERINTENDENTS OFFICE / NO / YES / CHEMPAT!

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): YES / YES / YES (HAZCOM TRAINING) PROBABLY NEED TO DEVELOP A MODULE SPECIFICALLY FOR REACTIVE CHEMICALS.

Describe your training program and provide the most recent documentation: ANNUAL HAZCOM TRAINING

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): REACTIVE CHEMICALS INCIDENTS RELATING TO PROCESS ARE POSTED IN THE CONTROL ROOM AND REVIEWED W/ OPERATIONS AS NEEDED (STAFF).

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): YES/YES OPERATING DISCIPLINE, JOB PROCEDURES - NOT ALL EMPLOYEES ~~ARE~~ IN BLOCK ARE TRAINED JUST THE ONES INVOLVED

* 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?

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Response(s): HAVE QUARTERLY, NOT ALL SPECIFIC TO REACTIVE CHEMICALS - TWO SO FAR REACTIVE CHEMICAL RELATED. DIFFERENT SHIFT / QTR.

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): YES/YES/YES (NICKEL SPEC CHANGE).

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/YES/YES

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

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 HANDLED VIA MOC PROCESS / N/A NO INFREQUENT PROCESSES.

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

Response(s): N/A NO FORMULATION CHANGES

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

CRITICAL INSTRUMENTS REVIEW
OPERATING DISCIPLINE REVIEW