CORPORATE SAFETY AND LOSS PREVENTION

Reactive Chemicals News

Number 294 January 15, 1997

The summary of the 1996 reactive chemicals performance has been completed and is provided in the attached tables. Some key points and conclusions that we can make from this data are:

- The number of major incidents and losses improved in 1996 when compared to 1994 and 1995, although many of the incidents clearly had the potential to be more serious.
- None of the incidents in 1994 through 1996 involved new or unknown chemistry. (All the chemistry was known by the technical community within Dow but not necessarily by the folks involved in the incidents.)
- The ratio of major incidents reported to total incidents has improved the previous two years. (The "Iceberg Theory" says we need to work on leveraging the learning from the "Near Miss" incidents so as to minimize the serious accidents.)
- There continues to be a large number of incidents resulting from not following or inadequate operating procedures. Startups seem to be especially vulnerable to this type of deficiency.
- We are now tracking the major and significant reactive chemicals incidents by technology. A more detailed summary of the performance and trends can be found off the Process Safety Web Page under the Reactive Chemicals button and then Incidents. (Process Safety Services Home Page address: *http://intranet.nam.dow.com/eh&s/Process_safety/psafety.htm.*)

As we go into 1997 with significant, continuing change occurring in our work areas, there are several key things we might consider focusing our Reactive Chemicals prevention efforts on. I would like to offer three key areas of emphasis. If we can accomplish improvements in these areas, it will no doubt have a significant, favorable impact on our ability to protect our people, assets and environment.

1. Making sure that we follow a rigorous Management of Change Process that includes Reactive Chemicals.
2. Making sure that reactive chemicals potential is considered in our operating procedures. (Startup and shutdown procedures need special attention.)
3. Challenge everyone to improve on the reporting of the "near miss" or "learning experience" Reactive Chemicals incidents so that the learning and awareness can be leveraged across the entire company.

Good Luck in 1997!

If I can be of any help in your efforts to improve reactive chemicals performance, please give me a call.

Gary Phillips

Gary Phillips
Process Safety Services

For address change, contact Sharon Hartnagle, Process Safety Services, 2020 Dow Center, Midland. MI

REACTIVE CHEMICALS
1996 INCIDENT SUMMARY

SUMMARY OF REACTIVE CHEMICALS INCIDENTS*

	1992	1993	1994	1995	1996
Total Incidents/Learning Experiences	99	88	74	85	61
Major Incidents ($50,000/DAWC)	3	5	9	7	3
% Ratio Major Incidents to Total Incidents	3.0	5.6	12.0	8.2	4.9
Total Injuries	11	1	3	4	3
DAWC	0	0	1	2	2
Fatality	0	0	1	0	1
Total Dollar Loss (Thousands, US)	$680	$1,522	$5,552	$2,471	$1,320

*Data from joint ventures and contract manufacturing not included even though incidents were reported and communicated.

MAJOR FACTORS FOR REACTIVE CHEMICALS INCIDENTS

	1992	1993	1994	1995	1996
Known Chemistry	85	72	74	85	61
Operating Procedures	55	40	25	60	32
Autoignition	28	22	34	32	29
Polymerization	16	24	17	15	8
No Positive ID of Material	14	8	3	19	7
Materials of Construction	9	3	4	2	0
Critical Instruments and Devices	4	4	9	17	11

CORPORATE SAFETY AND LOSS PREVENTION

Reactive Chemicals News

Number 298 June 12, 1996

The following Dow reactive chemicals incident has been thoroughly analyzed by Linda Peerey, Doug Merrick and Bruce Powers, Analytical Sciences Laboratory, Midland. They have proposed this month's Reactive Chemicals News to leverage this learning across Dow.

Vapor Flammability

What happened?

Recently, a fire incident occurred during a "normal" centrifuge clean-out procedure. Following a solvent wash, a centrifuge (48" wide and 30" deep) was opened for entry. It was then noted that a ½" layer of xylene (approximately 2 gallons) remained in the bottom dam surrounding the wheel of the centrifuge. A manual wash-out of the xylene with warm water from a Strahman hose was initiated. Almost immediately after the wash began, a "puff" sound was noted and orange flames became visible around the entire perimeter of the basket. The operator immediately activated the automated lid-closure sequence, which took approximately 1 minute. During this brief time, the fire grew to having visible flames some 6 feet high and generating a lot of black smoke. The lid closure successfully quenched the fire.

Data

In the above incident, the following factors were noted:

a) xylene is immiscible with water and less dense,
b) the initial water dispensed from the Strahman was 140 °F,
c) the flash point of xylene is approximately 85 °F,
d) xylene is highly non-conductive, having a resistivity of ~10^{13} ohm-meter,
e) neither the operator nor the Strahman hose were grounded to building steel,
f) the centrifuge was grounded.

What was the cause?

The root cause investigation surrounding this incident generated significant discussion because the utilized clean-out procedure is "standard practice" in many production plants throughout Dow. A similar problematic procedure encountered frequently with centrifuges is the manual removal of product that is wet with organic solvent. In such operations, ***fuel*** (organic-vapor) ***and air*** are inherently present in the system, and the only leg lacking in the fuel-air-heat "fire triangle" is the "heat" or ignition source. With the minimum ignition energy (MIE) of typical organic vapors being around 0.2 mJ, even a weak static spark meets the necessary energy for an ignition source. Potential sources of a static spark in the above incident include:

a) discharge from the ungrounded hose or operator to the centrifuge, and
b) a brush discharge from the xylene to the centrifuge. Any turbulence in the xylene (such as resulted from the water spray) can produce a potential charge in the xylene liquid.

Specific prevention/risk-reduction measures for this incident might have included:

a) re-inert the system prior to water wash-out (eliminating need for additional prevention measures),
b) use water below 85 °F in temperature,
c) ground the hose nozzle, and
d) use non-turbulent water spray on the xylene.

General: Vapor Flammability Prevention and Risk-Reduction

There are two approaches for integrating "loss prevention" into operating procedures where vapor flammability issues exist.

1) The preferred approach is to ***eliminate*** the "oxygen" or "fuel" leg of the fire triangle. This may be accomplished by maintaining oxygen levels below 8-10%, or maintaining the fuel concentration below the lower flammable limit (LFL). This ***guarantees*** safety by ensuring operations are outside the flammable region.
2) Only when it is not operationally feasible to eliminate the "oxygen" or "fuel" leg of the fire triangle should efforts focus on ***minimizing the probability*** of the "heat" (ignition source) leg of the fire triangle. Note that the MIE of typical organic vapor is so low that it is impossible to eliminate all potential ignition sources. Rather, loss prevention efforts focus on minimizing the probability of such an event. This can be facilitated by:
   a) maintaining a distance of at least 2 feet between any ungrounded operator (hose nozzle, etc.) and the grounded vessel containing the fuel/air mixture (if there is a static discharge, it is not likely to result in an incident),
   b) minimizing turbulence in highly non-conductive fluids so as to reduce the probability of static brush discharges from these liquids, or
   c) considering complete grounding of the operator (including their clothing, protective equipment, tools, etc.) as the scenario dictates (for example, those involving very low flash point materials and the necessity of manual removal of wet cake from a centrifuge).

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CORPORATE SAFETY AND LOSS PREVENTION Dow

Reactive Chemicals News

Number 297 April 15, 1996

This Reactive Chemicals News article was written by Dave Leggett of the Texas Operations Analytical Sciences, Core R&D group. Dave has done an excellent job developing CHEMPAT for us to use. The article provides a brief overview of the how CHEMPAT works.

Disseminating Compatibility Information Using CHEMPAT

Knowledge of the impact of inadvertent mixing of chemicals, and what to do if such occurs, is an important part of process safety and hazard evaluation. A chemical compatibility chart provides this information, in a compact and easy-to-read format, as well as valuable safety and reactivity information within the chart's database. We suggest that each operating plant has a prominently displayed and up-to-date chart. Using CHEMPAT satisfies these requirements.

CHEMPAT is a PC-DOS based, Windows-compatible program designed to organize and display inadvertent mixing information. The program produces a compatibility, or inter-reactivity, chart and manages the user-supplied information. Because this process is computer-based, data integrity is assured and maintaining up-to-date charts is straightforward. Additionally, the thought process required to develop the database and chart for the plant demands a thorough and exhaustive examination of the plant's handling of its process and associated materials.

A compatibility chart, displayed throughout the plant, provides information to all personnel on what to do if an unplanned mixing of chemicals occurs. It is, therefore, important that plant personnel are trained on the significance of the various hazard levels and the appropriate actions to take. A hypothetical set of actions, for each hazard level, is shown in below.

Hazard Level	Action Classification
0	Report inadvertent mixing event to supervision; no further action necessary.
1	Report event to supervision; devise and implement plan(s) to manage the situation; no emergency procedures to be initiated
2	Report event to supervision; prepare to initiate unit emergency plan if needed; notify personnel in immediate area; consider halting normal activities until extent of situation is fully assessed.
3	Report event to supervision; initiate unit emergency plan; notify all plant personnel; cease normal activities until extent of situation is fully assessed; consider need to evacuate the plant; report event to plant industrial security and other ER groups.
4	Initiate unit emergency plan; notify all plant personnel to evacuate the area; cease normal activities, if possible, before evacuating; report event to plant industrial security and other ER groups once evacuation is underway or complete.

The above set of actions derives from the potential severity of the event. The severity of the event is determined from expert knowledge and/or RC data associated with the particular binary mixture. In practice, each user will establish a set of actions, based on the associated hazard levels, for a variety of mixing scenarios. Once the actions to be taken are linked to the mixture scenarios, the complete CHEMPAT database and chart are easily developed.

The data regarding the chemical and physical results of mixing A and B, together with the plant's in-place lines of defense and emergency response procedures for that particular event, are used to assess the potential hazard. Other factors, such as proximity of the mixing event to storage areas, tank farms, potential sources ignition, etc., are also considered when evaluating the mixing hazards.

Once the chart is complete, it is reviewed jointly by plant supervision and the hazard evaluation and/or process safety groups. The chart should be predominantly a combination of level zero and level one ratings with *some* level two hazards. "Some" is obviously arbitrary, but is typically in the range of 0 – 10%. Review the overall assessment and assignment scheme if a *significant* number of level three and level four hazards were assigned. It is possible that the hazard assessment has been too conservative resulting in too many "3"s and "4"s. It is also possible that the number of "3"s and "4"s is an accurate reflection of the potential hazards that may exist in the plant. In the latter case, *the plant should undertake an orderly program to reduce the potential for hazardous interactions of materials.*

Space prevents a full description of all the aspects of developing and using compatibility charts and how to use CHEMPAT to accomplish this. A comprehensive manual is available for downloading; the CHEMPAT program is also available. The network paths for the manual and program are below. (The node number is 10.15.) Follow the instructions in the README.TXT file to load CHEMPAT onto your machine.

For the Manual: \\TXUS02\PCCOMMON\PERM\SFTYLOSS\RC_INFO\CHMP_MAN.DOC
For CHEMPAT: \\TXUS02\PCCOMMON\PERM\SFTYLOSS\RC_INFO\SETUP.EXE

Incidentally, CHEMPAT is now publicly available from AIChE. Dow donated the program to the chemical industry and AIChE volunteered to administer the distribution. This is in keeping with our on-going out-reach efforts in the area of Process Safety. Other donations from Dow are the *Fire and Explosions Index Hazard Classification Guide* and the *Chemical Exposure Index Guide.*

Do not hesitate to contact us in Core R&D for more information regarding this topic or any other matters relating to RC data generation and/or interpretation.

David Leggett /sm

David Leggett
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Analytical Sciences, Core R&D

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CORPORATE SAFETY AND LOSS PREVENTION Dow

Reactive Chemicals News

Number 296 March 15, 1996

This month's Reactive Chemicals News was written by Duane Koch, Process Engineering Leader, Texas Operations. Duane is also a key member of the our Reactive Chemicals Steering Team.

****** A W A R E N E S S ******

AN ESSENTIAL ELEMENT OF WORKING SAFELY WITH REACTIVE CHEMICALS

Dow is a leader in the caliber of resources available to assist operations and research personnel with reactive chemicals issues. But all of these resources do not deliver value if not effectively utilized. An important element in applying these resources to the reactive chemical challenges in our operations is – AWARENESS.

We have not had a large reactive chemicals accident within Dow in several years. As a result, there are a number of employees who have not seen or read about a significant reactive chemicals incident occurring in the company during their Dow career. Bill Knee, former Technology Center Director, and Gary Phillips addressed this concern last year by developing a book of photos that provides a "memory" to graphically revisit serious reactive chemicals incidents to be used as part of a training program. This action is aimed at providing the organization with reactive chemicals AWARENESS.

I have always found it beneficial to think of AWARENESS as being composed of three elements – ***knowledge***, ***attention*** and ***attitude*** – where:

- ***Knowledge*** represents knowing the right way to do things
- ***Attention*** represents the focus to actually do things the way we know they should be done
- ***Attitude*** represents the personal desire and commitment to strive towards a safe, injury-free workplace

One can think of this definition of AWARENESS as a three-legged stool – take any one of the legs away and you have a potentially hazardous situation.

Nearly all incident reviews show an opportunity to improve in one or more of these awareness elements. The leadership in Dow has historically worked very hard to remind everyone that we have a personal responsibility as an employee of Dow to maintain a high level of awareness in the workplace.

Knowledge

The Reactive Chemicals Program in Dow has very successfully established a world class base of knowledge. Innovations such as the accelerating rate calorimeter (ARC) are internationally recognized within the industry. Our laboratories and focal point networks for analyzing chemicals and assessing potential plant and lab situations are outstanding. Where each of us may have an opportunity to improve is in our own personal knowledge about the reactive chemicals in our operations. It is interesting to note that none of the reactive chemicals incidents experienced in the last 2 years had any unknown chemistry. Individuals involved in these incidents typically were not fully knowledgeable of this known chemistry. Everyone needs to assess their role in the company and assure they have the right level of reactive chemicals knowledge. If you have any questions or concerns, contact your site Reactive Chemicals Focal Point and establish a plan to gain the necessary level of reactive chemicals knowledge.

GRETCHEN LEBLANC
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Attention

Just having the knowledge is not enough. It is also essential that a high level of attention exists. In operating chemical processes, the potential for a reactive chemical accident is ever present. Focusing on the task at hand and avoiding distraction is key to applying our reactive chemicals knowledge and completely eliminating accidents. This attention is necessary to successfully apply the knowledge.

Attitude

When a full commitment to knowledge and attention is applied with the right attitude, an effective reactive chemicals program is realized. By fully accepting our responsibilities as individuals and as a company to continuously strive toward an accident free operation, we will be motivated to acquire reactive chemicals knowledge and operate the plants within the proper operating procedures and constraints. A reactive chemical incident free operation can be achieved when each of us as individuals realize that an accident can occur if we do not have the correct know how and daily work practices.

With all of the changes occurring in the Company, attention and attitude are undoubtedly the most vulnerable elements of awareness. Everyone is encouraged to take a moment from busy activities. In this moment of reflection we should assess our reactive chemicals AWARENESS.

The following are also Process Engineering resources throughout the globe who are available to help enhance your process "knowledge" and understanding of the reactive chemical data and concerns. Additional Reactive Chemicals Resources are available on the Reactive Chemicals file service (\\USPWS7\REACTCHM\RESOURCE, node number 4.156).

Individual	Site	Area of Special Focus/Activity
John Thayer	Texas	HAZOP, QRA, Gas Dispersion
Val Janecek	Texas	Relief Design, Reactive Relief
Donald Brooks	Texas	Relief Design, Reactive Relief
Larry Deason	Louisiana	Relief Design, Reactive Relief
John Monroe	Louisiana	Relief Design Global Consultant
Don Eure	Louisiana	Relief Design, Reactive
David Starks	Louisiana	Relief Design, Reactive
Joel West	Louisiana	Relief Design, Reactive
Martin Cogswell	Sarnia	Relief Design, Reactive Relief
Charlie Chang	Fort Saskatchewan	Relief Design, Reactive Relief
Dave Davies	Fort Saskatchewan	Relief Design, Reactive Relief
Rudi Dauwe	Terneuzen	Risk Assessment, QRA, Consequence
Ton Lichteveld	Terneuzen	Relief Design
Thomas Dehn	Stade	Relief Design, Flame/Detonation Arrestor
Gunter Kleis	Stade	Dust Explosion consultency
Dave Winegardner	Michigan	Relief Design, Reactive Chemicals
Carl Schiappa	Michigan	Relief Design, Reactive Chemicals
Harold Johnstone	Research	Engr. Sci. Lab, Reactive Chemicals Engineering

Duane Koch/smh

Duane Koch
Process Engineering Leader

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CORPORATE SAFETY AND LOSS PREVENTION

Reactive Chemicals News

Number 295 February 14, 1996

Key Principles

Our Reactive Chemicals Steering Team spent time trying to define the "Key Principles" that guide our efforts to improve Reactive Chemicals within Dow. As many of you may know, the concept of understanding your principles is essential to guiding continuous improvement. Principles are the underlying beliefs that we have that cause us to be what we are. They remain constant through the test of time and adversity. Principles can be old or they can be newly defined or discovered. Often they are a mixture of both. In his book *Principled Centered Leadership,* Stephen R. Covey does an excellent job of defining the role of principles in effective leadership.

Our steering team defined the Key Principles for Dow Reactive Chemicals by looking at both what beliefs and practices have made us successful in the past as well as defining new beliefs or principles that should guide us in the future with our changing environment. As a test of our historic principles, we asked ourselves the question "What principles do we have in Reactive Chemicals today that we feel would survive the test of adversity that might come with a very serious reactive chemicals accident?" Union Carbide, Phillips Petroleum and Shell Chemical have all had serious reactive chemicals accidents that, in some cases, have significantly altered the structure of their companies.

The Reactive Chemicals Principles we felt would survive this kind of adversity are:

1. **"The Keystone of the Reactive Chemicals Program is Owner Responsibility"**
   We have a lot of resources available in analytical testing, Safety and Loss groups, engineering and Technology Centers that can "help" our safe management of reactive chemicals, but when everything is said and done, the final responsibility for success rests with the **Owner** (Superintendent, Manufacturing Leader or Research Group Leader, etc.).

2. **"The Focus of the Reactive Chemicals Program is Understanding the Inherent Energy of the Systems and the Conditions Under Which it Can Be Released"**

   Within Dow we have always operated with technical strength in our operational and research areas. The concept of fully understanding the process and the chemistry has been basic to the way we have historically managed our plants. This is the basis for requiring a New Superintendent (or manufacturing leader) Reactive Chemicals Review and the reason for keeping a high level of management involvement in approving changes using our Management of Change Process.

   Some companies do not require the level of process and chemistry knowledge or involvement that we do and several have paid the price through serious reactive chemicals and process safety accidents.

3. **"Reactive Chemicals Plays a Key Role in Avoiding Circumstances which put People, Environment, Equipment or Business at Risk"**
   - "An Effective Reactive Chemicals Program Creates Competitive Advantage for Dow"
   - "A Reactive Chemicals Program Aligned with Global Work Processes Facilitates Effective Risk Management"

   This third key principle looks more to the future in defining how we see reactive chemicals supporting our Business and Global Work Processes.

   We have seen this concept work when some of our competitors have been forced to reduce their presence in the market place because of serious reactive chemicals and process safety accidents. As just one of many examples, Exxon in Baton Rouge not long ago was forced to allocate ethylene to many of it's customers producing plastics and basic chemicals because of a serious explosion and fire. By aligning our efforts with the existing work processes we feel that reactive chemicals can effectively leverage the strengths of the Dow matrix organization without creating a new separate role or work process. We see reactive chemicals being able to add value to the business by applying itself as a "Core Competency," as part of "Process Safety," leveraged across all functions and businesses focused on protecting people and assets.

The other members of your Reactive Chemicals Steering Team are:

- Richard Gowland, Europe Safety and Loss
- Bill Jackson, Manufacturing
- Duane Koch, Process Engineering
- Hank Kohlbrand, Research
- Dave Leggett, Analytical Support
- Bruce Powers, Analytical Support
- Wil Vandenborn, Technology and Manufacturing

We have met once to twice per year with the objective of guiding Reactive Chemicals direction from a broad multi-functional and multi-geographical viewpoint. Please feel free to give these folks your thoughts and ideas on how we can improve. A couple of these folks have new job assignments; and, with the integration of "Reactive Chemicals" as part of "Process Safety," we will no doubt have some future changes in membership and direction for this group. In any case, I wanted to take this opportunity to recognize and thank this team for providing guidance and direction to the current Reactive Chemicals efforts.

Gary Phillips
Health & Safety Services

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CORPORATE SAFETY AND LOSS PREVENTION DOW

Reactive Chemicals News

Number 292 November 13, 1995

Standardize Aggregate and Leverage?

Does this sound like a "Purchasing Theme?" It sure is, but there are strong similarities to what we are trying to do in the other functions in developing new ways to generate value.

One of the opportunities we have in Reactive Chemicals and Process Safety to become more efficient and effective in our efforts is to leverage more of what we do across the rest of Dow. There are several excellent examples of how this can be effectively done. I thought I would share a few of them with you and ask for additional ideas that you might suggest along this same line:

- Utilization of a central focal point, like a Technology Center or a progressive plant or site, to develop *standardized,* basic reactive chemicals support materials for all the plants within the technology. For example:
  - Interpretation of Testing Data
  - Compatibility Charts
  - Training Materials and Programs
  - Worst Case Scenarios and Corresponding Operating Discipline

  Some of this is currently being done within several of our technologies. There is a significant opportunity for us to do a lot more.

- Development of ways to *aggregate and leverage* reactive chemicals training and information across technologies. Many different technologies utilize the same chemicals and have the same or similar reactive chemicals concerns. The following are several opportunities that we are currently doing or might consider doing.
  - Sharing of a common database for incident analysis and measurement .
  - Sharing a common database for reactive chemicals testing.

  (The REACHEM Data Base accomplishes both of the above, and there are many opportunities for us to use it more.)
  - Using the Reactive Chemicals Summary and contributing to the Reactive Chemicals News to share learning and ideas across technologies and businesses.
  - The development and use of common training materials that are chemistry specific and not just technology specific. Many different technologies deal with reactivity issues for common types of process materials and chemistries, for example chlorine, ethylene, ammonia, etc. There is currently a significant amount of training material that could be utilized across technologies. We need to develop viable ways of sharing and leveraging.

- One of the things we are evaluating to help us leverage across technologies and the company better is a Reactive Chemicals file service. The Reactive Chemicals file service (location: \\USPWS7\REACTCHM; node 4.156) contains several folders that provide training materials and presentations that have developed across the Dow world. Also included are folders for previous Reactive Chemicals News and Reactive Chemicals Summaries. We hope to eventually have a place for reactive chemicals discussions or a bulletin board-type operation where reactive chemicals questions, answers and ideas can be exchanged. The location is currently set up as a read-only location, but we are looking at ways we can change that. We would be interested in your thoughts and suggestions on this approach.

- Development of common processes for our Reactive Chemicals programs and audits. In the past, every site and area has spent considerable effort developing their own sometimes unique processes for safety programs, including reactive chemicals. The reasoning for doing this has been primarily creativity and cultural differences, as well as the difficulty in communicating caused by great distances between sites. Clearly our ability to communicate and share information effectively between sites has improved significantly over the last few years with the computer systems, file servers, e-mail and video systems. Cultural differences may be an important issue relative to work practice safety or what we refer to as "Hard Hat Safety;" however, process safety, including reactive chemicals, is probably closer related to technology, which should have little cultural difference site to site and area to area.

As a result of these changes and new management view, most people now feel that there are truly significant opportunities here to ***standardize aggregate*** and ***leverage*** our work processes across the company not only for reactive chemicals and process safety but many more of the things we do functionally. What are your thoughts and ideas on this?

Gary Phillips

Gary Phillips
Health & Safety Services

CORPORATE SAFETY AND LOSS PREVENTION DOW

Reactive Chemicals News

Number 291 October 19, 1995

HAZOP and Reactive Chemicals

This month's Reactive Chemicals News is written by Richard Gowland, Manager, Process Safety, Dow Europe.

Sometimes in my work in trying to maintain reactive chemicals awareness, I have seen that the "stand alone" or independent reactive chemicals programme as something which needs more linkage to the process safety concept. Historically, we have had a successful effort with Reactive Chemicals Reviews and some of our training efforts. Reactive Chemicals News is unique in its ability to reach all areas of the company and speak to people of all levels of understanding.

Integration of Reactive Chemicals into Process Safety has been helped by the Consolidated Audit Process. However, the reactive chemicals file for a particular plant may be a thing which reaches maturity. By this I mean that as time passes and a process matures, the review may become "routine" and consist of "dusting off" what we already know without a critical examination of changes and deviations to the process. I have felt that the drive for risk reduction in the reactive chemicals area needed a catalyst. I believe that HAZOP can be that catalyst.

For those people who understand HAZOP, I risk repeating what they already know. But I shall explain a little about the HAZOP process. When a project or an established plant has a complete information set including Piping and Instrument Diagrams (P&IDs), equipment specifications and knowledge of the chemistry and technology a HAZOP study is a valuable way of finding potential hazards. Using the P&ID or a flow sheet, a team typically comprising of a process specialist or chemist; a MOD V programmer/ production engineer; a shift leader or operator; a maintenance specialist and an instrument specialist is put together to study the process as it is supposed to work. Using the P&IDs, the parts of the plant defined to have the largest risk (typically F&EI > 128 or CEI > 200) are separated into "nodes" or small sections. For example, a pump and its immediately connected pipework and supply tank could be a single node. The unit operation will be split into several of these nodes. The important thing is to make sure that the whole of the potentially hazardous operation is covered by the nodes of the study.

In each node, the **design intention** is clearly stated. This is:

What is supposed to happen (normal operation, shutdown, etc.) in the node?

For the pump example, the pressure, temperature, flow rates, materials being pumped are defined at this stage. These are the **parameters.**

Then the node is examined in detail for **deviations** from this design intent for each parameter:

- Is deviation outside the design possible?
- If yes, what are all the possible causes?
- For each cause, evaluate the possible consequences
- For each cause and consequence, list our lines of defense
- Make a decision if the system is acceptable or further action needed

This approach is taken for each parameter by matching the parameters each in turn with **guide words**. These are usually: No or None; Less; More; Reverse; Instead of (Something different). The combination of **guide words** and **parameters** produce our **deviations** means that we look at for the parameter flow: No Flow; Less Flow; More Flow; Reverse Flow; Instead of (Something other than the expected material is flowing). We work through all the parameters until the node is complete, and we have a record of all the possible deviations and hazards they could cause. When I think of all the HAZOP studies I have done, the following has become obvious. Just consider the parameter of flow:

No Flow

- Causes related to reactive chemicals:
  - blockage (residues, impurities, polymerization)
  - pump deadheaded
  - pump not running when required
  - line rupture from corrosion
- Consequences related to reactive chemicals
  - pump overheats – possible runaway
  - residues may be auto catalytic
  - an ingredient may be missed from a reactor
  - flow may be going somewhere unexpected
  - major leak

More Flow

- Causes related to reactive chemicals:
  - relief system could be flowing
  - high pressure from runaway
  - line rupture from corrosion
- Consequences related to reactive chemicals
  - relief is operating
  - possible line or pump rupture
  - flow may be going somewhere unexpected
  - major leak

Reverse Flow

- Causes of back flow related to reactive chemicals:
  - line rupture
  - high pressure from runaway
- Consequences related to reactive chemicals
  - back flow of reactive materials from a reactor to another part of the plant not designed for them
  - corrosion

Composition

- Causes of composition deviations related to reactive chemicals:
  - wrong recipe
  - blockage causes an ingredient to be missed
  - degraded material in line
  - wrong material loaded
- Consequences from wrong composition related to reactive chemicals
  - wrong reaction
  - slow reaction
  - runaway
  - toxic release
  - high impurity levels

The same relevance for Reactive Chemicals exists in all the parameters I habitually address in HAZOP. Temperature, pressure, composition (as part of flow), agitation and so on. Reactive Chemicals is the golden thread running through it all!

HAZOP is a proven but not always used tool of Process Safety and Risk Assessment. I suggest that there are cases where HAZOP is justified as a part of a Reactive Chemicals Review to make sure that we see as many of the deviations as possible and eliminate or control them.

What criteria in our Dow Reactive Chemicals process do you think should justify a HAZOP?

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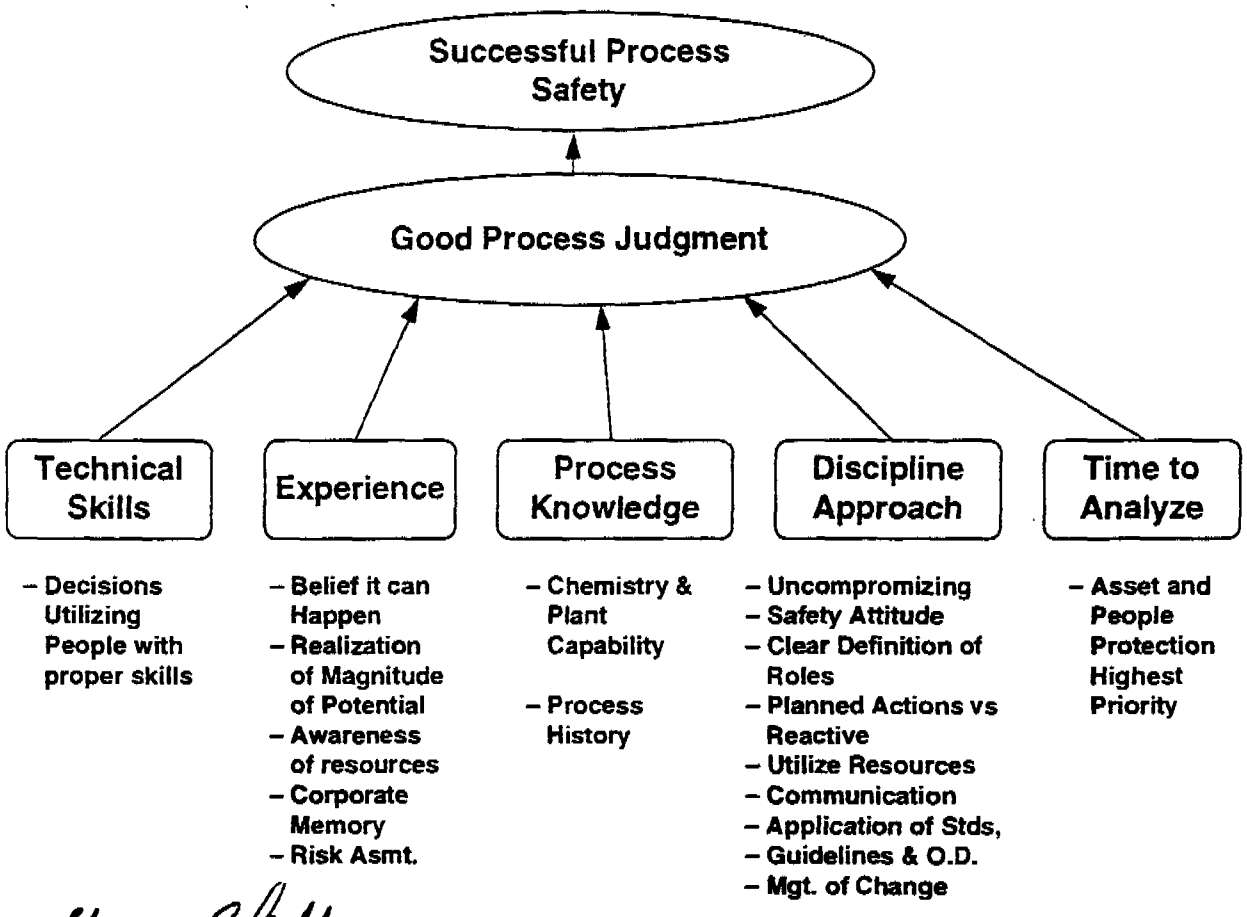
CORPORATE SAFETY AND LOSS PREVENTION Dow

Reactive Chemicals News

Number 289 August 21, 1995

In an effort to better understand the key elements that drive reactive chemicals and process safety in our plants the attached draft was prepared to attempt to relate my view of five key areas of emphasis. This model assumes that an acceptable plant design exists and focuses on how we manage change and operate daily. The primary driver of successful process safety is "Good Process Judgment" on the part of everyone involved with the plant. The five key drivers of Good Process Judgment are defined and partially explained. A deficiency in any of these five areas may be an opportunity for a safety problem in the future. It is also interesting to note that these drivers of Process Safety also drive overall smooth efficient plant operation. How does your area rate relative to these drivers?



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CORPORATE SAFETY AND LOSS PREVENTION Dow

Reactive Chemicals News

Number 285 March 1, 1995

Dave Leggett, Manager of the Reactive Chemicals Analytical Group in Texas Operations, sent a note summarizing a reactive chemicals incident that has had a major impact on a Dow competitor. The primary reasons we have worked to eliminate this type of an incident is to avoid injury and loss. Dave highlights another reason of growing importance:

The following article, summarized below, appeared in *Chemical Process Safety Report* (Volume 5, January 1995). The citations issued by OSHA amounted to $3MM in fines.

An accident at a Shell plant in Belpre, OH, destroyed one of four units that made thermoplastic resins. Three workers were killed in the explosion. It is believed that iso-pentane was added to the reactor rather than butadiene, resulting in overpressure and an explosion. Most of the citations were related to the process safety management standard (29 CFR 1910.119, September, 1992). The following are the reasons for most of the citations:

- An alarm to detect mischarges could be overridden because it was a nuisance after process type changes.
- Process safety information did not address:
  - safe upper and lower limits for process parameters
  - consequences of incomplete transfers from one reactor to the next
  - consequences of deviations from the planned procedures, for example, overcharging, mischarging; both could lead to a runaway
  - safety systems and their functions
  - special or unique hazards of the process
- Relief vent sizing did not reflect past experience (previous incident) nor current technology (i.e., DIERS technology not used).
- A partial process hazard analysis (PHA) did not include at least one person knowledgeable and experienced with the process.
- The PHA team did not address steps to avoid or correct deviations beyond normal operating conditions.
- Inspections, test procedures and inspection frequencies did not follow recognized and generally accepted practices (API/ASME Standards).
- Noted discrepancies in earlier inspections (1984) were never resolved.
- Initial operator training did not address hazards unique to the process, emergency operations, and safe work practices.
- Inspection frequency was not increased despite experience of severe fouling and plugging in the polymerization reactor.

- A January 1994 incident, involving the overcharging of 1,3-butadiene, was not fully investigated or followed up.
- Shell has agreed to accelerate its process hazard analyses schedule.

So, the next time you sit around the table with the PS&LP folks wondering "Why are we spending the time to audit?" — there are several reasons: its required by Dow, it is part of the Global Reactive Chemicals and PS&LP program and it allows us to comply with OSHA's PSM standard.

By working together on process safety management we can avoid the difficulties that Shell experienced.

Note: Although 29 CFR 1910.119 is a US regulation, the vast majority of foreign countries where Dow conducts its business have, or are developing, similar regulations.

Dave Leggett
Analytical Sciences

Reactive Chemicals Tip: The Reactive Chemicals database – REACHEM – on the Research VAX is a tremendous source of knowledge both on reactivity of various combinations of chemicals as well as previous incidents that may have occurred involving those chemicals. Use of this database information could be an excellent way to enhance the operating discipline in your area or to evaluate some of the "Management of Change" reactive chemicals issues you might be considering. Bob Thomas of the Thermal Lab in Midland is the system administrator and is planning on offering some courses on how to use REACHEM. Contact Bob if you have a specific interest – USRND::U057027 or (517) 636-5317.

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Rea... News

Number 284 February 1, 1995

Attached is the summary of our 1994 reactive chemicals safety performance.

In this data we can see definite cause for concern in that we have had our first reactive chemicals fatality in 13 years as well as a number of significant accidents and near misses. Over the last several years, our Dow performance has been among the best in the industry, but the trend and potential of some of the incidents should send us notice to not become complacent with our previous performance.

One only needs to look at the headlines relating to the experience of some of our competitors who have had major reactive chemicals incidents to understand the magnitude of the potential injuries and production losses that can occur. Most of us subscribe to the "Iceberg" principle of safety severity. This basic model assumes that for every so many minor incidents there is going to occur a smaller but proportionate number of serious accidents (i.e., the tip of the iceberg). Back in 1982 the ratio was about one extremely serious accident for every 150 reactive chemicals incidents. We were having about 85 incidents per year in just the US Area back then. The analysis of the 1994 Dow global reactive chemicals incidents shows our performance has greatly improved, but the ratio of extremely serious accidents to total incidents is still approximately the same. We have not had any of the big explosive types of events that we had back then, but we have had enough close calls to convince ourselves that it can still happen. This leads us to the conclusion that in order to eliminate the serious accident we must work on eliminating the smaller, less serious incident. Until that occurs we cannot feel overly secure.

One of the things missing as a result of our terrific safety and reactive chemicals performance is an awareness and respect that occurs from having seen the reality of a significant reactive chemicals incident. The old saying that "those who do not remember history are doomed to relive it" can sometimes prove to be all too true. Our challenge is to come up with reasonable ways to understand and remember what can happen so as to create the appropriate awareness and attention. I would like to hear and share your thoughts on how we might accomplish this. Please send me a e-mail or give me a call.

There are a couple of safety video tapes available that help create awareness to the potential of reactive chemicals:

- "A Look Back In Time," 15 minutes, Corporate Safety and Loss Prevention, 1990
- "Reactive Chemicals," 20 minutes, Gordon Miller, Texas Operations, 1982 (VT82-644)

Your local safety department may have a copy, if not please give me a call and I will try to help find one for you.

The current high production demands on our plants and the tremendous improvements in productivity that we have been implementing are a true test of our abilities to manage all the aspects of our operations. In a sense, we are charting our way through new territory. Our hope is that the tremendous improvements being made in our "operating disciplines" and the extra vigilance that you are directing at priorities, such as reactive chemicals, will enable us to be successful in this period of change.

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