Case Histories

Case histories

- **Case histories** are written descriptions of accidents, including the causes, consequences and methods required to prevent similar events.
- They are descriptions written by plant managers and operating personnel.
- These are the people with the hands-on experience,
- The ones who know and appreciate the accident and accident prevention methods.
- These case histories are categorized into five sections:
    - Static electricity
    - Chemical reactivity
    - System design
    - Procedures
    - Training

Case histories

- Anyone familiar with the specific equipment or procedures will appreciate the lessons learned.
- Accidents occur rapidly and unexpectedly.
- There is usually inadequate time to manually return a situation back into control
- Those who believe that they can successfully control accident deviations manually are doomed to repeat history.

Static Electricity

fires and explosions are the result of a flammable

mixture being ignited by a spark caused by static electricity.

Static Electricity

- The following series of case histories

Tank Car Loading Explosion

filling a tank car with vinyl acetate

- One operator was on the ground, and the other was on top of the car with the nozzle end of a loading hose
- A few seconds after the loading operation started, the contents of the tank exploded.
- The operator on top of the tank was thrown to the ground; he sustained a fractured skull and multiple body burns and died from these injuries.
- investigation indicated that the explosion was caused by a static spark that jumped from the steel nozzle to the tank car.
- The nozzle was not bonded to the tank car to prevent static accumulation.
- The use of a non metallic hose probably also contributed.

Explosion in a Centrifuge

- A slurry containing a solvent mixture of 90% ethyl cyclohexane and 10% toluene was being fed into a basket centrifuge.
- The lid was lifted and a flame was released between the centrifuge and the lid. The foreman’s hand was burned.
- The fill line from the reactor to the centrifuge was Teflon-lined steel, running to a point 3 ft from the centrifuge where there was a rubber sleeve connector.
- The short line from the sleeve to the centrifuge was steel. The centrifuge was lined.
- The accident investigation indicated that a flammable atmosphere had developed because of an air leak.
- The lined centrifuge was the source of ignition as a result of static accumulation and discharge.
- Later (and successful) processing grounded stainless steel centrifuge that was inerted with nitrogen.

Duct System Explosion

- Two duct systems in the same vicinity contained dust transport lines, dryers, and hoppers.
- One system was recently repaired and left open. The open system emitted some methanol vapors.
- The other system was being charged through a funnel with a dry organic intermediate.
- The charge line consisted of a new glass pipe and a 6-ft section of plastic pipe.
- The duct system that was being charged exploded violently, and the explosion initiated other fires.
- Fortunately, no one was seriously injured.
- The transportation of the intermediate dust through the glass and plastic line generated a static charge and spark.
- Open lines should be blanked off when the discharge of flammable vapors is possible.
- Also, proper grounding and bonding techniques must be used to prevent static buildup.

Conductor in a Solids Storage Bin

- A dry organic powder was collected in a hopper. A piece of tramp metal entered the hopper with the solids.
- As it rolled down the solids, it accumulated a charge by the charging method called separation.
- At some point in the operation the tramp metal approached the metal wall of the hopper, which was grounded.
- A spark jumped from the tramp metal to the grounded wall.
- The spark was energetic compared to the minimum ignition energy of the dust.
- Because the storage hopper's atmosphere was air (plus the dust), the dust exploded and the storage hopper ruptured.
- This explosion could have been prevented with a tramp metal collector, for example, a magnetic trap or a screen.
- An additional safeguard would be the addition of an inerting gas.

Pigment and Filter

- A low-flash-point solvent containing pigment was pumped through a bag filter into an open drum.
- The pigment drum was grounded by means of a grounding rod.
- Although the operation ran successfully for some time, one day there was a fire.
- Possibly, the grounding rod was placed closer to the filter than previously, giving the conditions for a brush discharge between the filter and the grounding rod.
- It is also possible that the grounding rod wire was closer to the isolated drum than previously; in this case a spark could have jumped between the drum and the grounding wire.

- This system was modified to include an inerting system and a dip pipe charging line,

- And all metal parts were bonded.

Pipefitter's Helper

- Pipefitter's helper was transporting tools to the boss. The helper walked through a cloud of steam before handing the tool to his boss.
- Upon each transfer, the boss received a rather large shock.
- The problem was the steam; it became charged as it exited a manifold.
- Then the charge was transferred to the helper and to the tools when the helper passed through the steam cloud.
- Charge loss was prevented because the helper was wearing insulated shoes.
- The boss was grounded because he was kneeling on a damp grounded grating.
- Using conductive shoes and changing the location of the toolbox solved this problem.
- This example may have been a disaster if the pipefitter was repairing a flammable gas leak,

Lessons Learned Concerning Static Electricity

A number of recommendations are also developed:

(1) Operators must be cautioned against drawing pipes or tubing through their rubber gloves, resulting in static buildup;

(2) Clothing that generates static electricity must be prohibited;

(3) Recirculation lines must be extended into the liquid to prevent static build up;

(4) Shoes with conductive soles are required when handling flammable materials;

(5) Bonding, grounding, humidification, ionization, or combinations are recommended when static electricity is a fire hazard;

(6) A small water spray will rapidly drain electrical charges during chopping operations;

Lessons Learned Concerning Static Electricity

(7) Inert gas blankets must be used when handling flammable materials;
(8) Drums, scoops, and bags should be physically bonded and grounded;
(9) Ground connections must be verified with a resistance tester;
(10) spring-loaded grounding or bonding clips should be replaced with screw type C-clamps;
(11) conductive grease should be used in bearing seals that need to conduct static charges;
(12) Sodium hydride must be handled in static-proof bags;
(13) Stainless steel centrifuges must be used when handling flammable materials;
(14) Flanges in piping and duct systems must be bonded

Chemical Reactivity

reactions resulting from the accidental and wrong combination of chemicals or reaction conditions (wrong type, wrong concentrations, or the wrong temperature).

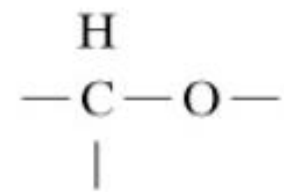
- **Functional Groups:** Specific functional groups that contribute to the explosive properties of a chemical through rapid combustion or detonation

Azide	N_3
Diazo	$-N=N-$
Diazonium	$-N_2^+ X^-$
Nitro	$-NO_2$
Nitroso	$-NO$
Nitrite	$-ONO$
Nitrate	$-ONO_2$
Fulminate	$-ONC$
Peroxide	$-O-O-$
Peracid	$-CO_3H$

Peroxides

- Peroxides *and* peroxidizable compounds are dangerous sources of explosions.
- Some examples of peroxidizable compounds

1. Ethers, acetals:

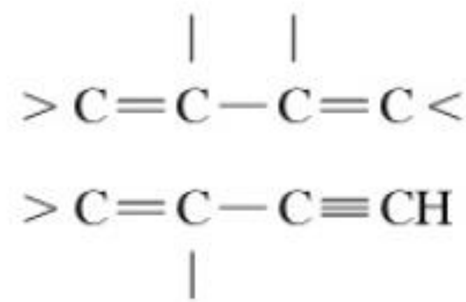


2. Olefins with allylic hydrogen, chloro- and fluoroolefins, terpenes, tetrahydronaphthalene:

$$>C=C<$$

3. Dienes, vinyl acetylenes:

   and



Peroxides *and* peroxidizable compounds

Peroxidizable hazard on concentration

- Diethyl ether
- Tetrahydrofuran
- Dioxane
- Acetal
- Methyl *i*-butyl ketone
- Ethylene glycol dimethyl ether (glyme)
- Vinyl ethers
- Dicyctapentadiene
- Diacetylene
- Methyl acetylene
- Cumene
- Tetrahydronaphthalene
- Cyclohexane
- Methylcyclopentane

Peroxidizable hazard on storage

- Isopropyl ether
- Divinyl acetylene
- Vinylidene chloride
- Potassium metal
- Sodium amide

Hazardous when exposed to oxygen due to peroxide formation and subsequent peroxide initiation of polymerization

- Styrene
- Butadiene
- Tetrafluoroethylene
- Chlorotrifluoroethylene
- Vinyl acetylene
- Vinyl acetate
- Vinyl chloride
- Vinyl pyridine
- Chloroprene

Reaction Hazard Index

- Rating system to establish the relative potential hazards of specific chemicals; the rating is called the reaction hazard index (RHI).
- The RHI is related to the maximum adiabatic temperature reached by the products of a decomposition reaction.
- It is defined as

$$\mathrm{RHI} = \frac{10T_d}{T_d + 30E_a},$$

*T*d is the decomposition temperature (K) and
*E*a is the Arrhenius activation energy (kcal/mol

- The RHI has a low value (1 to 3) for relatively low relativities and higher values (5 to 8) for high reactivities.

Reaction Hazard Index

Formula	Compound	Decom-position temperature (K)	Activation energy (kcal/mol)	RHI
$CHCl_3$	chloroform	683	47	3.26
C_2H_6	ethane	597	89.5	1.82
C_7H_8	toluene	859	85	2.52
$C_2H_4O_2$	acetic acid	634	67.5	2.38
C_3H_6	propylene	866	78	2.70
$C_6H_{14}O$	isopropyl ether	712	63.5	2.72
C_2H_4	ethylene	1005	46.5	4.19
C_2H_2	acetylene	2898	40.5	7.05
$C_3H_5N_3O_9$	nitroglycerine	2895	40.3	7.05
$C_4H_{10}O_2$	diethyl peroxide	968	37.3	4.64

Bottle of Isopropyl Ether

- Just as the cap broke loose, the bottle exploded,
- Practically disemboweling the man and tearing off several fingers.
- The victim remained conscious and, in fact, coherently described how the accident happened.
- The man was taken to a hospital and died within 2 hr of the accident of massive internal hemorrhage.
- An accident investigation identified the cause of the accident to be the rapid decomposition of peroxides, which formed in the ether while the bottle sat in storage.

Bottle of Isopropyl Ether

- Some of the peroxides crystallized in the threads of the cap and exploded when the cap was turned.
- As ethers age, especially isopropyl ether, they form peroxides.
- The peroxides react further to form additional hazardous by-products, such as triacetone peroxide.
- These materials are unstable. Light, air, and heat accelerate the formation of peroxides.
- Ethers should be stored in metal containers. Only small quantities should be purchased.
- Ethers should not be kept over 6 months.

Nitrobenzene Sulfonic Acid Decomposition

- 300-gal reactor experienced a violent reaction, resulting in the tank being driven through the floor, out the wall of the building, and through the roof of an adjoining building.
- The reactor was designed to contain 60 gal of sulfuric acid and nitrobenzene sulfonic acid, which was known to decompose at 200°C.
- The investigation indicated that the vessel contents were held for 11 hr. A steam leak into the jacket brought the temperature to about 150°C.
- Subsequent tests showed exothermic decomposition above 145°C.

- The underlying cause of this accident was the lack of precise reaction decomposition data.
- With good data, engineers can design safeguards to absolutely prevent accidental heat-up.

Organic Oxidation

- Chemical operators were preparing for an organic oxidation.
- Steam was applied to the reactor jacket to heat the sulfuric acid and an organic material to a temperature of 70°C.
- The rate of heating was slower than normal. The two operators turned the agitator off and also shut off the steam.
- One operator went to find a thermometer. Approximately 1 hour later, the operator was ready to take a temperature reading through the manhole.
- He turned on the agitator. At this point the material in the kettle erupted through the manhole.
- The two operators were drenched and both died from these injuries.

Organic Oxidation

- The accident investigation stated that the agitator should never be turned off for this type of reaction.
- Without agitation, cooling is no longer efficient; so heat-up occurs.
- Without agitation, segregation of chemicals also occurs.
- When the agitator is subsequently activated, the hotter chemicals mix and react violently.
- This type of problem is currently preventable through better operator training.
- Installation of electronic safeguards to prevent operators from making this mistake.

System Designs

- The following case histories emphasize the importance of these special safety design features.

Ethylene Oxide Explosion

- A process storage tank contained 6500 gal of ethylene oxide. It was accidentally contaminated with ammonia. The tank ruptured and dispersed ethylene oxide into the air.
- A vapor cloud was formed and almost immediately exploded.
- It created an explosive force equivalent to 18 tons of TNT, as evidenced by the damage.
- One person was killed and nine were injured; property losses exceeded $16.5 million.

- This accident was attributed to the lack of design protection to prevent the backup of ammonia into this storage tank.
- It also appears that mitigation techniques were not part of the system (deluge systems, dikes, and the like).

Ethylene Explosion

- Failure of a 3/8-in compression fitting on a 1000–2500-psi ethylene line in a pipe trench resulted in a spill of 200–500 lb of ethylene.
- A cloud was formed and ignited, giving an explosion equivalent to 0.12–0.30 ton of TNT. This accident took place in a courtyard, giving a partially confined vapor cloud explosion.
- Two people were killed and 17 were injured; property loss was $6.5 million.

- The probable causes of this accident include
  (1) use of non welded pipe,
  (2) installation of pipe in trenches, resulting in an accumulation of flammable vapors, and
  (3) lack of automated vapor detection analyzers and alarms.

Pump Vibration:

- Vibration from a bad pump bearing caused a pump seal to fail in a cumene section of a phenol acetone unit.
- The released flammable liquids and vapors ignited.
- An explosion ruptured other process pipes, adding fuel to the original fire.
- **This accident could have been prevented by a good inspection and maintenance program.**
- **Potential design improvements include vibration detectors, gas analyzers, block valves, and deluge systems.**

Leak Testing a Vessel

- A 2-ft-diameter float was fabricated using stainless steel and welded seam construction.
- Pipefitters were given the job of checking the welds for leaks.
- They were instructed to use 5 psi of air pressure and a soap solution to identify the leaks.
- A short time later, as the fitters were carrying out the tests, the float ruptured violently.
- Fortunately, there was no fragmentation of the metal, and the two fitters escaped injury.
- The accident investigation found that the leak test should have been conducted with a hydraulic procedure and not air.
- The vessel should have been protected with a relief device.

Dangerous Water Expansion

- A hot oil distillation system was being prepared for operation.
- The temperature was gradually raised to 500°F.
- A valve at the bottom of the tower was opened to initiate the transfer of heavy hot oil to a process pump.
- When the bottom valve was opened, the pocket of water came in contact with the hot oil.
- Flashing steam surged upward through the tower. The steam created excessive pressures at the bottom of the tower, and all the trays dropped within the tower.

- In this case the pressure luckily did not exceed the vessel rupture pressure.
- Although no injuries were sustained, the tower was destroyed by this accident.
- If these scenarios are possible, relief valves should also be installed to mitigate these events, or adequate safeguards should be added to the system to prevent the specific hazard scenario.

Thanks