Hazards of Hydrogen Peroxide handling

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Content

- **Hydrogen Peroxide properties**
- **Influence of Hydrogen Peroxide on Fire & Explosion Hazards**
  - Gas-phase explosion
  - Thermal runaway
  - Condensed-phase explosion
- **Real-life experiences**
  - Gas-phase explosions: 3 events
  - Thermal runaway: 3 events
  - Condensed-phase explosion: 1 event
- **Lessons learned**

1. Hydrogen Peroxide properties

Properties of Hydrogen Peroxide (HP)

- **A common and versatile chemical compound**
  - A reactive oxygen species
  - Clean byproducts: water and oxygen
  - Main uses at low concentration: oxidizing, bleaching, disinfectant.
  - Grades up to 70% are used in the chemical industry
  - … higher grades used as rocket propellant -out of today's scope.

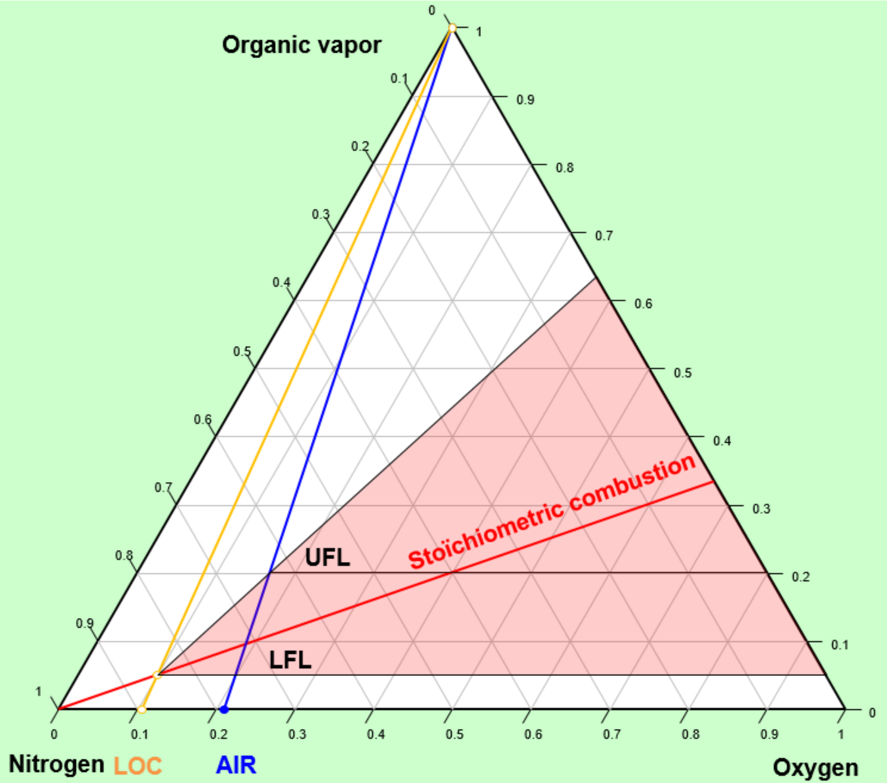
- **Labelling**
  - Grades ≥50%

  - Grades < 50% to ≥22%

2. Impact of Hydrogen Peroxide on Fire and Explosion Hazards

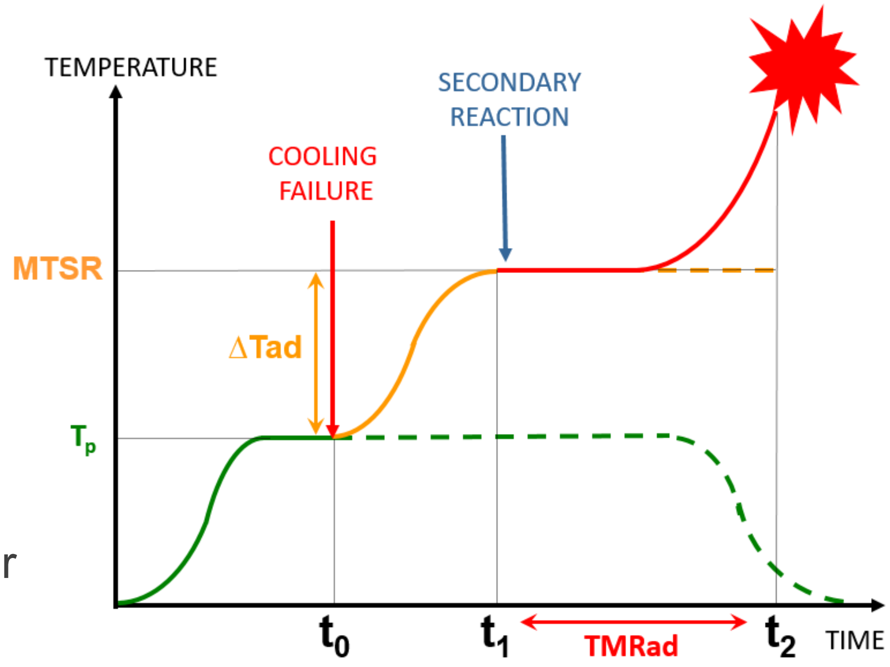
Gas-phase Explosion Hazard

- **Ternary diagram presentation (% vol)**
  - Lower Flammability Limit in air
  - Upper Flammability Limit in air
  - Limiting Oxygen Concentration
  - Stoïchiometric combustion line
- **In presence of Hydrogen Peroxide**
  - H_2O_2 in gas phase usually negligible
  - Generation of O_2 may exceed LOC
  - For $[O_2] >> 21\%$
    - UFL increases
    - Minimum Ignition Energy drops
    - Explosion pressure Pmax increases
    - Deflagration to Detonation Transition more likely



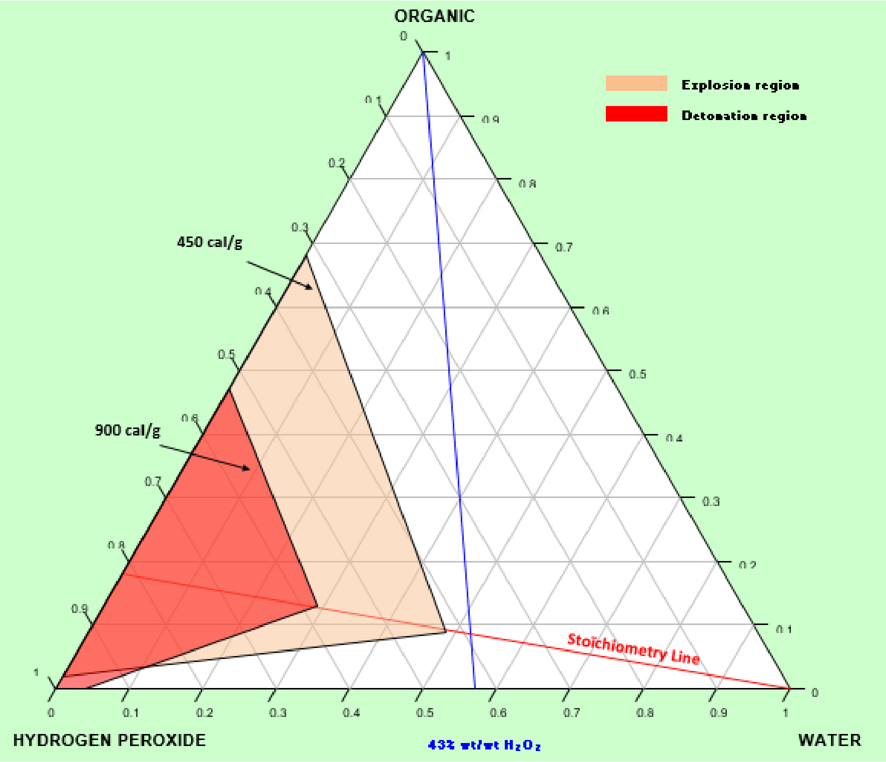
Reaction Runaway Hazard

- **Classical approach: Gygax/Stoessel**
  - Loss of cooling scenario
  - Runaway of desired reaction by accumulation of unreacted reagents
  - Triggers the secondary reaction
  - Stoessel: process criticality classes
- **In presence of Hydrogen Peroxide**
  - Side reaction: $H_2O_2 \Rightarrow H_2O + ½ O_2$
  - Catalyzed by alkalis, metals, salts, etc…
  - Any HP accumulation scenario can trigger the side reaction & overpressure
  - Obviously a gassy reaction:
    => Two-phase venting likely...



Condensed-Phase Explosion Hazard

- **Ternary diagram presentation (% mass)**
  - Generic diagram for an organic miscible in HP solutions
  - Illustrate decomposition energy and trials with high initiation energy (falhammer, detonation tube…)
  - Decomposition Energy limits:
    - Deflagration > 450 cal/g
    - Detonation > 900 cal/g
  - Zone boundaries depend on the chemical
  - Some special cases eg methanol: slowly transforms into performic acid
  - Maximum concentration to avoid explosive mixtures: ~35%.



adapted from Merrifield, HSE, 1988

Let’s see what happens in real life

- **Statistics on Solvay’s internal Lessons Learned Bulletins**
  - Process Safety Bulletins issued monthly to raise awareness
  - “Making the headlines” involves subjectivity
  - However HP is involved in 15 out of the 206 bulletins
- **Selected events taken from these Lessons Learned Bulletins**
  - Vast majority occurred at HP users sites
  - HP users represent >95% of Solvay’s workforce

3. Accidents
Gas-Phase Explosions

Event #1 - Manufacturing facility, France, 2015

- **Unit description**
  - Complex vent header system collecting vents from 23 different equipments
  - Off-gases are sent either to a scrubber, or to an oxidizer

- **The process carried out in one of the reactors that day**
  - Heating applied to vaporize traces of dichloromethane
  - Feeding HP 35% over 10 hours
  - Adding KOH solution to decompose the excess HP

- **Sequence of events**
  - The oxidizer was in maintenance during the first two steps: off-gases sent to the scrubber

Event #1 - Manufacturing facility, France, 2015

- **The accident**
  - Explosion in the vent pipe from the oxidizer to a glass seal pot
  - Shrapnels were sent dozens of meters away
  - One temporary hearing loss, no damages to the environment
- **The causes**
  - Dichloromethane condensed in the vent pipe low points
  - Dichloromethane is not classified “flammable liquid”, but vapors are flammable!
  - Oxygen from HP decomposition generated a flammable gas mixture in the vent header
  - The mixture was ignited at the oxidizer

Event #2 - Research facility, Belgium, 2017

- **The research field**
  - Hydrocarbon oxidation with O_2 and H_2O_2
  - Reactor: 0.25 liter, MAWP 200 bar, located in a bunker
  - Temperature 90°C, different pressures, DoE on compositions (~250 trials)
- **The process for each trial**
  - Loading 75 g hydrocarbon, solvent and catalyst in the reactor
  - Pressurize to 30 bar with nitrogen
  - Start agitation and heat to 90°C
  - Co-injection of O_2 and H_2O_2 in quantities according to test plan
- **Safety assessment**
  - Process temperature is above the mixture's flash point
  - Keep O_2 below the Limiting Oxygen Concentration = 7% vol.

Event #2 - Research facility, Belgium, 2017

- **The accident**
  - Poor yields observed when $O_2/(O_2+N_2) < 7\%$
  - O_2 quantities were increased gradually
  - Explosion occurred during test where $[O_2] = 52\%$
  - Flexible pipe shattered (detonation)
  - One hearing injury, no damage to the environment.
- **The causes**
  - Constraint to keep O_2 concentration below the LOC was misunderstood
  - Ignition source during trial at highest $[O_2]$
  - SOP not followed: operator in the bunker

Event #3 - Manufacturing facility, France, 2022

- **The process**
  - Processing a natural raw material
  - Solubilized in a flammable solvent
  - Addition of hydrogen peroxide 35%
  - Addition of caustic soda
  - “Cooking” step

- **Sequence of events**
  - Various recipes of this process operated since decades without accidents
  - Development of a new recipe at laboratory and pilot scale
  - Transfer of the new recipe at the Plant: explosion during the first batch!

Event #3 - Manufacturing facility, France, 2022

- **The accident**
  - Process carried out exactly as intended
  - Explosion in the reactor and fire
  - Rupture of glass seal pot on the vent line
  - No injuries and no damages to the environment
- **The causes**
  - O_2 generation by side reaction known to experts
    - Not quantified
    - Not communicated to Plant & Hazop teams
  - The new recipe implied 20 times more HP
  - At lab and pilot scale, the O_2 was displaced by N_2 sweep
  - There was no N_2 sweep at this Plant

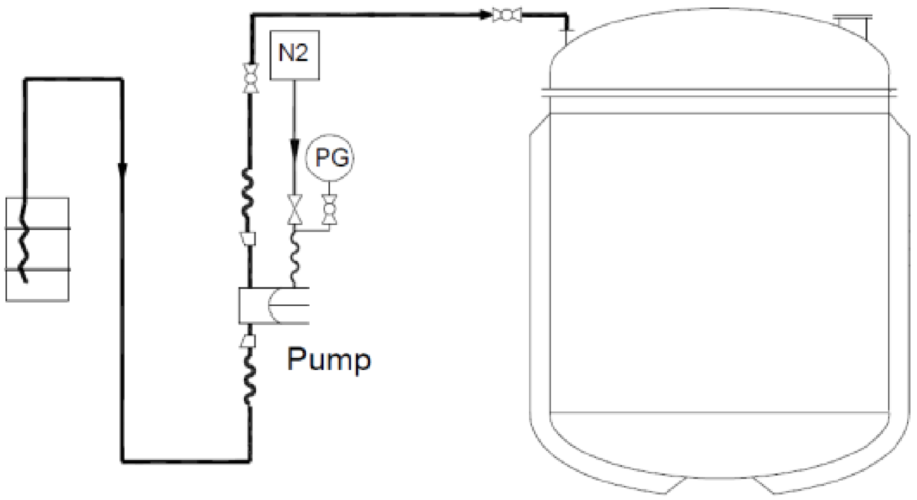
4. Accidents
Thermal Runaway

Event #4 - Manufacturing facility, USA - 2023

- **Process description**
  - HP 30% is fed to a reactor from drums
  - Pump & pipe previously used to load ethanol
- **The accident**
  - The partial HP drum heated-up and bulged
  - The drum tilted over and burst
  - Nobody was injured and the spill was contained
- **The cause**
  - Contamination of HP initiated its decomposition
  - Either dirty suction cane, or liquid backflow
- **Some basic rules not respected**
  - Suction cane not rinsed thoroughly with water
  - Drum’s breathing vent replaced by standard cap

Event #5 - Manufacturing facility, China - 2022

- **Process description**
  - HP 35% is fed to a reactor from drums
  - Use of a PTFE-coated diaphragm pump
  - After feeding HP, the pump & pipe are rinsed by pumping an organic solvent to the reactor

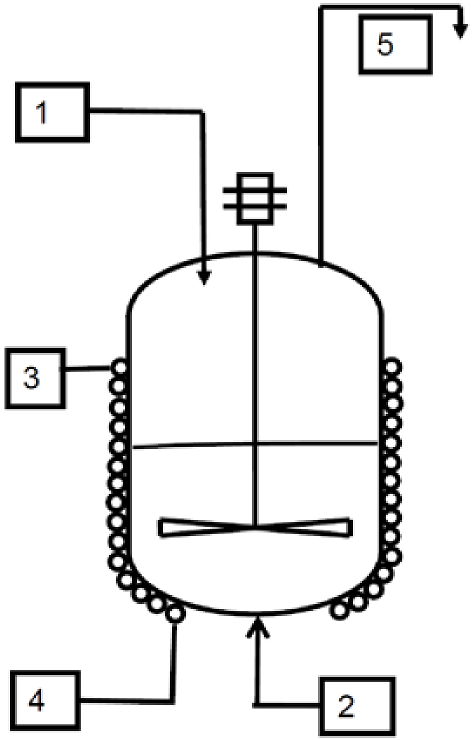


Event #5 - Manufacturing facility, China - 2022

- **The accident**
  - Transfer of 20 kg HP to the reactor
  - Pump & pipe are rinsed with solvent
  - 10 minutes after flushing, the pump burst
  - Fragments send few meters away
  - Nobody was injured and the spill was contained
- **The causes**
  - Damaged PTFE membrane put HP in contact with rust: decomposition to O_2 and H_2O
  - Lack of venting provision on piping & pump
- **Several basics not respected**
  - Pump & pipe not dedicated to HP / Not rinsed
  - Coatings on incompatible materials to be avoided

Event #6 - Manufacturing facility, Germany - 2018

- **Process description**
  - Semi-batch process
  - Raw materials are loaded in the reactor and cooled to 20°C - 25°C
  - Catalyst (CO_2) is bubbled through the mixture for 30 min
  - HP 35% is metered to the reactor over 5 hours, with cooling to maintain 60°C



- **The day before**
  - Replacement of the CO_2 flowmeter

Event #6 - Manufacturing facility, Germany - 2018

- **The accident**
  - When metering the HP35%, the normal initial exotherm was not observed
  - Temperature was raised with heating coils
  - … Runaway
  - 30% of the reactor mass vented via the Safety Valve and discharged to the roof
- **The causes**
  - Flowmeter units mismatch =>lack of catalyst
  - Heating initiated the side reaction: H_2O_2 (liq) $\rightarrow$ H_2O (liq) + ½ O_2 (gas)
  - The hazard of HP accumulation was known, but the SOP was not detailed enough

5. Accident
Condensed-phase explosion

Event #7 - Manufacturing facility, China, 2015

- **The process**
  - Continuous reaction of an organic with HP 70%
  - Performed in a cascade of stirred reactors under atmospheric pressure
  - Shut down sequence:
    - Flush the HP feed line with water into the reactors in normal conditions
    - Then, drain the reactors content into the holding tank
- **Sequence of events**
  - A planned shutdown turned into an emergency shutdown by steam outage
  - Reactors containing organics were drained to the holding tank
  - The following shift identified that the HP feed line was not flushed
  - A Low level interlock on the 1st reactor was bypassed to flush the HP line to the reactor with drain line open to the holding tank

Event #7 - Manufacturing facility, China, 2015

- **The accident**
  - Condensed-phase detonation in the drain pipe, fortunately located in a trench
  - Shrapnels found dozens of meter away
  - No injuries and no damages to the environment
- **The causes**
  - HP 70% displaced during flushing contacted organic product in the (heated) drain pipe
  - Mixtures of organics with HP > 40% can become explosive
  - Scenario identified in Hazop, however:
    - The SOP was not sufficiently detailed
    - Poor Bypass management

6. Lessons learned

Root cause by PSM element

- **For these 7 events, the main root causes relates to:**

- **Process Safety Information**
  - Relevant information was not available (4 event) or misunderstood (1 event)

    => Do not rely only on SDS's content & Involve multidisciplinary groups
- **Operating Procedures**
  - Not detailed enough (2 events) or not respected (1 event)

    => Barriers to major scenarios in SOP should be clearly defined & understood
- **Process Hazard Analysis**
  - Internal method limitation (1 event) and Layer of protection rating (1 event)

    => Method was updated

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