2025 Calendar

A year of process safety incident case studies

Forget not those who were needlessly killed and injured in the process safety incidents described herein.

Important notice:

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This calendar of process safety incident case studies was prepared by Peter Davern, Department of Chemical Sciences, University of Limerick, Ireland. All case study descriptions were drafted by referring to or extracting content directly from the following sources.

January – Ciba-Geigy Limited, Grimsby (UK):

- Rantell, M., *Historical runaway reaction case study (January 1992)*, Loss Prevention Bulletin, 273, June 2000
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February – Packaging Corporation of America Paper Mill, Louisiana (USA):

- U.S. Chemical Safety and Hazard Investigation Board, *Non-Condensable Gas System Explosion at PCA DeRidder Paper Mill*, Report Number: 2017-03-I-LA, April 2018 <https://www.csb.gov/packaging-corporation-of-america-hot-work-explosion-/>
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March – Intercontinental Terminals Company, LLC, Texas (USA):

• U.S. Chemical Safety and Hazard Investigation Board, *Storage Tank Fire at Intercontinental Terminals Company, LLC (ITC) Terminal*, No. 2019-01-I-TX, July 2023 <https://www.csb.gov/intercontinental-terminals-company-itc-tank-fire/>

April – Corden Pharma Limited, Cork (Ireland):

- Gakhar, S.J., Rowe, S.M., Boylan, M., Conneely, P., *Runaway chemical reaction at Corden Pharmachem, Cork*, Loss Prevention Bulletin, 237, June 2014
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May – Kuraray America Inc., Texas (USA):

- U.S. Chemical Safety and Hazard Investigation Board, *Ethylene Release and Fire at Kuraray America, Inc. EVAL Plant*, No. 2018-03-I-TX, December 2022 <https://www.csb.gov/kuraray-pasadena-release-and-fire/>
- U.S. Chemical Safety and Hazard Investigation Board (2022), *Animation of 2018 Ethylene Release and Fire at Kuraray in Pasadena, Texas*, [video online], available: <https://www.youtube.com/watch?v=0DA--nMkWeA>

June – Shell Nederland Chemie, Moerdijk (The Netherlands):

• Dutch Safety Board, *Explosions MSPO2 Shell Moerdijk*, July 2015 https://onderzoeksraad.nl/wp-content/uploads/2023/11/823457063632interactief_shell_moerdijk_en.pdf

July – ICMESA, Meda, near Seveso (Italy):

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- Hailwood, M., *Seveso – 40 years on*, Loss Prevention Bulletin, 251, October 2016
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- Marshall, V.C., *The Seveso Disaster: An appraisal of its causes and circumstances*, Loss Prevention Bulletin, 104, April 1992
- United States Environmental Protection Agency, *Learn about Dioxin* <https://www.epa.gov/dioxin/learn-about-dioxin>

August – Exxon Mobil (Esso) Refinery, Rotterdam (The Netherlands):

- Dutch Safety Board, *Brand bij Esso 21 augustus 2017 (translated, Dutch to English: "Fire at Esso 21 August 2017")*, July 2019; translated, Dutch to English using DeepL Translate [\(https://www.deepl.com/en/translator\)](https://www.deepl.com/en/translator)
- IChemE, *Major Process Safety Incident vs Root Cause Map*, Rev. 11, 21 July 2023, [https://www.icheme.org/media/20722/icheme-lessons-learned-database-rev-11.pdf,](https://www.icheme.org/media/20722/icheme-lessons-learned-database-rev-11.pdf) which links to: Lessons Learned Database, *Xylene Column Reboiler Tube Rupture and Major Fire*, [https://www.icheme.org/media/18789/rotterdam-incident-summary-21](https://www.icheme.org/media/18789/rotterdam-incident-summary-21-aug-17.pdf) [aug-17.pdf](https://www.icheme.org/media/18789/rotterdam-incident-summary-21-aug-17.pdf)

September – Esso Longford Gas Plant, Victoria (Australia):

- Atherton, J., Gil, F., *Incidents That Define Process Safety*, John Wiley & Sons, Inc., New Jersey, 2008, pp. 167–174
- Government of Victoria, *The Esso Longford Gas Plant Incident, Report of the Longford Royal Commission*, 1999, <https://vgls.sdp.sirsidynix.net.au/client/search/asset/1266205>
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- Weiss, B., *Lessons from Longford – 20 years on*, Loss Prevention Bulletin, 262, August 2018
- *Preventing Disaster: Learning from Longford – An interactive training workshop with Professor Andrew Hopkins*, Futuremedia Training Resources, Sydney, 2007

October – BASF, Ludwigshafen (Germany):

- ARIA BARPI No. 48716 https://www.aria.developpement-durable.gouv.fr/accident/48716_en/?lang=en
- BASF: Site Brochure Ludwigshafen entitled *Ludwigshafen Site – Strong in the Verbund*, downloaded from:
- <https://www.basf.com/global/en/who-we-are/organization/locations/europe/german-sites/ludwigshafen/the-site>
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November – Total Refinery, Antwerp (Belgium):

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December – Buncefield Oil Storage and Transfer Depot, Hertfordshire (UK):

- Buncefield Major Incident Investigation Board, *The Buncefield Investigation – Third progress report* [http://news.bbc.co.uk/2/shared/bsp/hi/pdfs/09_05_06_buncefield_report.pdf](https://eur03.safelinks.protection.outlook.com/?url=http%3A%2F%2Fnews.bbc.co.uk%2F2%2Fshared%2Fbsp%2Fhi%2Fpdfs%2F09_05_06_buncefield_report.pdf&data=05%7C02%7CPeter.Davern%40ul.ie%7Cd44e4f1f0c4f46807bf508dcb091a6de%7C0084b9243ab4411692519939f695e54c%7C0%7C0%7C638579386812049459%7CUnknown%7CTWFpbGZsb3d8eyJWIjoiMC4wLjAwMDAiLCJQIjoiV2luMzIiLCJBTiI6Ik1haWwiLCJXVCI6Mn0%3D%7C0%7C%7C%7C&sdata=ccMaKKqhxyuJ7TxWrPdJhTJ%2B5o%2Bn0t1AdJkFokEu%2FlM%3D&reserved=0)
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JANUARY – CIBA-GEIGY LIMITED, GRIMSBY (UK)

Figure 1: The reactor floor of Building B62, pre-incident. Image source: Loss Prevention Bulletin

Figure 2: The reactor floor of Building B62, post-incident. Image source: Loss Prevention Bulletin

Figure 3: Graphical summary of the thermal risks for the synthesis reaction; note – the axes are not to scale. Image source: Loss Prevention Bulletin (adapted)

Incident type: Synthesis reaction thermal runaway (near miss)

Day, date: Saturday, 04 January 1992

Location: Grimsby, Lincolnshire, UK

Industrial sector: Chemical intermediates and bulk pharmaceuticals manufacturing

Substance(s) involved:

Dichloronitrobenzene, aniline, sodium carbonate

Number killed: 0 **Number injured:** 0

Organisation: Ciba-Geigy Limited

Description:

This near miss incident occurred during the synthesis of a batch of chloronitrophenylamine in a jacketed, continuously-stirred, tank reactor located in Building B62 of the (then) Ciba-Geigy Limited plant at Grimsby, UK. The reactor's jacket was supplied with pressurised water/steam for heating and water for cooling. Ordinarily, the process began when sodium carbonate was charged to the reactor followed by aniline from bulk storage. Molten dichloronitrobenzene (DCNB) at 70 to 80°C was then charged from bulk storage while stirring. The reaction mass was then heated to ca. 160°C and held there until the reaction was complete. Specifically, production operators were instructed to increase the reactor temperature to ca. 150°C and then shut off the jacket and allow the mildly exothermic synthesis reaction to heat the reaction mixture further. However, for the incident batch, the reactor temperature continued to rise slowly until it reached the temperature gauge's upper limit of 170 $^{\circ}$ C. Even though the reactor was under atmospheric pressure, aniline (boiling point 184 $^{\circ}$ C) began to distil by itself to a receiver, indicating the temperature had risen further. The distillation rate increased further and became very vigorous. The pressurised water/steam in the jacket was now at a higher pressure than normal, but an attempt to manually drain the jacket had to be aborted because the flow of steam was "deafening". Thereafter, the reaction mass rose up the reactor's glass riser vent pipe (6-inch diameter), prompting an evacuation of the building. The rising reaction mass ruptured two bursting discs and emitted from the roof vent as black particulate matter and fumes. The emission lasted 10 to 20 minutes. Inside Building B62, the joints on the glass riser vent pipe failed, releasing black, tar-like material that contaminated the area (Figure 1 versus Figure 2). Nobody was harmed during the incident.

Contributing factors:

• The procedure to heat to ca. 150°C and then shut off the jacket meant the system was thereafter operating adiabatically with no cooling provided by the jacket. The mildly exothermic synthesis reaction had an adiabatic temperature rise (ΔT_{ad}) of 25°C. Thus, without cooling, the maximum temperature of the synthesis reaction (MTSR) was 175°C (Figure 3), and the final temperature of synthesis reaction depended solely on the jacket shut-off temperature and any variation in the reaction mixture. This MTSR was only 65°C below the onset temperature of a highly exothermic decomposition reaction with $\Delta T_{ad} = 938^{\circ}\text{C}$ (Figure 3); but decomposition reactions can be active at temperatures below their onset temperature. The jacket shut-off temperature varied among production operators; on this occasion it was 154°C, the upper end of the range of normal control. Thus, from this elevated starting temperature, the synthesis reaction's subsequent ΔT_{ad} was likely enough to trigger the decomposition reaction, which slowly caused the temperature to rise until a thermal runaway scenario developed. \bullet The hazardous decomposition was known prior to the incident. The main basis of safety relied on the boiling (and distillation) of aniline to remove the energy released during the decomposition reaction. But there was only enough aniline to remove 20% of this energy. \bullet Two years earlier, the batch size was increased by 10% in the same reactor; furthermore, the incident batch had a ca. 3% overcharge of one raw material. Cumulatively, both actions caused a small increase in the final temperature of a synthesis reaction already operating in a thermally sensitive region. ● Starting from a given MTSR, the time for a decomposition reaction to reach thermal runaway (TMR_{ad}, Figure 3) is a measure of the <u>likelihood</u> of triggering the decomposition. If TMR_{ad} is >24hours, the likelihood of triggering the decomposition reaction is deemed low. Here, the TMR_{ad} was calculated to be <8 hours for the MTSR of 175°C, meaning a high likelihood of triggering the decomposition reaction. • The ΔT_{ad} of a decomposition reaction reflects the severity of a runaway reaction. If ΔT_{ad} is >400°C (as was the case in this incident), the severity is deemed catastrophic. **Some lessons learned:**

For a process, the importance of (i) having full thermal safety data and re-visiting the data prior to any process changes, (ii) having a valid, reliable and robust basis of safety for thermal risks.

JANUARY ²⁰²⁵

FEBRUARY – PACKAGING CORPORATION OF AMERICA PAPER MILL, LOUISIANA (USA)

Foul Condensate Tank

Figure 1: Simplified drawing of the foul condensate tank. The top of the weir (dotted line) sits approximately 6 meters from the base of the tank. As the liquid inside the tank rises above 6 meters, liquid is "skimmed" into the weir and sent to a turpentine recovery system. Image source: U.S. CSB (adapted)

Figure 2: A computer-generated image depicting the hot work being performed on the pipework above the foul condensate tank. Image Source: U.S. CSB (adapted)

Incident type: Non-condensable gas system explosion

Time, day, date: approximately 11:05 a.m., Wednesday, 08 February 2017 **Location:** DeRidder, Louisiana, USA **Industrial sector:** Pulp and paper **Substance(s) involved:** Non-condensable gas

Number killed: 3 **Number injured:** 7

Organisation: Packaging Corporation of America

Description:

The Packaging Corporation of America's (PCA) DeRidder, Louisiana pulp and paper mill produces containerboard used in products such as boxes and cardboard displays. The containerboard is made from pulp produced at the mill. During the process of creating pulp, vapours are generated. These vapours, which contain turpentine, water, and other non-condensable gases (including sulfur compounds), are collected and separated. To separate the vapours, they first enter a turpentine stripping column. There, most of the turpentine is removed and sent to a condenser. The remaining vapours condense to a liquid (known as "foul condensate") that contains mostly water but also residual amounts of sulfur compounds and turpentine. The foul condensate is sent from the turpentine stripping column to an approximately 380,000 liter-capacity atmospheric storage tank, used to store the liquid at, or close to, ambient pressure. This foul condensate tank is primarily used to regulate the flow of liquid between the turpentine stripping column upstream and a downstream unit that removes the remaining sulfur components from the water. At the time of the incident, the mill was undergoing its annual shutdown. One of the shutdown tasks was to repair water piping located above, and connected to, the foul condensate tank; the piping had shifted and cracked months earlier. The repair required welding to be done on the piping. To prepare for this hot work, valves were closed leading into and out of the tank and the piping was separated from the tank, while 3 meters of liquid remained inside. The liquid was left within the tank, partly because there were no plans to work directly on the tank. The company also assumed that the tank contained mostly water, was sealed off from the atmosphere, and thus did not pose a safety risk. Residual turpentine, normally present in foul condensate, collected on top of the liquid in the tank due to its density. The tank was equipped with a weir to skim turpentine off the surface of the foul condensate liquid once the liquid had reached a height of 6 meters (Figure 1). The skimmed turpentine was sent to a turpentine recovery system. But in the months before the incident, the turpentine was not removed due to confusion as to who at the mill was responsible for operating the tank. Due to this confusion, a valve designed to direct skimmed turpentine to the mill's turpentine recovery system remained closed for months. Thus, leading up to the incident, there was more flammable turpentine in the tank than anyone expected. In addition, there are normally vapours in the tank's headspace. Although these vapours can become flammable, they are supposed to be kept at a concentration too rich to burn. However, due to the non-routine conditions experienced during the annual shutdown, the tank's contents likely cooled, creating low pressure within the tank. This most likely triggered a relief valve on the tank's roof to draw in more air to avoid damaging the tank from the vacuum created by low pressure, thus creating an explosive atmosphere. Ahead of the hot work, in addition to the process isolations, a mill employee used a gas detector to check for a flammable atmosphere in and around the water piping, and found none. As a result, the company issued a hot work permit for the welding work. But even though a flammable atmosphere was not present outside the tank, a flammable atmosphere existed inside the tank. Without knowing that the tank posed a serious hazard, three contract workers began welding on the water piping located above it (Figure 2). Though it was not possible to confirm, it is likely that sparks or molten slag from the hot work landed on or near the tank, heating up the tank wall or otherwise igniting the contents inside. Alternatively, it may be that the hot work was complete but as the tools were lowered, a welding torch fell and created an electric arc on the tank or its vent piping. Regardless, the hot work activities likely ignited the flammable vapours and liquid turpentine inside the tank resulting in a large explosion. The tank separated from its base and launched up and over a six-storey structure, landing approximately 114 meters away. Three people were killed and seven were injured; all were contract employees working near the tank.

Contributing factors:

● PCA did not voluntarily apply its process safety management (PSM) system, which was required by OSHA elsewhere in the mill, to the non-condensable gas system that included the foul condensate tank. Thus, no process hazard analysis was ever done, which could have identified the scenario of a flammable atmosphere arising inside the foul condensate tank and thereafter could have defined safeguards to address this scenario, especially when planning hot work. ● It was unclear who was responsible for the foul condensate tank. Over time, this led to few workers knowing much about the tank, its contents, and its explosion potential. ● The tank's design did not adequately address the scenario of a flammable atmosphere developing within it. It could have been (i) fitted with a lowpressure alarm to alert that the vacuum relief valve may open and thus allow air in, (ii) fitted with an oxygen analyser to alert workers and trigger a nitrogen inertion step, or (iii) vacuum-rated to avoid the need for a vacuum relief valve entirely.

Some lessons learned:

The merits of (i) applying a PSM system site-wide, (ii) clearly defining roles and responsibilities, and (iii) designing tanks to adequately address foreseeable hazardous scenarios.

FEBRUARY ²⁰²⁵

MARCH – INTERCONTINENTAL TERMINALS COMPANY, LLC, TEXAS (USA)

Figure 1: Plume of black smoke rising from ITC's tank farm fire.

Figure 2: Schematic of ITC's Truck Butane Injection System. Image source: U.S. CSB (adapted)

Incident type: Storage tank release and fire

Time, day, date: approximately 10:00 a.m., Sunday, 17 March 2019

Location: Deer Park, Texas, USA

Industrial sector: Petrochemicals storage

Substance(s) involved: Butane-enriched naphtha

Number killed: 0 **Number injured:** 0

Organisation: Intercontinental Terminals Company, LLC

Description:

Image source: U.S. CSB

At the time of the incident Intercontinental Terminals Company, LLC (ITC) was a terminal and storage facility operator that had been servicing the petrochemical industry for over five decades. ITC's facility at Deer Park, Texas was situated on an inlet in the Houston Ship Channel. It housed 242 fixed storage tanks whose capacities ranged from 8,000 to 160,000 barrels (1,272,000 to 25,440,000) liters). The terminal was separated into various tank farms, each containing multiple tanks within a common secondary containment area intended to capture the entire contents of the largest tank in the containment area in the event of a leak or spill. The tanks stored petrochemical liquids and gases, fuel oil, bunker oil, and distillates for various oil and chemical companies that leased the tanks from ITC. One such tank, Tank 80-8, was an 80,000-barrel aboveground atmospheric storage tank that held flammable butane-enriched naphtha; naphtha is a complex mixture of petroleum hydrocarbons in the C4–C10 range. It was equipped with a Truck Butane Injection System to boost the naphtha's octane level by allowing butane to be unloaded into the tank from a truck under nitrogen pressure, via pipework connected to the tank's external naphtha circulation loop (Figure 2). On the evening before the incident, two butane truck deliveries were unloaded into Tank 80-8 over an approximately three-hour period. The tank's circulation pump was started before unloading began. It remained on during the unloading process, and stayed running through the night and into the following morning to mix the roughly 70,300 barrels of butane-enriched naphtha within the tank. At around 9:30 a.m. on the following morning, the pump's mechanical seal failed and butaneenriched naphtha began releasing to the atmosphere. Between 9:30 and 10:00 a.m., Tank 80-8's volume decreased by more than 177 barrels as the butane-enriched naphtha continued to release from the failed (though still running) pump. At 10:00:46 a.m., the released product ignited. After the fire had started, ITC was unable to isolate or stop the release. As a result, the fire burned, intensified, and spread to the other 14 tanks located in the same containment area. The fire burned for three days before being extinguished. The fire caused substantial property damage at the terminal, including the destruction of fifteen 80,000-barrel aboveground atmospheric storage tanks and their contents. The incident also significantly impacted the environment. A containment wall around the tanks breached and released an estimated 470,000–523,000 barrels of hydrocarbon and petrochemical products, firefighting aqueous film-forming foam, and contaminated water into the nearby waterways, sediments, and habitats, ultimately reaching the Houston Ship Channel and surrounding waters. An approximately 11-kilometer stretch of the Houston Ship Channel was closed, as were several waterfront parks in the vicinity, due to the contamination. The incident did not result in any injuries or fatalities; however, the local community experienced serious disruptions, including several shelter-in-place orders because of benzene-related air quality concerns. The estimated property damage from the incident exceeded \$150 million.

Contributing factors:

● ITC did not have a formal mechanical integrity procedure in place to cover Tank 80-8 and its associated equipment, including the circulation pump. The investigation concluded that the pump continued circulating butane-enriched naphtha despite the failure of its outboard bearing. The bearing failure likely led to significant pump vibration, which loosened the gland nuts that secured the mechanical seal in place, causing the seal to separate and allow the release of the flammable mixture. ● Tank 80-8 was not equipped with a flammable gas detection system to alert personnel of a hazardous atmosphere resulting from loss of containment from the tank or its associated equipment. A 2014 hazard review recommended the addition of flammable gas detection systems near Tank 80-8; however, this was never done. ● Tank 80-8 and the other storage tanks nearby were not equipped with remotely operated emergency isolation valves designed to mitigate process releases remotely from a safe location. ● Although mostly designed to the relevant standards when built, parts of the tank farm design (e.g., tank spacing, subdivisions, engineering controls for pumps, and drainage systems) made it hard for emergency responders to slow or prevent the initial fire's spread, thus the fire spread to other tanks in the tank farm. The resulting accumulation of hydrocarbon and petrochemical products, firefighting foam, and contaminated water in the secondary containment area ultimately contributed to a breach of the containment wall and a release of materials to the local waterways. • Tank 80-8 was not covered under OSHA's Process Safety Management Standard or the U.S. EPA's Risk Management Program Rule. Thus, no process safety management program was applied to it.

Some lessons learned:

For companies that handle large volumes of flammable or highly hazardous substances, the importance of (i) having multiple preventive and mitigation safeguards in place such that a single safeguard failure does not result in a catastrophic event, (ii) having strategically located gas detection systems, (iii) having appropriate remote isolation capability, (iv) applying tank farm design criteria that facilitate (rather than hinder) emergency response efforts, and (v) applying a process safety management program even when not a regulatory requirement.

MARCH ²⁰²⁵

APRIL – CORDEN PHARMA LIMITED, CORK (IRELAND)

Figure 1: The north side of production Building No. 2 (PB2), post-incident, with the upper roller-shutter door (circled) missing. Image source: Loss Prevention Bulletin

Figure 2: (a) The upper roller-shutter door found on the ground outside PB2 near the drum storage area, **(b)** the cover of the solids charge chute found on the ground outside PB2, and **(c)** part of the solids charge chute butterfly valve found on the 3rd floor. Image source: Loss Prevention Bulletin

Description:

Corden Pharma Limited, a toll chemical manufacturer, produced 2-cyano-3-methylpyridine (CMP) via the two-stage process (Reaction Scheme 1) in Production Building No. 2 (PB2). The first stage was carried out in reactor K6003 and involved reacting picoline-N-oxide (PNO) with diethylcarbamoyl chloride (DECC) in acetone. The resultant intermediate, an acyloxypyridinium salt, was then reacted with an aqueous solution of sodium cyanide (NaCN) in another reactor to yield the final product CMP. K6003 was a glass-lined, carbon steel, jacketed and agitated reaction vessel with an operating volume of 2.5 m³ and a design pressure of 6 barg. The reactor had a bolted manway on top (sealed with gasket material), a bursting disc and relief valve in series (both set at 6 barg), a parallel relief line to a dump tank (containing a bursting disc set at 7 barg), and a solids charge chute. The key process steps in the preparation of the acyloxypyridinium salt in K6003 were to (i) charge molten PNO (566 kg) under vacuum to the previously nitrogen-inerted and acetone-rinsed vessel, (ii) charge acetone (1,020 L) and cool the contents to 15 to 25°C, and (iii) charge DECC (702 kg) from drums under vacuum over 45 to 60 minutes while keeping the reactor temperature below 40°C by applying jacket cooling. For the incident batch, the acetone solvent charge was omitted prior to adding the DECC to the reactor. A runaway chemical reaction ensued, which generated enough energy to deform the vessel's dished end, distort significantly the manway flange, and completely 'blow out' the manway gasket leaving a ca. 10 mm gap through which reactor contents were ejected. The cover of the solids charge chute was torn off the top of the chute (this required four bolts to be sheared), and was found on the ground outside PB2, Figure 2(b). The solids charge chute butterfly valve was also sheared off, projected out of the chute and was found on the 3rd floor of PB2, Figure 2(c). Loss of containment of the reactor contents occurred at both $2nd$ and $3rd$ floor levels in PB2. Two operators present at the time were severely injured, one of whom subsequently died from his injuries. Substantial damage also occurred to the building; see, for example, Figures 1 and 2(a). Company management decided to close the facility some months after the incident. **Contributing factors:**

• The acetone charge provided a 'heat sink' for the exothermic reaction of PNO and DECC. The absence of this heat sink (due to omitting the acetone charge) most likely resulted in a runaway exothermic decomposition of the thermally unstable acyloxypyridinium salt and thereafter of the PNO. ● The potential for violent decomposition of the acyloxypyridinium salt and subsequent decomposition of PNO was known from calorimetry data available prior to the incident, and the importance of the acetone charge was commonly understood. But the complete omission of the acetone charge was missed as a process deviation during the related process HAZOP. Thus, apart from requiring a 'double sign-off' in the batch procedure to confirm acetone had been charged, there was no warning that this was a safety critical step. ● It is understood from the surviving operator that the omission of acetone was realised and the increase in batch temperature was also noticed on the DCS. However, the operators' response was to go to the reactor and isolate it from the overheads equipment (mainly glass), to protect them. However, this action, instead of evacuating or even staying in the control room, cost one of the operators his life. The company should have understood, based on calorimetric data, that charging DECC without acetone present would likely be unrecoverable once done, and so without a suitable protection system, the mandatory response should have been to evacuate. ● The reactor's emergency relief systems were unable to deal with the pressure generated during the runaway scenario. That said, the solids charge chute unintentionally provided additional emergency relief capacity, which may have prevented the catastrophic failure of the reactor. **Some lessons learned:**

● Properly conduct HAZOPs of hazardous processes. ● Process control and protection measures should be commensurate with the risk of the related loss of control scenarios.

Incident type: Runaway chemical reaction

Time, day, date: ca. 1:25 a.m., Monday, 28 April 2008

Location: Cork, Ireland

Industrial sector: Toll chemical manufacturing

Substance(s) involved: Picoline-N-oxide and diethylcarbamoyl chloride

Number killed: 1 **Number injured:** 1

Organisation: Corden Pharma Limited

APRIL ²⁰²⁵

MAY – KURARAY AMERICA, INC., TEXAS (USA)

Figure 1: A computer-generated image depicting the horizontal release of ethylene vapour from EVAL Reactor 2's emergency pressure relief system. Image source: U.S. CSB

Figure 2: The welding machine on the back of the pickup truck, post-incident. Image source: U.S. CSB

Incident type: Ethylene release and fire

Time, day, date: 10:28 a.m., Saturday, 19 May 2018 **Location:** Pasadena, Texas, USA **Industrial sector:** Polymer production **Substance(s) involved:** Ethylene **Number killed:** 0 **Number injured:** 23 **Organisation:** Kuraray America, Inc.

Description:

Kuraray America, Inc. manufactures EVAL, a copolymer made from ethylene and vinyl alcohol, which is used in food packaging and storage containers. Leading up to the incident, operations personnel were taking steps to bring one of four reactors (namely, EVAL Reactor 2) back online following a weeks-long, scheduled, plant-wide shutdown for maintenance and equipment upgrades. All four reactors looked similar, but EVAL Reactor 2 had a lower maximum design pressure (740 psi) than the other three (1,150 psi). EVAL Reactor 2 already contained liquid methanol and ethylene vapour when operators began incrementally raising the reactor's pressure by adding more ethylene vapour. This was done to reach the target pressure for reaction start-up, while also checking for leaks. Meanwhile, chilled liquid (from a newly commissioned refrigeration system) was unnecessarily circulating through the reactor's heat exchanger. After 11:20 p.m. on the night before the incident, the combination of reactor pressure and the low temperature from the chilled liquid caused ethylene vapour to condense in the reactor. This caused the reactor temperature to decrease. Around 7 a.m. on the morning of the incident, a supervisor noticed the reactor's low temperature and instructed operators to stop circulating the chilled liquid through the heat exchanger and to periodically added steam to the reactor's water-filled jacket. As the reactor temperature increased with each injection of steam to the jacket, some liquid ethylene inside the reactor vapourised, thus raising the reactor pressure. By about 8:45 a.m., the reactor's pressure had reached the operating target of nearly 600 psi but was still increasing. Around 9 a.m., the pressure reached 640 psi and the high-pressure alarm went off. A board operator responded by periodically opening a pressure control valve (PCV) to send some of the vapour inside the reactor to a flare. However, being concerned about exceeding the flare's environmental emissions limits, he did not fully open the PCV. He was also focused on other start-up activities and did not realise the valve was not open enough to bring the pressure under control. The pressure inside the reactor continued to rise. Despite this, shortly after 10 a.m., operators initiated the next step in the start-up. At that time, a new board operator took over and noticed the reactor pressure was over 700 psi. But he did not recall the reactor's maximum design pressure of 740 psi and thought it could withstand a higher pressure, like the other three reactors. Similar to the first board operator, the new operator only partially opened the PCV, not realising how dangerously close the pressure was to the reactor's limit. But the control valve was not open enough to relieve the reactor's pressure. At 10:28 a.m., the reactor's emergency pressure relief system activated. High-pressure ethylene vapour discharged from the reactor into the atmosphere. It was released horizontally toward an area where contractors were working (Figure 1), rather than vertically to a safe location. Soon after, a welding machine operating on a pickup truck nearby (Figure 2) likely ignited the vapour. A large fire erupted. 23 people were injured, many as they urgently tried to evacuate. The ethylene-fuelled fire stopped after about three minutes when the spring-loaded emergency relief valve closed as the reactor's pressure normalised. In total, around 1,000 kg of ethylene was ejected to the atmosphere.

Contributing factors:

● Kuraray's long-standing design of its emergency pressure-relief systems deviated from industry standards by discharging flammable ethylene vapour through horizontally-aimed piping into the air, near workers. • The decision to design EVAL Reactor 2 with a lower maximum design pressure than the other three EVAL reactors. • Operators were not provided with specific warnings about EVAL Reactor 2's lower maximum design pressure, nor were they trained on alarm setpoints or how to respond to high-pressure scenarios. ● A high-high-pressure safety interlock, designed to automatically relieve excess ethylene pressure via the PCV to the flare, had been disabled earlier in the start-up when troubleshooting an issue with a misaligned valve. ● An emergency open valve (EOV), designed to relieve excess ethylene pressure to the flare, was not used because written supervisor approval was needed to physically unlock and thereafter activate its control room switch. ● A 2015 Kuraray process hazard analysis team recommended upgrading the EOV to allow it to be taken over by the control system and fully opened at pressures above the high-high-pressure alarm; however, this recommendation's implementation had been pushed out to 2019. ● The presence of non-essential workers, i.e., contractors, during start-up and upset conditions. ● The control system "flooded" the operators with about 160 alarms per hour on the morning of the incident. ● Kuraray had a long chain of weakly implemented management system elements within its overall process safety management (PSM) system but failed to identify these weaknesses during periodic self-audits.

Some lessons learned:

The importance of (i) abiding by recognized and generally accepted good engineering practices (RAGAGEP), and (ii) fully implementing the management system elements of a PSM system.

MAY ²⁰²⁵

JUNE – SHELL NEDERLAND CHEMIE, MOERDIJK (THE NETHERLANDS)

Figure 1: MSPO2's Unit 4800 during the circulation and heat-up steps; EB = ethylbenzene. Image source: Dutch Safety Board (adapted)

Incident type: Runaway chemical reaction

Time, day, date: 10:48 p.m., Tuesday, 03 June 2014

Location: Moerdijk, the Netherlands

Industrial sector: Base chemicals production

Substance(s) involved:

Ethylbenzene, G-22/2 (a hydrogenation catalyst) and nitrogen

Number killed: 0 **Number injured:** 2

Organisation: Shell Nederland Chemie

Description:

On 25 May 2014, Shell Nederland Chemie in Moerdijk (Shell Moerdijk) shut down one of its *styrene monomer and propylene oxide* plants (namely, MSPO2) for a short, scheduled maintenance period (a 'pitstop') to replace the catalyst pellets (a copper-chromium based hydrogenation catalyst) in two trickle-bed reactors within Unit 4800 (Figure 1). These trickle-bed reactors were catalystfilled columns designed to allow a gas-liquid mixture to gravity-flow down through them and wet the catalyst pellets; by contrast, liquid-full reactors fill the entire column from the bottom up and fully immerse the catalyst pellets. In normal operation, Unit 4800 was used to make methylphenylcarbinol (MPC) from methylphenyl ketone (MPK) via catalytic hydrogenation. Before restarting normal operation after such a pitstop, it was first necessary to (i) wet the catalyst pellets in both reactors by circulating a mixture of ethylbenzene (EB, liquid) and nitrogen through Unit 4800, (ii) heat the unit to 130°C via heat exchanger E4804 on the EB circulation line, and (iii) chemically reduce the 'fresh' catalyst using hydrogen, thus readying it for the MPC process. During these steps, liquids and gases leaving the reactors were separated in separator vessels, and the liquids recirculated to the reactors via central pump P4803. The gases from the 1st separator went to Reactor 2 and those from the 2nd separator were burned in a flare stack. On the day of the incident, a Panel Operator began the process start-up by circulating EB through both reactors. By 21:00, the Panel Operator deemed the flows through both reactors had stabilised (Figure 2) and, after consulting the Production Team Leader, began the complex task of manually raising the circulating EB's temperature to 130°C at a heating rate of 50°C/h. From that point on, the EB level in both separators and the EB flow towards Reactor 2 fluctuated considerably and were unstable. Around 21:30, the Panel Operator felt the temperature was rising too slowly and increased the heating rate above the agreed 50°C/h. At around 22:16, a high level in Reactor 2's separator triggered an automatic shut-off of the gas flow to the flare stack. Soon after, the level returned to a safe value, but the Panel Operator did not re-open the gas flow. Thus, Unit 4800 could no longer discharge gases, and the system's pressure gradually rose to 7.8 bar by 22:45. At 22:48:03, the Panel Operator first noticed alarm signals indicating the gas discharge system was at 12 bar and the temperature of both reactors was above set alarm limits. At 22:48:26, Reactor 2 exploded. About 20 seconds later, the 1st separator also exploded. The MSPO2 plant was engulfed in flames and two contractors working close by were injured. **Contributing factors:**

● In 1977, Shell successfully chemically reduced a sample of 'fresh' catalyst CU-1808T in a lab-scale liquid-full reactor by circulating EB and hydrogen, thus confirming EB's 'inertness' under the processing conditions for catalyst reduction. Based on this, CU-1808T was used in MSPO1's plant-scale liquid-full reactor from its start-up in 1979 onwards; note, MSPO2's trickle-bed reactor started up in 2000. During 1999-2002, a catalyst supplier successfully chemically reduced another catalyst (G-22/2) in a lab-scale trickle-bed reactor using nitrogen and hydrogen, but without EB. From this, G-22/2 was approved as a 'like-for-like' replacement for CU-1808T, and thereafter, according to Shell, G-22/2 was chemically reduced in its other *styrene monomer and propylene oxide* plants five times prior to the incident. But the chromium(VI) content of the G-22/2 batch used in MSPO2 during this incident was 4.5-5% w/w instead of 0.2-0.3% w/w for the G-22/2 and CU-1808T batches used historically. This elevated chromium(VI) inadvertently facilitated the exothermic oxidation of EB at ca. 90°C (during the heat-up to 130°C). But the fluctuating/unstable EB flow through Reactor 2 (plus the much-reduced nitrogen flow due to the back pressure from the gas flow shut-off) meant that catalyst pellets were inadequately wetted and unable to dissipate the heat generated. Thus, adiabatic hot spots developed within the catalyst bed and heated to 180°C, whereupon the catalyst's copper oxide content facilitated another exothermic oxidation of EB that developed into a runaway chemical reaction within the (by now) sealed system. • Fluctuating/unstable flows (and the associated array of alarm signals) were known to occur during start-ups after such pitstops; they were not deemed a concern due to EB's perceived 'inertness'. • This was the Panel Operator and the Production Team Leader's first time to start up Unit 4800 after such a pitstop. • When work instructions were drawn up, some key process parameters defined during Unit 4800's design (e.g., the minimum EB and nitrogen flowrates needed to ensure wetting of the catalyst pellets; having a 30 °C/h heating rate) were either not always incorporated or failed to be incorporated in the correct manner. Thus, important information was lost between Unit 4800's design and its ultimate (day-to-day) management. **Some lessons learned:**

The importance of (i) management of change, specifically here in terms of changes to raw materials and process parameters, and (ii) having suitably experienced personnel in place during start-ups.

JUNE ²⁰²⁵

JULY – ICMESA, MEDA, NEAR SEVESO (ITALY)

Description:

The ICMESA chemical plant in Meda near Seveso, Italy (25 km north of Milan) was founded in 1946. At the time of the incident, ICMESA produced 2,4,5-trichlorophenol (TCP), which was an intermediate in the production of hexachlorophene (a disinfectant used in medicinal soaps) and 2,4,5-T (a herbicide). TCP was produced via a two-stage process (Figure 3, top) in a 10,000 L batch reactor (Figure 1). The reactor was heated by an external steam coil which used the exhaust steam (at 12 barg and ca. 190°C) from a turbine located elsewhere on the plant. Stage 1 of the process saw 1,2,4,5-tetrachlorobenzene (TCB) undergo nucleophilic aromatic substitution with sodium hydroxide (NaOH) in ethylene glycol as solvent, and xylene was also included to subsequently remove (via azeotropic distillation) the water formed. As such, the reaction mixture was heated to ca. 150° C until no more water was formed. The temperature was slowly increased to ca. 170° C to distil off the xylene and water, and ethylene glycol was then distilled under vacuum. Thereafter, the reaction mixture was quenched by adding cold water in large excess. Stage 2 then involved acidifying the resulting aqueous solution of sodium 2,4,5-trichlorophenolate with HCl to liberate the desired 2,4,5-trichlorophenol (TCP). At the time of the incident, Italian law required plants like ICMESA to shut down over weekends. Thus, around 5 a.m. on the Saturday morning of the incident, a TCP batch was duly shut down. At that point, the reaction was complete but not all the ethylene glycol had been removed by vacuum distillation. No batch of TCP had ever before been shut down at this point in the process. That said, the reaction mixture was now at 158° C, well below the temperature (230 $^{\circ}$ C) at which an exothermic decomposition reaction (postulated to be the decomposition of the sodium salt of ethylene glycol, formed when NaOH reacts with ethylene glycol) was believed possible. Following shutdown, the reactor idled unattended at 158°C, no longer stirred or heated or actively cooled. At 12:37 p.m., the reactor's bursting disc ruptured, discharging over about 20 minutes ca. 6 tonnes of hazardous substances, including ca. 1 kg of 2,3,7,8-tetrachlorodibenzodioxin (informally known as 'dioxin'), a highly toxic and persistent organic pollutant (POP) formed at high temperatures (Figure 3, bottom). The discharge contaminated about 17 km² of land (Figure 2). About 4 km² was made uninhabitable and 736 residents in Zone A were evacuated; Zones B and R were not evacuated. About 250 people developed the skin disease chloracne and about 450 suffered NaOH burns. Over several years, buildings were demolished or decontaminated, and as far as possible the land returned to agricultural and horticultural use. Though no one was killed, 'Seveso' is one of the best known of all chemical plant incidents. It led the then European Community to enact the Seveso Directive in 1982 (since amended in 1996 and 2012), which requires all companies that handle greater than defined 'threshold' quantities of hazardous substances to demonstrate their capability to do so safely. **Contributing factors:**

● It is now known that the exothermic decomposition reaction can occur at 180°C, albeit slowly. ICMESA's turbine was on reduced load because other processes on site were also shutting down for the weekend. Thus, the steam's temperature rose to ca. 300°C. In the idle TCP reactor (then ca. 33% full), the bulk liquid temperature could not get much above 158°C because of its heat capacity, thus the reactor's wall below the liquid level cooled from 300°C on the outside to 158°C on the inside. However, above the liquid level, the wall was at 300°C throughout. When the steam was isolated and, 15 minutes later, the stirrer was switched off, heat passed via radiation from the hot walls above the liquid and heated the top few centimetres of the liquid to 180–190°C. This triggered the slow exothermic decomposition reaction, which progressed adiabatically over the next seven hours or so, at which point runaway occurred. ● The TCP reactor was not equipped with an emergency relief receiver vessel, perhaps because a runaway was not envisaged given the prevailing processing conditions. However, three runaway reactions in similar plants had occurred prior to the 'Seveso' incident. For example, a runaway and pressure rupture occurred during the production of TCP from TCB and NaOH in ethylene glycol in a batch reactor at Coalite and Chemical Products, Bolsover, UK in 1968. The escaping gases exploded, killing one employee and injuring seven others. In that case, the reactor was heated by hot oil at 300°C and the manual heating control system had failed. **Some lessons learned:**

The importance of thoroughly interrogating chemical processes for thermal and reactive hazards, and thereafter (i) defining the maximum temperature for heating media to avoid runaway reactions, and (ii) designing pressure relief systems that exhaust to containment systems, thus preventing hazardous releases to the work and/or external environment.

JULY ²⁰²⁵

AUGUST – EXXON MOBIL (ESSO) REFINERY, ROTTERDAM (THE NETHERLANDS)

Figure 1: A simplified view of the Powerformer plant showing only the units and detail relevant to this incident. Figure 2: A diagram of a **Organisation:** Exxon Mobil (Esso) *(Figures 1 and 2 have been created by adapting images sourced from the Dutch Safety Board)*

Powerformer plant furnace.

Incident type: Fire **Time, day, date:** Shortly before 9:22 p.m., Tuesday, 21 August 2017 **Location:** Rotterdam, the **Netherlands Industrial sector:** Oil and gas **Substance(s) involved:** Toluene and xylenes **Number killed:** 0 **Number injured:** 0

Description:

The Powerformer (catalytic reforming) plant is part of the Exxon Mobil (Esso) Refinery in Rotterdam, the Netherlands. The plant converts naphtha (a petroleum fraction) into a blend of various hydrocarbons used to produce, among other things, petrol and aromatic hydrocarbons like benzene, toluene and xylenes. It consists of a naphtha pre-treatment section, a reaction section (the 'Powerformer') where the naphtha is converted, and a feed fractionation section where the output from the Powerformer is separated into product streams (Figure 1; naphtha pre-treatment section not shown). Of relevance to this incident, the plant has two distillation towers: T1001 produces benzene/toluene concentrate and its bottom stream feeds T1002 which produces a xylenes concentrate. The plant also has six furnaces (Figure 2). Of note are furnaces F561, F562 and F563 which heat the product stream in the Powerformer, and F1001 which, being configured to circulation pumps P1003A and P1003B (duty-standby arrangement), serves as the reboiler for T1002. During normal operation, the hot exhaust gases from the six furnaces are routed to a waste heat boiler (WHB), but they can be re-routed to a flue stack, if needed. Around 7:35 p.m. on the day of the incident, one of the Powerformer plant's two compressors tripped and a field operator was unable to restart it. However, the Powerformer continued to run using its second compressor, albeit at a somewhat reduced level. Almost at the same time, a problem arose with the WHB, which triggered the exhaust gases from the six furnaces to automatically re-route to the flue stack. Since the operators could find nothing wrong with the WHB's status to warrant this automatic re-routing of the exhaust gases, they closed (on a second attempt) the route to the flue stack, thus restoring the flow of exhaust gases to the WHB. Shortly after, however, the pressure within the WHB rose such that a 'high pressure cut-out' activated, causing all six furnaces to trip and a "flood" of alarms to activate. Once appraised of events, the shift team leader and the refinery shift manager instructed the operators to initiate promptly an approved procedure to 'hot restart' the furnaces – if the furnaces cooled down too much, condensation would form in the reactors and damage the catalyst. The approved 'hot restart' procedure required various protection systems on the furnaces to be bypassed. However, to prevent multiple trips of the furnaces due to fluctuating gas pressures during the restart, the operators manually bypassed the protection systems instead of using the five-minute automatic bypass feature approved for such restarts; the operators deemed the five-minute window to be too short, and they were used to bypassing manually during restarts. Between 7:45 p.m. and 8:15 p.m., all the furnaces and the WHB had started up, although many alarms still sounded in the busy control room. At 8:15 p.m., an operator acknowledged a 'thermal overload' alarm for circulation pump P1003B. At 8:25 p.m., P1003B stopped but no one noticed this (likely because the small number of staff were still so busy stabilising the now restarted plant). P1003B's failure duly triggered F1001 to trip on 'low-flow cut-out'. However, no one linked F1001's trip to P1003B's failure, nor could anyone find an obvious reason why F1001 had tripped. Therefore, F1001 was restarted at 8:31 p.m. At 9:22 p.m., flames were seen coming from F1001 and the flue stack. A large fire took hold, fuelled by ca. 110 tonnes of mostly toluene and xylenes that drained from T1002 into F1001. There were no casualties and no on-site contamination, but F1001 had to be demolished and rebuilt, and the Powerformer was shut down for about a year. **Contributing factors:**

● It only emerged days after the incident that the compressor had tripped due to a short circuit in its power cable, and that the same short circuit had also led to a voltage dip in the WHB's switching station; this caused the WHB's fan to stop and, ultimately, the WHB to fail. It is possible that the field operator mistook the wind-down of the WHB's fan (as it stopped) as evidence the fan was still running. ● Thereafter, the failed WHB was unable to deal with the restored flow of furnace exhaust gases, thus triggering the 'high pressure cut-out' which tripped all six furnaces. Only at that point did it become clear that the WHB's fan had stopped, but not why it had stopped. Despite this, instructions were still given to 'hot restart' the furnaces – the WHB was not essential for the Powerformer plant to operate because exhaust gases could anyway be routed to the flue stack while troubleshooting the WHB's fan issue. ● In deciding to 'hot restart' the furnaces, not enough consideration was given to how difficult it would be for the small number of staff to (i) oversee and control all the actions needed, and (ii) respond to the ca. 250 alarms that activated every 10 minutes during the 'hot restart' of the six furnaces. ● The tripping of all six furnaces decreased the heat supply to other parts of the Powerformer plant. Among other things, this caused T1001's distillation performance to deteriorate such that the proportion of heavy fractions increased. Downstream, this ultimately put more pressure on P1003B, which initially overheated and then failed, thus triggering F1001 to trip on 'low-flow cut-out'. The operator (busy warming up and stabilising the plant) likely did not deem P1003B's failure a high enough priority since P1003A was on automatic standby. However, unknown to the operator, P1003A was under maintenance and thus not available. Therefore, not linking F1001's trip to P1003B's failure, the operators restarted F1001's burners, but with its lowflow protection still manually bypassed. F1001's fluid coil duly overheated without a steady flow of product fluid through it, and then ruptured. Product fluid leaked from the ruptured coil (called a 'split tube') and ignited inside F1001. Thereafter, most of the contents of T1002 drained into F1001 through the ruptured coil and fuelled the fire.

Some lessons learned:

The importance of (i) prioritising safety over production, not least, during complex start-up activities, (ii) not bypassing safety-critical trips regardless of inconvenience, except for cases of maintenance/testing, (iii) having enough staff on plant to support routine and start-up activities, and (iv) communicating effectively the maintenance status of safety-critical plant equipment.

AUGUST ²⁰²⁵

SEPTEMBER – ESSO LONGFORD GAS PLANT, VICTORIA (AUSTRALIA)

Figure: An overview of Gas Plant 1's lean oil circulation system (created by adapting an image sourced from Loss Prevention Bulletin)

Incident type: Explosion and fire **Time, day, date:** 12:25 p.m., Friday, 25 September 1998 **Location:** Longford, Victoria, Australia **Industrial sector:** Oil and gas **Substance(s) involved:** Hydrocarbons **Number killed:** 2 **Number injured:** 8 **Organisation:** Esso

Description:

In Gas Plant 1 (Figure) of the Esso Longford site, raw natural gas (from offshore, ca. -25° C, partly pre-treated but still containing some hydrocarbon condensate) was continuously fed under pressure to parallel absorbers (A and B) where it encountered a descending flow of 'lean' oil (kerosene-like, ca. -20C). The lean oil extracted ethane/propane/butane from the natural gas to become 'rich' oil, leaving the resultant methane-enriched natural gas to exit the top of the absorbers as natural gas for sale. The rich oil exiting the absorbers flashed off lighter materials at lower pressure in a Rich Oil Flash Tank (ROFT), was heated via heat exchangers (containing returning lean oil in the circulation loop) and flowed to the Rich Oil Deethaniser (ROD) fractionation column. Here, ethane exited at the top, and the heavier fractions that collected at the bottom were recirculated by

reboiler GP905. The ROD bottoms were passed via heat exchanger GP922 to the Rich Oil Fractionator (ROF) where final fractionation of the rich oil occurred, thus regenerating the lean oil in the ROF bottoms. Some of this regenerated lean oil flowed through a fired reboiler (GP501) and returned to the bottom of the ROF, while the remainder was saturated with methane from the top of the ROD and passed through a series of heat exchangers and an Oil Saturator Tank (to flash off any unabsorbed methane) before returning to the absorbers in a closed loop. The evening/night before the incident, the operators had difficulty controlling Absorber B to handle a greater than normal amount of hydrocarbon condensate in the raw natural gas feed. As a result, and unknown to them, the level of condensate in Absorber B likely rose such that it escaped from the absorber in the rich oil stream. This caused the stream to flash more than usual in the ROFT, and thus to drop in temperature. This temperature drop should not have been a major problem provided the lean oil circulation continued. However, for reason(s) unclear, sometime before 7 a.m. on the morning of the incident, liquid likely began carrying over into the ROD overheads. This caused the Oil Saturator Tank's level to rise sufficiently such that the lean oil booster pumps (GP1201 A/B/C) tripped at 8:19 a.m. The resulting low level in the Oil Saturator Tank caused pumps GP1202 A/B to stop at 8:30 a.m., thus the lean oil circulation stopped also. Within five minutes of this, the rich oil stream exiting Absorber B was pure condensate, which flashed at lower and lower temperatures. By 9:30 a.m., the ROD system had cooled to an estimated -48°C in the absence of heating from lean oil, causing ice to form on GP905 and GP922. GP922's cold flanges distorted and then leaked. After unsuccessful attempts to stop the leak and restore the lean oil flow, Gas Plant 1 was shut down around 11:14 a.m. Troubleshooting continued thereafter. GP1201 and GP1204 were restarted at 12:17 p.m. in the hope that lean oil (now < 285°C) might warm GP922 enough to seal its leak. In doing so, some warm lean oil entered GP905, creating a thermal shock that caused brittle fracture of the reboiler at 12:25 p.m. The reboiler failed catastrophically, releasing 20 to 25 tonnes of hydrocarbon vapour which travelled ca. 170 m towards some fired heaters, where it ignited causing an explosion and fire. Two employees were killed, eight others were injured. Due to the high degree of pipeline interconnections on the site, it took two days to isolate all the hydrocarbon streams and finally extinguish the fire. Natural gas supplies to domestic and industrial users were halted for between 9 to 19 days. **Contributing factors:**

● Exxon, the parent company, had written into its HAZOP guidelines the need to be particularly aware of the hazards of cold temperature. However, no HAZOP had been conducted on Gas Plant 1. Therefore, the opportunity was missed to address the known hazard of cold temperature embrittlement of carbon steel equipment (like GP905) arising from a failure of the lean oil circulation. Furthermore, the prevailing regulatory regime did not require Esso to draft a "Safety Case" for the site; drafting a Safety Case would have compelled the company to conduct a HAZOP. Also, an Exxon audit of the site a few months before the incident failed to identify that Gas Plant 1 had not undergone a HAZOP. ● About a month before the incident, the lean oil circulation system shut down unexpectedly and a heat exchanger became so cold that ice formed on its exterior and leaks occurred. The lean oil system was restarted before the heat exchanger became brittle cold. But this process upset was not investigated further because it was not logged on Esso's incident reporting system; Esso used this system as its primary safety metric, but only to track lost-time-injury rates. ● Esso relocated its fulltime engineers from the Longford site to the head office in Melbourne in 1992, thus adversely impacting the level of real-time on-plant technical and troubleshooting support available to operators. ● Operators were routinely exposed to 'alarm flooding' in the control room, which likely distracted them when attempting to troubleshoot the shutdown of the lean oil circulation system. **Some lessons learned:**

At high hazard facilities, the importance of (i) always conducting a HAZOP of new or modified processes, (ii) maintaining a state of chronic unease, especially after 'successful' facility safety audits, (iii) maintaining a level of on-plant technical support commensurate with the hazardous nature of the process(es) being undertaken, (iv) having realistic expectations of operators' capacity to manage safety critical alarms, and thus designing processes accordingly, and (v) defining and routinely tracking meaningful leading/lagging indicators of process safety performance.

SEPTEMBER ²⁰²⁵

OCTOBER – BASF, LUDWIGSHAFEN (GERMANY)

Figure 1: The pall of smoke rising from the fires at the North Harbour of BASF's Ludwigshafen site. Image source: C&E News

Description:

Figure 2: Hours after the initial explosion at Ludwigshafen, the fire at the harbour was still burning. Image source: BBC News

Figure 3: A section of the pipeline trench, postincident. Image source: Fränkische Nachrichten

Figure 4: Memorial at the yard of the BASF North Fire Station. Image source: BASF

Incident type: Fire and explosions

Time, day, date: about 11:30 a.m., Monday, 17 October 2016 **Location:** North Harbour, Ludwigshafen, Germany

Industrial sector: Petrochemicals production

Substance(s) involved:

Ethylene, propylene, a butylene product mix (raffinate), pyrolysis gasoline, and ethylhexanol

Number killed: 6 **Number injured:** 28

Organisation: BASF

BASF's headquarters site at Ludwigshafen is the world's largest integrated chemical complex. It comprises ca. 2,000 buildings, has ca. 39,000 employees, produces an array of chemicals, and covers an area of ca. 10 km² on the bank of the Rhine in the southwest of Germany. A few days before the incident, a specialised pipeline construction company began scheduled assembly works on a depressurised and secured propylene pipeline, which was one of several pipelines that ran in an open trench between the Ludwigshafen complex and its harbour on the Rhine. The aim of the assembly works was to exchange several parts of the pipeline as a preventive maintenance measure. On the day of the incident, a fire started at approximately 11:30 a.m. near the assembly works. Forces of the BASF fire department, emergency service and environmental protection arrived a few minutes later at the incident area and immediately started emergency operations. During the initiation of emergency operations, an explosion at an ethylene pipeline occurred. A 30-metre piece of the pipeline broke loose from its anchorage and was projected towards the harbour where BASF firefighters had established their position, killing four of the firefighters and severely injuring seven. The explosion led to subsequent fires at various points along the pipeline trench, damaging further product and supply pipelines. A tanker anchored in the harbour also caught fire. Additional emergency forces immediately began rescue measures as well as extinguishing and cooling measures. The fire brigade performed controlled burning of the leaking products in accordance with the firefighting concept for compressed gases. The pipelines involved in the initial fire included those used for ethylene, propylene, a butylene product mix (raffinate), pyrolysis gasoline and ethylhexanol. By 9.30 p.m. on the day of the incident, the emergency services had extinguished the fire. Measurements on-site and in the vicinity revealed the absence of abnormally high concentrations of hazardous substances in the air, except in the immediate environment of the incident zone. In addition to the four BASF firefighters who were killed, one sailor from a tanker anchored at the harbour was also killed. A further 22 people suffered slight injuries. A fifth BASF firefighter succumbed to his injuries 11 months later.

Contributing factors:

On the Friday before the incident, a hand-held auger was used to perforate a 3-mm hole in the propylene pipeline due for repair, and measurements taken using a portable gas detector confirmed the absence of a hydrocarbon-related explosive atmosphere. Several cut-outs were then made in the propylene pipeline and a number of pipe pieces were removed from a U-shaped expansion loop and also from the pipeline on one side of the expansion loop. On the following Monday (the day of the incident), the work was proceeding on the other side of the expansion loop when an angle grinder inadvertently cut into a 'live' pipeline next to the propylene pipeline under repair; this live pipeline contained a butylene mixture under 4 bar pressure. The butylene mixture escaped via the cut left in the line and ignited due to the sparks produced by the angle grinder. The flames heated the adjacent ethylene pipeline (88 bar, approximately 250 mm diameter) until it burst by fast decomposition, causing a massive explosion with a 200 m fireball and a mass fire.

Some lessons learned:

The importance of maintaining a heightened awareness of nearby hazards when undertaking non-routine and/or intrusive work on isolated plant within a live plant environment; and thereafter implementing measures to control adequately these hazards – for example, of relevance to this incident, the systematic prior labelling of pipework cut-out locations.

OCTOBER ²⁰²⁵

NOVEMBER – TOTAL REFINERY, ANTWERP (BELGIUM)

Figure 1: A leak-sealing clamp (blue) fitted to a flange. Image not related to this incident. Image source:<https://leaksealing.com/>

Figure 5: The valve, post-incident, showing the absence of the bonnet. Image source: Team / Total

Contributing factors:

Figure 2: A *bonnet / valve body* flange with a steam leak. Image not related to this incident. Image source:<https://leaksealing.com/>

Description:

Figure 3: (a) A ring type joint (RTJ) flange, and (b) cut-through detail showing the metal ring in place. Image not related to this incident. Image source: https://www.micronsteel.com

Figure 4: Example of a 1½-inch stud bolt with two heavy hexagonal nuts (ASTM A193 Grade B7). Image not related to this incident. Image source: <https://www.fabory.com/>

Incident type: A steam BLEVE

Day, date: Tuesday, 19 November 2013

Location: Antwerp, Belgium **Industrial sector:** Oil and gas

Substance(s) involved: Steam **Number killed:** 2 **Number injured:** 0 **Organisation:** Total

Figure 6: The separated bonnet, post-incident. Image source: Team / Total

Figure 7: A bolt showing light thread galling after the seized nut was removed. Image not related to this incident. Image source[: https://boltdepot.com](https://boltdepot.com/)

Figure 8: Stud bolts, postincident, showing evidence of SCC and "normal" fracture. Image source: Team / Total

In March 2011 at the Total refinery in Antwerp, a leak-sealing clamp (Figure 1) was installed around the leaking 16 inch *bonnet / valve body* flange (Figure 2) of a motorised gate valve located on the circulating water circuit of a steam generation system; the steam system was part of a continuous catalytic reforming (CCR) platformer plant. The *bonnet*

/ valve body flange had a ring type joint (RTJ) flange assembly**(1)**. At the time of its installation, the clamp created a leak-free joint. After the clamp's installation, the section was out of service for five months between April and November 2011, and again in 2012 for about six weeks. When out of service, the valve remained under pressure, albeit at low temperatures, i.e., a dead end. After the section returned to service at the end of 2011, the joint leaked several times and re-injections of sealant into the clamp were performed. On the day of the incident in November 2013, two TEAM Industrial Services technicians were performing a reinjection of sealant into the leak-sealing clamp. At the time, the motorised valve was in the open position and boiler water (70 barg and 290C) was flowing through it. Almost immediately after starting their work, all 20 of the 1½-inch stud blots**(2)** securing the bonnet suddenly failed, causing the bonnet-motor assembly to separate forcefully from the valve body (Figures 5 and 6) . The sudden release of boiler water resulted in a boiling liquid expanding vapour explosion (BLEVE). Both technicians were killed.

• The diameter of the RTJ groove in the bonnet flange was 5 mm too small; the acceptable ASME tolerance is 0.13 mm. Therefore, the standard RTJ metal ring did not fit properly into the groove. This meant that extra torque had been applied to several stud bolts to create the desired (leak-tight) parallel flange connection. Thus, these over-torqued stud bolts had stresses close to the minimum yield (ca. 600 N/mm² at 300 °C). The over-torquing may also have caused micro-cracks to develop due to 'galling'**(3)**. ● The joint leaked on one occasion during its period out of service and a re-injection of sealant was performed. Thereafter, with the valve still out of service (pressurised but cold), a minor leak re-occurred inside the flange-clamp assembly. This created a wet corrosive environment which caused several stud bolts to start corroding and also to become more susceptible to stress corrosion cracking, SCC⁽⁴⁾. Then, when the joint leaked several times following its return to service (at high temperature and pressure) at the end of 2011, the leaked boiler water inside the hot flange-clamp assembly evaporated, leaving behind a corrosive residue of caustic (sodium hydroxide, NaOH) on the already corroding stud bolts**(5)**. Thus, all the conditions needed for the rapid degradation of the stud bolts via SCC were now in place, namely: high stress, a corrosive medium (NaOH), a susceptible material, and a high enough temperature ($>70^{\circ}$ C). On the day of the incident, the additional stress from the re-injection process was enough to trigger the failure of the one or more of the (by now) severely degraded stud bolts. This caused stress on the weakened bolts nearby, prompting a chain reaction of overload and fracture of all 20 bolts (Figure 8) that culminated in the bonnet's separation from the valve body, and then the BLEVE.

Some lessons learned:

● Visual inspection is not conclusive regarding the condition of stud bolts. ● Stud bolts in good condition can (under the right circumstances) degrade rapidly due to SCC. • When risk assessing a re-injection process, pay added attention when the condition of the stud bolts and the stresses on them are unknown. • Pay particular attention to (i) recurring leaks on live boiler water systems because caustic residues may develop on the stud bolts if the leaked water evaporates within the flanged assembly, and (ii) the build-up of white solid deposits on bolts and/or flanges. ● Leak-sealing clamps are temporary repairs; replace them with permanent repairs at the first opportunity, e.g., a planned outage or turnaround. \bullet Injecting sealant into leak-sealing clamps can increase the tensile stress on stud bolts by 10 – 20%.

(1): A ring type joint (RTJ) flange is a machined metallic flange with a deep circular groove cut into its face (see Figure 3 for an example). The groove accommodates a metal ring which gets compressed into the flange when the connecting bolts are tightened. This compression results in a leak-proof, close-fitting seal on the pipe or connection. The RTJ flange was designed for the petroleum and petrochemical industries where higher pressures and temperatures are present.

(2): The stud bolts were made from heat-treated, chromium-molybdenum alloy steel, ASTM A193 Grade B7; see Figure 4 for an example.

(3): Thread galling occurs during installation of bolts when pressure and friction cause bolt threads to seize to the threads of a nut. Once an assembly has seized up from galling it is typically impossible to remove without cutting the bolt or splitting the nut (see Figure 7 for an illustration).

(4): Stress corrosion cracking (SCC) is a crack-inducing form of corrosion caused by the simultaneous influence of (high) tensile stresses and a corrosive medium. **(5)**: Caustic can arise in boiler water when residual sodium carbonate (Na₂CO₃, used to 'soften' boiler water) reacts with water: Na₂CO₃ + H₂O \rightarrow 2NaOH + CO₂.

NOVEMBER ²⁰²⁵

DECEMBER – BUNCEFIELD OIL STORAGE & TRANSFER DEPOT, HERTFORDSHIRE (UK)

Figure 1: Schematic of Tank 912 – the three level alarms (each shown with a red X) are included for illustrative purposes only. Image source: BMIIB (adapted)

Time, day, date: 6.01a.m., Sunday, 11 December 2005

Location: Hemel Hempstead, Hertfordshire, UK

Incident type: Explosion and fire

Industrial sector: Hydrocarbon fuel storage and distribution

Substance(s) involved: Unleaded petrol (gasoline)

Number killed: 0 **Number injured:** 43

Organisation: Hertfordshire Oil Storage Limited

Description:

At the time of the incident, the Buncefield oil storage and transfer depot was a tank farm facility that accommodated three operating sites authorised to store 194,000 tonnes in total of hydrocarbon fuels, and was the UK's fifth largest fuel distribution facility. The three operating sites were: Hertfordshire Oil Storage Ltd (HOSL), British Pipeline Agency Ltd (BPA), and BP Oil UK Ltd. Various grades of fuel were transported in batches to these operating sites via pipelines from three UK oil refineries, and were separated into dedicated tanks according to fuel type. The majority of fuel was then taken from the depot by road tankers. Jet aviation fuel left the BPA operating site via two pipelines for distribution to Heathrow and Gatwick airports. From 6.50 p.m. on the evening before the incident, HOSL's Tank 912 began receiving a batch of 8,400 m³ of unleaded petrol at a flow rate of 550 m³/h. At this time, Tank 912 contained 1,079 m³ of unleaded petrol and had ullage of 4,971 m³. At 3.05 a.m. on the day of the incident, Tank 912's level gauge 'flat-lined' at two-thirds full on the control room display even though the tank continued to fill. The three level alarms (namely, the 'user level', the 'high level' and the 'high-high level') could not operate because the tank reading was always below these alarm levels; the tank farm supervisors relied on these alarms to control filling processes. At about 5.35 a.m., the fuel in Tank 912 began to overflow through the vents on its roof. By about 6 a.m., more than 250 m³ of fuel had overflowed. A combination of the weather conditions, the flow rate of fuel, and the shape of Tank 912's roof and wall caused the overflowing fuel to cascade downwards and outwards from the tank such that a fuel-rich vapour rapidly formed and flowed off-site via the ground topography. The vapour cloud was noticed by members of the public off-site and by tanker drivers on-site waiting to fill their vehicles. They alerted employees on-site. The fire alarm button was pressed at 6.01 a.m., which sounded the alarm and started the firewater pump. A vapour cloud explosion occurred almost immediately, probably ignited by a spark caused by the firewater pump starting. The resulting devastation was enormous. There were no fatalities but over 40 people were injured; the harm to humans may have been more if the incident had not occurred early on a Sunday morning when the adjacent industrial area was relatively quiet. The ensuing fire, the largest seen in peacetime UK, engulfed over 20 fuel tanks on the HOSL and adjacent sites and burnt for several days. Fire crews attended from many parts of the country. Fuel and firefighting chemicals (including environmentally hazardous perfluorooctane sulfonate, PFOS) flowed from leaking bunds down drains and 'soakaways', both on- and off-site. The environmental, social and economic toll was considerable.

render the switch inoperable. Image source: HSE (UK)

Contributing factors:

• Tank 912's level display 'flat-lined' at two-thirds full because the tank's level gauge had stuck. It had stuck 14 times in the previous 3½ months; when it did, supervisors either managed to rectify the problem or called an external maintenance contractor to do so. That said, the definitive cause of the sticking had never been identified. ● Tank 912 was fitted with an independent high-level switch (IHLS), which was meant to shut down operations automatically if the tank was overfilled. The switch had been designed so that some of its functionality could be routinely tested. Those who installed and operated the switch did not fully understand how it worked, or the crucial role played by a padlock (see Figure 2). Therefore, the padlock was not fitted after the test. This meant the switch was left effectively inoperable and was therefore unable to prevent the tank from overfilling. ● There was only one control room display screen available to monitor a number of tanks, and on the night of the incident Tank 912's display was at or near the back of a stack of four other tank display 'windows'. ● The tank farm supervisors had limited visibility of and control over the flows of incoming fuel from the oil refineries. ● The increase in throughput at Buncefield over the years meant there was considerable pressure on ullage space, with batches diverted between tanks to prevent overfilling. ● There were few written procedures covering tank-filling processes, and those that existed were short on detail. ● In the context of secondary containment, the bunding had many flaws (at joints and at the walls where pipes penetrated them), which caused large volumes of fuel, firefighting water and foam to leak from the bunds. ● There was virtually no tertiary containment in place. The site's drainage systems were only designed for rainwater and minor spills/losses of product, which would flow to interceptors and the site's effluent treatment plant.

Some lessons learned:

● For a hazardous process, ensure the effectiveness and independence of the various layers of protection. In this incident, the three level alarms were not independent of the level gauge; thus, the alarms could not activate once the level gauge stuck at a level below the alarms' setpoints. • Fully understand the functionality of safety critical equipment. The IHLS needed a padlock to retain its test lever in the working (horizontal) position. But the switch supplier did not relay this critical point to the installer and maintenance contractor; also, HOSL did not act as an 'intelligent customer' and could not be assured of the service they were obtaining from their contractors. Ultimately, this lack of understanding meant the padlock was not fitted and the switch was inoperable. ● Ensure the reliability and adequacy of secondary containment (bunds) and, where appropriate, tertiary containment (drainage collection and treatment systems).

DECEMBER ²⁰²⁵

