1298510 August 2000

Source : CHEMICAL SAFETY AND HAZARDS INVESTIGATION BOARD, AUGUST 14, 2000, (http://www.chemsafety.gov).
Disclaimer: The Chemical Incident Reports Center (CIRC) is an information service provided by the U.S. Chemical Safety and Hazard Investigation Board (CSB). Users of this service should note that the contents of the CIRC are not intended to be a comprehensive listing of all incidents that have occurred; many incidents go unreported or are not entered into the database. Therefore, it is not appropriate to use the CIRC database to perfrom statistical analysis that extends conclusions beyond the content of the CIRC. Also, although the CSB never knowingly posts inaccurate information, the CSB is unable to independently verify all information that it receives from its various sources, much of which is based on initial reports. CIRC users should also note that the CSB receives more comprehensive reports about incidents that occur in the U.S.; comparisons made between U.S. incidents and those in other nations should take this fact into consideration.

Location : Honolulu, USA

Injured : 1 **Dead :** 0

Abstract

A plant was shut down due to an accidental mixing of two incompatible chemicals causing a release of approximately 20 pounds of chlorine gas.
The incident occurred when an operator accidentally pumped sodium hypochlorite, bleach, into a 200-gallon storage tank containing phosphoric acid. The operator was injured in the incident.
[plant shutdown, people, gas / vapour release, storage tanks, normal operations, injury]

Lessons

[None Reported]

1277230 June 2000

Source : CHEMICAL SAFETY AND HAZARD INVESTIGATION BOARD, JULY 3, 2000, (http://www.chemsafety.gov). (http://www.chemsafety.gov).

Location : Dover, USA

Injured : 4 **Dead :** 0

Abstract

Fumes were released when an operator inadvertently mixed two chemicals together forcing the evacuation of a printing company. Four people were affected by the release.
[gas / vapour release, people, accidental mixing, injury]

Lessons

[None Reported]

12363 23 March 2000

Source : CHEMICAL SAFETY AND HAZARD INVESTIGATION BOARD, 24 MARCH, 2000, (http://www.chemsafety.gov).
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Location : Lily, USA

Injured : 48 **Dead :** 0

Abstract

Sulphuric and hydrochloric acid were accidentally mixed resulting in two accidental releases of chlorine gas. The building was evacuated.
Forty eight people were treated for minor respiratory problems.
[sulphuric acid, gas / vapour release, evacuation, accidental mixing, mixer, injury]

Lessons

[None Reported]

1218106 February 2000

Source : CHEMICAL SAFETY AND HAZARD INVESTIGATION BOARD, FEBRUARY 7, 2000. (http://www.chemsafety.gov).
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Location : , USA

Injured : 0 **Dead :** 0

Abstract

A spill occurred at an electroplating company causing the evacuation of nearby residents.
The incident occurred when a malfunctioning water line or valve at the electroplating plant caused excess water at the small shop to mix with chemical residue used in the electroplating process.
[mechanical equipment failure, accidental mixing, normal operations, unknown chemicals]

Lessons

[None Reported]

132232000

Source : EUROPEAN CHEMICAL NEWS, 18 DECEMBER 2000 - 7 JANUARY 2001.
Location : Ludwigshafen, GERMANY

Injured : 0 **Dead :** 0

Abstract

A chemical spill occurred at a chemical plant. The incident occurred when a drum of isopropanol and methyl vinyl ketone burst injuring a worker and affecting several others including visitors at the site.
It is thought that a drum containing residue of caustic soda was accidentally filled with the mixture causing the drum to rupture.
[accidental mixing, drums]

Lessons

[None Reported]

1164819 August 1999

Source : YAHOO NEWS, 19 AUGUST, 1999, (http://www.yahoo.co.uk),; HAZARDOUS CARGO BULLETIN, NOVEMBER 1999.
Location : , UK

Injured : 2 **Dead :** 2

Abstract

Two factory workers were found dead on the ground floor of a paint-stripping factory after being overcome by fumes in a suspected chemical leak.
It is thought that they had mixed some chemicals, different to the normal process, causing a gas to be released, possibly methylene chloride which is a fast acting asphyxiant.
Fire crews were at the scene wearing protective clothing, but the first two ambulance attendants who had rushed in were unprotected. They attended hospital for a check up.
[fatality, asphyxiation, mixing, accidental mixing, gas / vapour release]

Lessons

[None Reported]

1105627 May 1999

Source : CHEMICAL WEEK, JUNE 9, 1999.
Location : Pasadena, Texas, USA

Injured : 1 **Dead :** 0

Abstract

An explosion occurred at a chemical plant critically injuring a worker who was cleaning a 10,000 gallon tank containing a ferric sulphate compound. The explosion was caused by water being mixed with residue inside the tank. The worker suffered second degree burns to the face, neck and hands. An investigation into the incident is being carried out.
[accidental mixing, injury]

Lessons

[None Reported]

11495September 1998

Source : CHEMICAL HAZARDS IN INDUSTRY, JUNE 1999.

Location : , UK

Injured : 2 **Dead :** 0

Abstract

An explosion occurred at a plant when nitric acid leaked from a valve as it was being transferred from one container to another, and mixed with cleaning fluid to create an explosion which blew workers of their feet. Workers from a nearby petroleum plant were evacuated due to the formation of a gas cloud.
The company were fined more than £25,000 (1999).
[accidental mixing, contamination, evacuation, gas / vapour release, material transfer]

Lessons

[None Reported]

11377September 1998

Source : THE CHEMICAL ENGINEER, APRIL 1999.

Location : , UK

Injured : 2 **Dead :** 0

Abstract

An explosion injured two workers and released a cloud of toxic gas. Nitric acid escaped from a leaking valve as it was being transferred. The leaking acid mixed with a cleaning fluid to create an explosion. The company was fined £24,000 (1998).
[accidental mixing, gas / vapour release, maintenance, injury]

Lessons

[None Reported]

868 02 July 1998

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

A cooling tower, on an ethylene plant, had been prepared for person-entry. A fitter noticed paint blistering near to the middle entry door.
The emergency services played water onto the tower externals until temperatures fell to 150 degrees C then the tower was repurged with nitrogen.
Prior to the incident, the tower had been purged with nitrogen, then steam purge to remove traces of hydrocarbons, and cooled. An air purge was then used to assist cooling, and the last (middle) of three entry doors removed. It was whilst removing this door that the blistering paint was noticed.
[pyrophoric carbon, iron sulphide, fire - consequence, autoignition]

Lessons

The tower had been shut down to investigate, and remove, blockages of coke and polymer. The coke is carried forward from upstream furnaces, and the polymer forms within the tower during normal operations. Before shutdown, several wash solutions, including xylene, were used to attempt to dissolve the polymer. None of these were successful in removing the blockage so a decision to open up the tower was taken.
Laboratory tests showed that washing with xylene produced fine, sooty carbon deposits that were self-heating in air at the temperatures in the tower. There could then self-ignite at 185 degrees C.
Also, traces of finely divided iron sulphide, also present in the xylene wash sampler, can be pyrophoric.
Either of these mechanisms could have let to glowing-hot sooty carbon, which then ignited the larger coke particles on the tower trays.
Manufacturing managers were recommended to review procedures for cleaning and opening (to air) equipment, containing material of a pyrophoric nature.
An outline procedure was developed, and referred to in the Report.
However, the procedure itself, was not included in the report received.

1188108 June 1998

Source : CHEMICAL HAZARDS IN INDUSTRY, SEPTEMBER 1999.
Location : , GERMANY

Injured : 0 **Dead :** 0

Abstract

An explosion occurred in a chemical plant. The incident occurred during production of toltrazuril, an ingredient used in production of a parasiticide.
It was originally thought that the explosion occurred during production of a fungicide.
Apparently a worker used potassium hydroxide instead of potassium carbonate in a reaction with 2-chloro-5-toluene and dimethyl sulphoxide.
The plant was completely destroyed.
[operator error, accidental mixing, processing, damage to equipment]

Lessons

[None Reported]

129451998

Source : CHEMICAL & ENGINEERING NEWS, JULY 24, 2000.

Location : New Jersey, USA

Injured : 9 **Dead :** 0

Abstract

An explosion occurred at a chemical plant injuring nine workers and releasing process chemicals into the surrounding area. The explosion occurred due to a runaway chemical reaction in a 2,000-gallon kettle being used to produce dye.
[gas / vapour release, runaway reaction, processing, injury]

Lessons

[None Reported]

8847 25 September 1997

Source : HAZARDOUS CARGO BULLETIN, 1997, NOV. REUTER. UPI.
Location : California, USA

Injured : 2   **Dead :** 0

Abstract

A leak of rain water mixed with chlorine occurred from a 200 litter drum causing an acrid, yellow cloud to spread over the area forcing evacuation of nearby homes.
[accidental mixing]

Lessons

[None Reported]

1119903 July 1997

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

During a routine switching over of coke pots at the bottom of a combination tower, hot vacuum tower bottoms oil (VTB) was released to atmosphere and auto-ignited. The resultant fire caused plant damage of $180,000 (1997) and loss of production of $410,000 (1997). It was very fortunate there were no injuries to personnel since operators were working above the coke pots at the time of the incident.
At 1420 hours, the fractionator operator was instructed to switch over the coke pots. These pots are designed to remove coke fines from the bottom of the combination tower on the outlet to the suction side of pump. Only one pot is in service at any one time, the other being on standby. They are normally switched over every Thursday or as necessary. The operation involved taking drain pot B out of service and replacing it with pot A. Before the contents of the pot can be drained, the pot has to be cooled with 32 degrees C/90 degreesF purge oil from 321 degrees C/610 degrees F to 121 degrees C/250 degrees F. At 1450 hours, the fractionator operator was advised by radio from the control board operator that the temperature of the pot was 232 degrees C/450 degrees F. There is no local temperature indicator at the pots, only a temperature transmitter back to the control room.
At 1500 hours, a coke drum change over commenced as this was already planned and also requires the assistance of the fractionator operator. As soon as the fractionator operator had completed the tasks associated with the coke drum change, around 1510 hours, he proceeded to drain the coke pot. The flow from the drain appeared excessive and as he was about to close the drain valve, the fire erupted.
The incident occurred on the last day of the work shift and the last day before a major holiday. It was unusual to have a major coke drum switch at the same time as a coke pot switch. The coke drum switch requires the efforts of three operators including the fractionator operator. The coke pot switch requires the efforts of the fractionator operator plus another operator. Both tasks are coordinated through the control board operator under the supervision of the chief operator. The fractionator operator had completed the switchover from coke pot B to A including alignment for purge oil cool down at 1430 hours without the usual assistance of a second operator. He returned again to the operation after he had finished his tasks associated with the coke drum switch. There is conflicting evidence as to whether the fractionator operator, in fact, had permission to drain the coke pot from the control room (radio communication). Coke fines present in the system tend to make it difficult to operate the valves which are often plugged.
Evidence suggests that the four-inch suction valve from pot B to pump was a quarter open (2-3 rounds) and that the purge oil valve was also open when the fire occurred. The pot had been pressured up and the operator had taken his wrench to #bang# the drain valve in order to clear the system and get flow started. Once the drain broke free, hot oil splashed out of the containment pit.
[operational activities, valve, design inadequate, autoignition, fire - consequence, spill]

Lessons

Effective controls including periodic task observations must be implemented where there is any possibility of oil being released to atmosphere above its auto-ignition temperature.

8804 April 1997

Source : CHEMICAL HAZARDS IN INDUSTRY, 1997, NOV.
Location : ,

Injured : 10 **Dead :** 0

Abstract

A chemical explosion occurred releasing small amounts of plutonium to the environment and exposed 10 workers to airborne chemical contamination. The incident occurred in a shut down plutonium reclamation facility when 370 gal of hydroxylamine nitrate in dilute nitric acid spontaneously exploded. The mixture had been in "short term" storage for four years, and water had been slowly evaporating from the solution. Eventually, a concentration was reached that resulted in the chemical explosion.
[accidental mixing, environmental]

Lessons

[None Reported]

1109705 March 1997

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

A minor explosion was heard in the crude unit area of this refinery. Smoke was seen from the vacuum tower overhead pipe.
On March 2, 1997, shutdown for maintenance turnaround commenced. The vacuum unit was depleted of oil, water washed/flushed and steam purged according to the shutdown/steam out checklist. A hydrant hose was connected to the suction side of the light vacuum gas oil pump ready for water wetting of the vacuum column. On March 4, 1997, the vacuum tower was steamed out. On March 5, 1997, the vacuum tower steaming was cut off. No water wetting was carried out immediately on the vacuum tower as the average tray temperature was still high around 90 degrees C (194 degrees F). At 8:20 am a cold work permit was issued for the installation of system blinds on the vacuum tower. At 8:30 am: A cold work permit was issued for installation of blinds on a number of heat exchangers, removal of the covers and the pulling of tube bundles. At 2:45 p.m. the vacuum tower overhead condenser (shell side) piping spool piece (40 inch) was taken out so as to facilitate the removal of the shell. At 3:15 pm a minor explosion was heard. Smoke was seen from the open flange on the tower's overhead line. All turnaround work was stopped. The Fire Brigade was alerted to stand by on site. Nitrogen was injected into the overhead line within a few minutes of the incident as it was thought there was a fire in the tower's overhead line. The tower top temperature started to fall immediately after the N2 injection. A water hoses were connected to the B-structure foam line at ground level and at the top platform of the condensers and water was injected into the open end of the tower's overhead line. At 3:45 pm It was observed that the vacuum tower (151E) tray temperatures continued to rise. Water was then injected via the top light vacuum gas oil reflux line through the pump suction. The tray temperatures dropped immediately after the water was introduced. At 4:00 pm The tower condenser overhead line temperature showed signs of increasing. A steam hose was connected to the inhibitor pump discharge bleeder and steam was introduced through the three quarter inch line to the overhead line. The overhead line temperature dropped after the steam was introduced. At 6:00 pm arrangements were made to install a 40 inch end flange to the overhead pipe's open end.
The following are the findings from an investigation of the incident:
· As per normal operating practice, water wetting of the column would only have commenced after the average tray temperature had cooled to below 60 degrees C.
· The planned column wetting arrangement (water was connected to the suction side of the light vacuum gas oil pump to be injected via the reflux line) was adequate.
· A cold work permit was issued for a number of heat exchangers including the vacuum tower's, overhead condensers 159CA/CB for installation of blinds, removal of heat exchanger covers, and the pulling of tube bundles. The 40 inch blinds should have been installed at the inlet nozzle on the shell side of the heat exchangers before any work on the heat exchangers had be carried out.
· No specific permit was issued for the removal of the shell side of heat exchanger 159CB or associated inlet piping spool piece. According to a mechanical technician, it was verbally communicated.
· The spool piece was taken off to facilitate the removal of the shell side of condenser/heat exchanger 159CB.
The open end of the 40 inch overhead line after the spool piece was removed was not fitted with a full face blind. This resulted in large ingress of air into the vacuum tower. The immediate cause of the minor explosion and fire in the vacuum tower was the autoignition of the pyrophoric iron sulfide from the ingress of air prior to the column wetting procedure.
[fire - consequence]

Lessons

The following recommendations were made
1. Both the Issuing Authority and the Performance Authority for the Work Permit System must discuss and understand in detail the exact job scope so that blinding is undertaken in the correct sequence of the maintenance preparations.
2. Operations Department should carry out the water wetting of the vacuum column as soon as practical.
3. Safety briefings on "Pyrophoric Iron Sulfide" should be carried out just prior to turnarounds.
Lessons Learned
A preparation of plant for maintenance procedure (a controlled document) must be strictly followed.
All parties involved in preparation of equipment for maintenance must be aware of the exact sequence of tasks to avoid auto ignition of pyrophoric iron sulfide.

1113708 January 1997

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

Passing diesel fuel oil valves on a burner allowed fuel to vaporise in a boiler, which had been shut down by interlock due to either low water level or low fuel pressure. The fuel reached the autoignition temperature in the economiser section and exploded twice. The first, smaller, explosion consumed the oxygen in the shutdown boiler, the main explosion occurred when mixed with air during the start-up purge cycle. The nitrile seats of the valves were affected by an additive in the fuel while those with fuel oil seats remained with tight shut off.
Three boilers were firing diesel fuel owing to a gas supply restriction. During the morning rounds the fuel supply was changed to tanks 2 and 3 from tanks 4 and 5 in readiness for the 11:00 am delivery to tanks 4 and 5. At approximately 2:30 pm, boilers 1 and 3 went to the lock-out position; and there was a dull thud in Boiler 3 with a smoky atmosphere and a smell of fuel oil. It was noticed that the fuel oil supply pressure was lower than usual and so the supply tanks were changed to feed from the refilled tanks 4 and 5. The Boilerhouse Supervisor decided to restart the lead boiler, Boiler 3, and switched off Boiler 1. The purge cycle for start-up of Boiler 3 was commenced and at 2:45 pm the explosion occurred within Boiler 3. The fire detection system was activated which automatically called the Fire Brigade. The operator isolated the fuel oil pumps and tanks from Boiler 3 before leaving the Boilerhouse, a major incident forward control team attended the site, along with the external emergency services.
An investigation concluded that fuel gas was not the source of the Boiler 3 incident. Isolation procedures used by the Boilerhouse Operator had been correct, and all valve interlocks on the gas isolation system had functioned correctly. Pressure tests carried out on the shutoff valves showed that one was passing. While reports of fluctuating oil pressure leading to boiler lock out could have been caused by air in the fuel, the tank levels were never low enough to allow ingress of air. After the boiler was depressured, a fuel oil deposit was found in the boilers. Analysers showed this to be the heavy ends of diesel fuel oil. After dismantling the fuel oil shut-off valves, it was found that the rubber "O" ring seals and associated diaphragms had been attacked by the fuel oil, causing swelling which had prevented the spring return from shutting the valve properly. The seal material was found to be "Nitrile" which was originally specified by, the valve manufacturer, to be suitable; but, due to later inclusion of certain additives within the fuel oil, was now the preferred material.
Investigation of the boiler showed that the economiser and flue gas ducting took the brunt of the damage rather than the boiler itself and indicated that the explosion occurred in the flue gas outlet.
The following corrective actions were taken:
1. Replace all fuel oil "Nitrile" valve seals and diaphragms with fuel oil on boilers 1 and 3.
2. Update maintenance schedules to inspect fuel oil shut-off valves every two years for signs of seal distortion.
3. Ensure that all plant and equipment in fuel oil service has been installed to the correct material specification.
4. When firing fuel oil, should a burner lock-out occur, the fuel oil supply line should be manually isolated and the boiler left idle for at least 20 minutes before the air purge is commissioned.
5. Produce an operations manual for all plant in, and associated with, the boilerhouse.
6. Ensure that any future modifications carried out to the boilers are covered by the "management of change" procedures at the site.
7. Produce up to date and accurate drawings of all boilers and the associated instrument and control systems. Field checking will be an integral part of this exercise.
8. Review the boiler level control system, identifying improvements which will lead to greater operational stability and therefore fewer trips during normal operation.
[low pressure, process causes, explosion, seal failure]

Lessons

A robust management of change procedure is essential to address subtle changes to equipment or changes to process materials, in this case additives to the fuel oil.
The integrity of the fuel isolation systems for boilers and heaters should be regularly inspected and reviewed.

1298 1997

Source : CHEMICL HAZARDS IN INDUSTRY, 1997, SEP.

Location : ,

Injured : 0 **Dead :** 0

Abstract

An incident occurred during a telescoped iron reduction/acetylation process. The reduction was carried out in the presence of an anhydride and the reduction product, an aromatic amine, was converted in situ to the corresponding acetylamino species. The process began when heat was generated in the normal manner but following the addition, the batch self heated at an increased rate. It boiled and the reactor over-pressurised. A substantial amount of the batch was subsequently ejected from the vessel.
[reactors and reaction equipment, overpressurisation, spill, processing, uncontrolled reaction, unknown chemicals]

Lessons

[None Reported]

1113512 October 1996

Source : ICHEME
Location : , USA

Injured : 0 **Dead :** 0

Abstract

A 6 inch untreated/raw naphtha line failed catastrophically near the base of the vacuum tower and the outflow autoignited. Both the reformer and the naphtha hydrotreater depressured in less than 15 minutes through the ruptured pipe. The resultant torch fire and subsequent fires from leaking flanges and pipe failures burned for approximately 10 hours. Two flare connections failed which contributed significantly to the duration of the fire as the plant was being shutdown and depressured to the flare system. Property damage is estimated at $10 million (£5.9 million) (1996). Commercial loss is estimated at $20 million (£11.9 million) (1996) as units, not directly affected by fire, were shutdown for weeks and the vacuum tower was down for over two months. An environmental release of FCC catalyst affected areas outside the plant, as the various units were shut down.
Untreated naphtha from the crude units were combined into a single stream prior to introduction into the naphtha hydrotreater. The failure occurred in the line from one of the crude units, downstream of the last exchanger and prior to the point where the two streams join. The naphtha line was at normal conditions prior to the incident at approximately 450 psig and 600 degrees F (317 degrees C). There were no indications from any of the alarms or any of the nearby employees that there was any problem with the line immediately prior to the fire. The piping was originally installed in 1965 and specified as aluminised (or "Alonised" as it is referred to) carbon steel piping. "Alonising" is an old process, no longer in common use for process piping, performed mainly to enhance the resistance of steels to high temperature, high sulfur environments. Although this piping was in service for over 30 years, sections of this same line near the failure had experienced only slight-to-moderate pitting and had retained nearly its original wall thickness.
[pipeline failure, fire - consequence, damage to equipment, autoignition, processing]

Lessons

The following recommendations were made:
1. Ensure that potential corrosion problems are adequately addressed with appropriate expertise and level of management.
2. Develop an action tracking system for all recommendations resulting from investigations, HAZOPS, audits, etc.
3. Re-evaluate piping inspection program.
4. Consider outside review of mechanical integrity program to share and incorporate best practices.
5. Replace alonized carbon steel pipe in high temperature/high sulfur services.
6. Consider amending emergency response plan to include call-out of personnel to assist in operational shutdown of units in major emergencies.
7. Emergency response drills should consider shutdown and isolation procedures and review of location of valves and switches.
8. Review the procedures in place for the emergency operation center and staging area including the need for a checklist and registration of first responders.
9. Develop a site specific plan for industrial hygiene exposure assessment on and off site during emergencies.
10. Review the adequacy of stationary fire protection in heavily congested areas.
11. Review the location, identification and accessibility of emergency isolation valves and switches.
12. Review the adequacy of existing emergency communication and notification systems within the refinery.
13. Make certain inspection thickness monitoring locations are sufficient to detect localized corrosion.
14. Conduct external audits of inspection programs and associated data management systems every 5 years to ensure continual mechanical integrity improvement and sharing of best practices.
15. Review adequacy of fire protection systems in congested areas and particularly for flare lines.
16. Check drainage in plant areas to remove expected quantity of fire water.
17. Ensure that all emergency systems are clearly identified and accessible.
18. Additional operational assistance is required in major emergencies to secure the safe shutdown or operation of other units.

1036909 June 1996

Source : LOSS CONTROL NEWSLETTER, ISSUE 3, 1996,; HEALTH AND SAFETY AT WORK JUNE 1997.
Location : Huddersfield, UK

Injured : 0 **Dead :** 0

Abstract

An explosion occurred causing the roof of a plant to be blown off. This was due to overpressurisation of the reactant tank.
The firm was fined £50,000 (1996) after an explosion demolished half of its premises. The reactor explosion happened after added a chemical nitrosyl sulphuric acid which was too low for it to react. He turned off the reactor's cooling water when he thought the process was complete. The temperature actually built up until the explosion occurred from a runaway reaction. The reactor top went through the roof and landed 100 metres away. The base went downwards through one floor and embedded itself in the concrete floor below. A previous incident in August 1995 2 tonnes contents of the reactor erupted through the lid at 270 degrees C.
[reactors and reaction equipment, methyl nitrophenol, runaway reaction, processing, methyl nitrophenol, nitrosyl sulphuric acid]

Lessons

[None Reported]

8701 28 February 1996

Source : SEDGWICK LOSS CONTROL NEWSLETTER, ISSUE 1, 1996.
Location : Samara, RUSSIA

Injured : 0 **Dead :** 2

Abstract

A mixture of fuel and air caused an explosion when a furnace was being lit to start-up a catalytic reforming facility. Fatality.
[catalytic reformer, residue]

Lessons

[None Reported]

8391 19 February 1996

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

Coker charge pump seal failure on a refinery. The inboard mechanical seal on a new Coker II Charge Pump failed. When coker feed was released, it auto-ignited.
The flange of the bellows, which is a sleeve made of Invar, had corroded away. The severity of the corrosion was a surprise since the seal had been in service only 6 weeks.
Losses including damage to equipment, product loss and the cost of maintenance amounted to $21,000 (1996). It was found that the flange of the bellows had corroded away and the seal stationary face separated from the bellows, allowing feed to leak to atmosphere. This was caused by the bellows material being susceptible to high temperature sulphur corrosion, however the engineering data sheet did not quantify the feed components, and the manufacturer had no data to quantify corrosion rates as a function of temperature and sulphur concentration.
[autoignition, material of construction failure, refining]

Lessons

Sulphur concentration needs to be stated on all seal and pump specifications.

8195 September 1995

Source : HAZARDOUS CARGO BULLETIN, 1995, NOV.
Location : Aqaba, JORDAN

Injured : 0 **Dead :** 0

Abstract

An explosion of a container with nitrocellulose at marshalling yard destroyed 20 and damaged 32 containers. Spontaneous combustion suspected.
[damage to equipment]

Lessons

[None Reported]

8379 01 August 1995

Source : ICHEME

Location : ,

Injured : 0 **Dead :** 0

Abstract

A substantial carryover of kerosene occurred from a section of the plant into the flare system. Liquid flowed from the overflow pipe at the base of the flare into the sewer system. The sewer overflowed and some 30 m 3 (cubic metres) spilled around the flare stack.
It was found that during water wash of the clay treater, the outlet valve of the treater was left in the open position. The incident was caused because the flushing operation for the clay treaters was not documented as a procedure.
[cleaning inadequate]

Lessons

Operating procedures and job tasks need to be evaluated and available in written format.
Checklists for verifying vessel isolations are useful.

3256 16 July 1995

Source : LLOYDS LIST, 1995, JUL, 18, JUL, 25,; EUROPEAN CHEMICAL NEWS, 1995, JUL.; CHEMICAL HAZARDS IN INDUSTRY, 1995, DEC.
Location : Ludwigshaven, GERMANY

Injured : 4 **Dead :** 0

Abstract

Explosion in laboratory caused considerable damage when solvent leaked from a 250 litre vessel. Sulphuric acid accidentally entered a distillation vessel being used to purify an intermediate for making an animal feed additive. The acid caused a runaway reaction that shattered the glass column and escaping vapours caught fire.
[fire - consequence, laboratory work, damage to equipment]

Lessons

[None Reported]

8527 15 February 1995

Source : HAZARDOUS CARGO BULLETIN, 1995, APR.; EUROPEAN CHEMICAL NEWS, 1995, FEB, 27.
Location : Essen, GERMANY

Injured : 4 **Dead :** 1

Abstract

An explosion and fire occurred at a chemical plant applying silicone coatings. The blast occurred when some polymethyl hydrogen siloxane was accidentally fed into a reactor, together with the correct feedstock, allyl glycidyl ether. The two epoxides reacted, overheated and hydrogen burst out of a ruptured pipe into the building, where it mixed with air and exploded. The 5 workers were caught in the resulting fire. According to the Company, the police believe that human error is to blame. Although both chemicals were labelled, they were stored in drums of the same colour. Damage is put at DM 10m $6.7m (1995). Fatality.
[fire - consequence, human causes, damage to equipment, identification inadequate, overheating, chemicals added incorrectly, charging reactor, reactors and reaction equipment]

Lessons

[None Reported]

7587 27 November 1994

Source : LOSS PREVENTION BULLETIN, 126, 3-6.

Location : ,

Injured : 13 **Dead :** 0

Abstract

A breakdown of operations occurred on plant which was caused by the bursting of an acrylic acid tank. This resulted in a large-scale fire fuelled by the escaping acrylic acid/polyacrylic acid. The polyvinyl alcohol storage facility nearby also caught fire

The following combination of events lead to the accident:

1. A power supply failure.
2. External temperature of around 5 degrees C, with a north wind.
3. The open-topped building.
4. Crystallising out by the acrylic acid in both pipeline circuits.
5. Warming-up and polymerisation caused by the pump working against a blocked delivery route.
6. Thawing of the crystallised acrylic acid in the bypass pipeline.
7. Transfer of polymers into the acrylic acid storage tank.
8. Slow warming of the tank's contents by around 0.5 degrees C/hr due to the pump passing against a throttled valve,
9. Ineffectiveness of the temperature monitoring system, since the large circulation pipeline remained blocked all the time.

[cold weather, rupture, fire - consequence, polymerisation, chemical missing, instrumentation failure, temperature meter/control]

Lessons

The following safety procedures were introduced to avoid the reoccurrence of a similar incident:

1. A continuous independent temperature measurement of the tank contents will be provided.
2. The circulation pump will be equipped with a temperature control safety switch.
3. Safeguards put in place to ensure that temperatures in acrylic acid storage facilities and in rooms containing acrylic acid pipelines do not fall below a certain level. This will avoid crystallisation of the acrylic acid in the event of a power failure.
4. Analytical surveillance will ensure that the inhibitor concentration within the acrylic acid does not fall below 200 ppm.
5. A measuring device will be installed to monitor the throughput of the major pipework.
6. An emergency reaction inhibition system will be installed.

6779 27 November 1994

Source : LOSS PREVENTION BULLETIN, 126, 03; EUROPEAN CHEMICAL NEWS, 1994, 5 DEC.; THE CHEMICAL ENGINEER, 1994, 15 DEC.
Location : Burghausen; Bavaria, GERMANY

Injured : 13 **Dead :** 1

Abstract

Incident at a polyvinyl acetate plant. A faulty power switch cut off the electricity supply to a circulating pump in an acrylic acid tank. The temperature of the acid in the pipes then fell from the safe range of 15 - 25 degrees C to 12 degrees C when it crystalised. The crystalised acid material polymerised uncontrollably destroying the storage unit, a manufacturing unit and a warehouse. Fatality.
[polymerisation, power supply failure, processing]

Lessons

1. The temperature of the tank to be monitored.
2. The circulation pump to be equipped with a temperature control safety switch.
3. Safeguards to ensure that the temperature of the storage tank and building do not fall below the crystallisation temperature.
4. Analytical surveillance to ensure inhibitor level does not fall below 200 ppm.
5. Measurement of large cycle throughput
6. A stopper system installed.
7. Pressure release system for storage tanks.

6671 19 August 1994

Source : SEDGWICK LOSS CONTROL NEWSLETTER, 3RD QUARTER, 1994.
Location : Houston; Texas, USA

Injured : 0 **Dead :** 0

Abstract

A runaway reaction led to a ruptured bursting disc and venting of about 2 tonnes of cyclopentadiene and fish oil. The vapour cloud ignited but was extinguished by plant personnel.
[fire - consequence]

Lessons

[None Reported]

6597 21 June 1994

Source : WASTE ENVIRONMENT TODAY, 1994, 7, (7)., 18
Location : Bristol; Pennyslvania, USA

Injured : 39 **Dead :** 0

Abstract

Violent explosion in plant during mixing of trichlorosilane and styrene in a steel drum. There was a heatwave prevailing at the time which may have caused the unusual reaction during this normally routine mixing operation. The resultant fire took 5 hours to control. Incident led to the evacuation of 200 people in a half mile radius.
[runaway reaction, fire - consequence, weather effects]

Lessons

[None Reported]

6567 27 May 1994

Source : LLOYDS LIST, 1994, 30 MAY., 3 JUN., 17 JUN., & 2 DEC.; EUROPEAN CHEMICAL NEWS, 1994, 6 JUN.; CHEMICAL WEEK, 1994, 1 JUN, 22 JUN, & 29 JUN.; CHEMISTRY IN BRITAIN, 1995, FEB.

Location : Belpre; Ohio, USA

Injured : 0 **Dead :** 3

Abstract

Explosion and fire in a styrene butadiene block polymers resins plant near 3 tanks containing up to 5000 tonnes of styrene. Some people evacuated. Fire lasted for 10 hours. Plant remained closed. 316 tonnes of styrene, 127 tonnes of cyclohexane and 12 tonnes of ethylene dibromide released. It is suspected that there was a disproportionate amount of butadiene in the reactor where it was added to other chemicals. This may have started a reaction which caused a pressure build up in the reactor leading to vessel failure and explosion. Company agreed to pay $3.02 m (1994). Fatality.
[high pressure, chemicals added incorrectly, unwanted chemical reaction, reaction vessel]

Lessons

[None Reported]

7599 May 1994

Source : LOSS PREVENTION BULLETIN, 128, 3-5.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A high pressure reactor ruptured during a catalyst activation operation. A gaseous stream of hydrogen and light hydrocarbons was released and spontaneously ignited. The unit was immediately shutdown and depressurised. The fire was limited to the vicinity of the ruptured reactor and was extinguished within twenty minutes by onsite emergency services. There were no injuries but damage to equipment included the reactor and some piping, instrumentation and air-fin heat exchangers on an adjacent structure.

An investigation was carried out and the causes identified. The operation in progress was a catalyst activation process which involved reducing an oxide coated form of the catalyst in the presence of hydrogen to its base metal form. The fresh catalyst to be activated was loaded in the top bed of a three bed reactor. The lower two beds of the reactor already contained previously used catalyst. In order to activate the fresh catalyst in the top bed, hydrogen had to be passed over the catalyst for a period of four hours at relatively high temperature and pressure. Target activation temperature was higher than the normal operating range of 300-380 degrees C, but within the reactor design temperature. The hydrogen used was from the site system and contained 70% hydrogen and 30% hydrocarbons in the range C1 to C5 with trace C6+. Since the reactor was a stacked bed reactor with entry at the top, the hydrogen rich gas had to pass over the fresh catalyst and then the older catalyst beds.

The gas was initially warmed-up via a furnace and passed through the reactor. As the inlet bed temperature target was approached, the furnace coil outlet temperature overshot its set point and three out of the four top bed temperature instruments went out of range, with the temperature at the bottom of that bed exceeding the vessel design temperature. In response, furnace firing was reduced and quench gas flows were increased to the reactor. Temperature control was poor as the furnace was tuned for normal process liquid/gas operation rather than gas-only activation. Two hours into the activation, the top bed temperatures had steadied out around the target activation temperature but the bottom temperature reading in that bed and all eight of the temperature readings in the two catalyst beds below remained offscale, beyond the design temperature of the reactor.

The activation step was completed two hours later and the reactor cooled down. Three hours into the cool down phase, the reactor, which had a diameter of one metre and a wall thickness of 50 mm, ruptured at the base of the middle catalyst bed.

[spontaneous combustion, fire - consequence, temperature meter/control, processing, operator error, reactors and reaction equipment]

Lessons

This was only the second time that the activation had been performed on this catalyst system. In hindsight, the actual processes occurring within the reactor were not fully understood and the job preparation could have been improved. However, the root cause of the incident was that temperature instrument readings were discounted. Safety refresher training must emphasise that instrumentation and alarms must not be discounted and, where data conflict, a defensive position should be chosen and a safe operating regime established at all times.

1170623 April 1994

Source : ICHEME
Location : , GERMANY

Injured : 0 **Dead :** 0

Abstract

A series of three explosion occurred within a few seconds in the waste incinerator of a chemical site during a night shift. There were no injuries and the damage sustained was slight. The incinerator burns waste from acrylics and viscose plants.The incinerator was operated for 20 years without any significant incidents. Salts (sodium sulphate and sodium hydroxide) were being charged and collecting as a molten pool in the rotary kiln section. A quantity of this residue had been allowed to build up. The explosion occurred within 2 minutes of a 14 drum charge being made to the system. On-site inspections suggested the damage caused was greater than that consistent with mild over-pressure but there had been no equipment failure. A Rapid Phase Transformation (or Physical explosion) caused by very hot molten salt entering the quench bath (containing water) from the kiln was seen as the most likely cause. This might have been triggered by a small transient over-pressurisation.
[charging, processing, overpressurisation, damage to equipment, accidental mixing]

Lessons

1. Inventories of molten salt to be minimised within the incinerator. The best means of achieving this is not to change salts containing metal ions to the system.
2. A programme of regular inspections of the kiln should be instigated to ensure that residues are not allowed to build up.
3. Restrict access to the area at the bottom of the kiln, especially during and after charging.

1092008 April 1994

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

A leak occurred on a main fractionator column of the CDU at a refinery resulted in a fire and shutdown of the unit. No injuries resulted from the incident and damage to the column was relatively minor. There was damage to access ladders and sections of grating, to a one inch service air line, and instrumentation cabling and lighting which was in the flame impingement path was destroyed.
The release of hydrocarbon vapours from the column was most likely caused by the relaxation of flange bolts on a 6 inch blanked nozzle. Relaxation of the bolts was not caused by any unusual action of the operators, but was probably due to thermal stresses created during shutdown and start-up of the unit, though a contributory factor could have been the introduction, in an uneven flow, of significant volumes of cool oil from the bottom pump-around circuit.
Autoignition of the vapours is considered as most likely.
Response to the incident was efficient, both the refinery and Central Regional Fire brigades responded rapidly to the emergency calls.
Initial fire fighting was hampered by the fact that the available fire monitors had difficulty reaching to the height of the fire source. However, additional monitors were brought from the nearby Alkylation Unit, and with these and better positioning it became possible to direct water at the fire area.
The local fire brigade was able to get additional water coverage by use of a hose from the elevated fin-fan air coolers deck.
[fire - consequence, damage to equipment, mechanical equipment failure]

Lessons

The incident demonstrated the difficulties in fighting fires located at an elevated location on processing units, with the need for pre-planning on simulated fire situations to assess adequacy of fire fighting equipment, fixed and mobile.
Processing plant operating procedures to be the subject of regular review to en-sure that thermal shocks to equipment are minimised at every point in procedures.
Redundant equipment/pipework on plant is best removed completely; if not, it must be adequately supported.
Operator routine walks through plants to include checking for flange leaks, especially during condition changes, also during dramatic weather condition changes, e.g., heavy rain may produce thermal stress on hot flanges sufficient to cause relaxation.

1172810 December 1993

Source : ICHEME
Location : ,

Injured : 1 **Dead :** 0

Abstract

During routine cleaning operations on a casting machine, a pipefitter was rendered briefly unconscious when hydrogen sulphide was emitted whilst chemicals were being drained from the machine tanks. The fitter fell, sustaining minor injuries.
The casting machine had being having some problems, during operation, which had lead to it being taken out of service so that washing operations and tank checks could be undertaken.
The drain valves on a sulphide tank were opened, allowing the contents of the tank to drain into a gully, beneath the machine. (From there the fluid would flow into the main drain).
The pipefitter was proceeding with the cleaning of the viscose feed to the casting machine. At this time other fitters were preparing to start jet washing tasks. This initially involved removing particles of viscose from the acid baths, where the jets had been dripping the viscose, prior to the cleaning operations commencing. Following removal of the viscose particles, the drain valves under the acid baths were opened, draining the baths' contents into the main drain. The main drain was flushed with water (as per normal operation) to dilute the contents of the drain.
It is believed that the sulphide tank and the acid baths were drained at the same time. The hydrogen sulphide was emitted and the incident occurred.
The plant Operating Manual did include a detailed warning of the dangers which would be faced in the event that the tanks / baths were drained simultaneously.
The Company investigated the incident. The Factory Inspector made a site inspection and considered the actions taken by the Company.
[draining, gas / vapour release, fall, asphyxiation, accidental mixing, injury]

Lessons

1. The Company reinforced it's Operating Procedure. Draining of the tanks / baths became an operation subject to a General Permit to Work.
2. The Factory Inspector made a number of recommendations to try and prevent a similar incident occurring. These included:
· That human error could still be the cause of such an incident and if possible the Operating Procedure should be tightened further.
· Consideration should be given to providing fixed audible alarms for hydrogen sulphide (and chlorine).
· The main drain should be checked for acidity before dropping alkaline baths into the drain.
· The potential for separate piping should be considered (although leakage could still provide a problem).
· Provision of suitable breathing apparatus.

6248 October 1993

Source : LOSS PREVENTION BULLETIN, 117, 17.
Location : Georgia, USA

Injured : 1 **Dead :** 0

Abstract

Workers were transferring a 93% solution of sulphuric acid from a 3785 litre storage tank to 378 litre "day tank" when a 2.5 cm carbon steel transfer pipe line failed. The failure caused sulphuric acid to be sprayed about 18 metres from the origin of the leak. A worker walking through the area was sprayed by the acid mist and received second degree burns on his back. After being washed down in a safety shower by fellow workers, he was taken to a medical facility for treatment. The procedure for transferring acid from the bulk tank to the day tank required that the valve at the dilute tank be closed and that a transfer pump be used to facilitate the transfer of acid from the bulk tank to the day tank. When the accident occurred, the valve at the dilute tank was closed and the transfer pump had been started. The pump built up pressure in the pipe, causing the mist of acid.

An inspection indicated that the failed line was constructed of carbon steel and appeared to be a "Schedule 40 pipe", although the engineering drawings specified use of "Schedule 160 pipe", which has walls approximately twice as thick. In addition, it was known that the flow of acid through the line normally reduces the thickness of the pipe wall by about 5 microns per year. The section of the line that failed had been replaced approximately 10 years ago. On this occasion, as soon as the leak was discovered and the transfer pump shut down, the area was barricaded and thoroughly washed. All piping was subsequently inspected using non-destructive evaluation (NDE) techniques, and pipes of insufficient thickness were replaced.

[pipeline failure, incorrect equipment installed, spill, material transfer]

Lessons

This incident provided several lessons relating to configuration control and the handing of corrosive materials:

1. Whenever system components are replaced or repaired, engineering documents must be checked to ensure that the correct materials are used. Engineering documents (especially drawings) must be carefully managed to ensure that they are kept up-to date. However, specifying the correct materials and components for maintenance and repairs is not enough. Follow up must be conducted to ensure that the entire process is performed correctly, appropriate replacement items must be ordered, inspected on receipt, adequately documented in work orders, installed, and functionally tested.

2. Management must ensure that all hazardous materials and processes are identified and that procedures are developed and implemented to ensure safety. A preventative maintenance programme, including a replacement schedule or through NDE testing, should be established to replace components where failure would result in serious safety or environmental consequences.

3. Implementation of relevant standards related to mechanical integrity, procedures, and training should have prevented the use of incorrect schedule piping. Although many standards apply to facilities with quantities of hazardous material above a certain thresholds, these recommended practices will prevent accidents even when applied to facilities that are not covered by the standard.

1090721 August 1993

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

A cone roofed tank in residue service violently ruptured at the roof to shell seam. A black plume rose in the air and was carried into the neighboring area. Steam was injected into the tank to snuff out the internal fire. About 3,400 bbls. of residue of left the tank, with approximately 95 percent of this captured in the tank dike area. The airborne portion (less than 150 bbls.) travelled outside the tank dike area. Damage inside the refinery was limited to the tank roof and its upper shell. There were no injuries.
The project incident cost to date is $212,000 (1993), including 652 car and 239 house insurance claims resolved to date. The total cost may increase to $364,000 (1993) due pending claims and the tank repair.
The incident occurred when the combination of hot residue vapours, oxygen and pyrophoric deposits in the vapour space completed the fire triangle with autoignition. The resulting combustion increased the tank vapour space pressure, overpressured the tank and ruptured the roof to wall seam. Combustion vapours and liquid oil was released from the tank.
The incident occurred after the tank had been isolated the previous night at a temperature of 405 degrees F. Just hours before the tank isolation, the vacuum distillation unit cooler box in atmospheric residue service was bypassed due to plugging, raising the rundown from its normal temperature of 400 degrees F to about 670 degrees F.
The combination of excessive temperature and available oxygen in the tank vapour space provided the scenario for autognition. Lack of communication and a previous tank roof seam split were contributory causes to the incident.
[storage tanks, material of construction failure, gas / vapour release, damage to equipment, design or procedure error, high temperature]

Lessons

The following recommendations were made:
1. Rundown temperatures of residue to storage must not exceed safe levels.
2. Damaged tanks retained in service may exacerbate problems at a later date.
3. For residue, bitumens, heavy oils, subject to deposition on tank walls and under roofs, autoignition is a potential hazard.
4. Tank heating coils must not be in operation without an adequate liquid level coverage.
5. Temperature indications for storage tanks are usually poorly provided giving operators.
6. limited reliable information, this needs to be considered when working close to safe temperature limits.

6096 03 June 1993

Source : OCCUPATIONAL SAFETY OBSERVER, 1994, FEB.
Location : Kenvil; New Jersey, USA

Injured : 3 **Dead :** 0

Abstract

Four explosions at gunpowder plant destroyed 4 buildings and 5 damaged. Windows were broken over an 8 mile radius and 80% of the business in a nearby town were damaged. 3 seriously injured. $6 million (1993) fines were imposed for 71 violations. Explosions caused by failure to clean equipment.
[cleaning inadequate, processing, black powder (gunpowder), injury]

Lessons

[None Reported]

8308 June 1993

Source : ICHEME
Location : ,
Injured : 0 **Dead :** 0

Abstract

DHT compressor explosion and fire at a refinery. An explosion and fire occurred at a reciprocating recycle H2 (hydrogen) compressor during commissioning of a new DHT Unit. It happened during the reactor presulphiding step, when the recycle gas contained 9000 ppm of H2S (hydrogen sulphide) and the pressure was at 940 psig. Failure of retaining bolts on head-end suction valve unloader of recycle cylinder on compressor allowed release of process gas.
Investigations revealed that the bolts failed due to inappropriate material (to prevent sulphide stress cracking) and inadequate design for the service. The manufacturer did not comply with the company's practice for reciprocating compressors in H2S applications.
Estimated at $100,000 (1993). Damage to compressor shelter, instrumentation. Estimated 250 manhours spent on investigation.
[fire - consequence, damage to equipment, design inadequate, refining, incorrect material of construction, stress corrosion cracking]

Lessons

Standards in design control, purchasing, construction, and inspection and testing of purchased equipment, are essential to the safety of any process plant project.
Each group involved in a project, whether projects, contractors, suppliers, designers, procurement, manufacture, construction, etc. plays a key role in assuring the equipment's fitness for use.
All possible process conditions must be detailed in the specification for the purchase of equipment.
HAZOP studies must include all deviations from the design operating conditions such as shutdown, start-up, maintenance, and other activities such as the presulphiding process to check the adequacy of the design.

6052 29 April 1993

Source : ICHEME
Location : , FRANCE

Injured : 0 **Dead :** 0

Abstract

Spontaneous combustion occurred in a pile of internals from cooling tower cell removed for maintenance reasons.
[cooling equipment, fire - consequence]

Lessons

[None Reported]

6038 19 April 1993

Source : LOSS PREVENTION BULLETIN, 113, 25-25.
Location : ,

Injured : 0 **Dead :** 0

Abstract

Vinyl acetate odour was noticed inside a reactor shed coming from an atmospheric Pre-Emulsion (PE) tank. The manway cover had lifted off the tank and emulsion was present on the deck in front of the manway. The PE tank held a complete pre-emulsion (monomers, maleic anhydride, surfactant, ferrous sulphate and water) since the previous shift on Friday night. Sometime between Friday evening and Sunday evening, a reaction began in the PE tank and was still taking place when the start-up crew arrived at midnight on Sunday. The Shift Supervisor shut the agitator off, recorded the PE tank temperature (60 degrees C) and evacuated the reactor area. Incident Command was established. Personnel donned breathing apparatus and rain gear and entered the area carrying an LEL/O2 meter. They started the agitator on the PE tank. A sudden pressure surge again lifted the manway cover off the tank. They stopped the agitator and evacuated the area. Moments later they returned to the PE tank, replaced the manway cover, began circulation of the pre-emulsion through the heat exchanger and left the area. Periodic entry to the area to monitor the PE tank temperature while the area was continually monitored for flammables and oxygen (O2). The Safety, Heath & Environment Manager arrived and called the Fire Department. She also contacted the Distribution Safety Manager who advised her to create a water quench in the reactor and transfer the pre-emulsion from the PE tank into the quench. Water and inhibitor were added into the cleaned reactor. The pre-emulsion was slowly metered into the reactor while monitoring the PE tank temperature and the filled space inside the reactor. Once they confirmed that the temperature was holding steady, they increased the pre-emulsion transfer rate. Approximately two-thirds of the pre-emulsion was transferred into the reactor resulting in a temperature drop to 23 degrees C effectively quenching the reaction. Water and inhibitor were added to the remaining pre-emulsion in the PE tank and the material was circulated through the heat exchanger. After confirming that the PE tank temperature was stable, the PE agitator was started. The PE tank temperature dropped from 54 to 37 degrees C. Conditions remained stable on both the reactor and the PE tank and an end to the emergency was declared.
The key findings were:
1. There were a number of problems associated with the emergency response actions and equipment availability.
2. Some formulations called for adding catalyst or other additives to the pre-emulsion tank.
3. The pre-emulsion tank was not monitored.
[reactors and reaction equipment, runaway reaction, spill]

Lessons

Key actions taken were:
1. No monomer mix or pre-emulsion will be left unattended or monitored.
2. Remove catalyst and activators from the pre-emulsion tank.
3. Establish written procedures for minimising hold times of pre-emulsion and monomer mix for handling non-typical (e.g. polymerisation) situations.
4. Improve written emergency response procedures and employee emergency response training.
5. Remove heat sources from pre-emulsion vessels.
6. Complete the ongoing process vessel high temperature/high level alarm project.

1194306 April 1993

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

An explosion and fire occurred in the final powder degasser on a polyethylene plant. There were no injuries or danger outside the factory, and no loss of planned production. However, significant repair and cleaning costs were incurred. Leading up to the incident, the plant was in the process of shutting down. A trial had been running, and difficulties had been experienced with the vent recover unit (VRU), which could not cope with the hydrocarbon quantities being degassed at the given reactor withdrawal rates. This affected the operation of the secondary degasser to the extent that eventually there was no effective degassing of the powder in this unit. Significant quantities of hydrocarbon therefore passed into the final air degasser where a flammable atmosphere was established.The source of ignition was static. Vessel earthing was adequate but static generated inherently in the degasser fluidised bed would have provided sufficient ignition energy to ignite the flammable hydrocarbon/ air mixture.The damaged vessel was found to have only minor damage; during the fire it had been subjected to temperatures of 600-700 degrees C and some slight deformation had occurred because of reduced mechanical strength at such conditions.An analyser was highlighted as a key area in monitoring hydrocarbon in the degassing train. Following the incident the alarm setting was reduced and equipment redundancy provided to ensure a reliable reading. Relevant operating instructions were reviewed and training carried out to ensure that appropriate actions are taken when there are high hydrocarbon levels in the system. Limitations of the VRU and associated systems were established and corrective engineering identified. Response from the emergency services was excellent and only minor concerns were raised.
[fire - consequence, shutdown, vapour recovery system, polymerisation, incorrect chemical concentration, hydrocarbon]

Lessons

Root cause analysis identified the following:
1. Immediate causes:·
Breakthrough of hydrocarbon into the final degasser creating a flammable hydrocarbon/ air mixture.
Source of ignition was static, inherently generated in the fluidised bed.
The resulting fire was burning polymer
2. Basic causes:·
The degassing system was unable to achieve the required degassing of the powder during the shutdown phase at the given reactor product withdrawal rates. This allowed increased quantities of hydrocarbon to pass into the air degasser.For over four hours prior to the explosion, a flammable atmosphere existed in the interface between the inert powder conveying system and the air degasse.
Plant operating instructions were inadequate and the potential risks associated with increasing hydrocarbon levels in the degassing system were not recognised.
Equipment constraints in the VRU significantly impacted the hydrocarbon removal capability of the degassing system.

6841 February 1993

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

Corrosion probe stress. Significant release of hydrocarbon gases when withdrawing a corrosion probe from a live piping system on the crude distillation unit. The outer probe holder had suffered stress corrosion in service, and a piece of the probe holder broken away when it was being withdrawn (defective equipment). The basic cause was that the probe holder material could not resist corrosion cracking, it was improperly selected.
[material of construction failure, incorrect material of construction]

Lessons

Materials for all components in a system subject to corrosion must be such that sudden failure will not occur leading to release of hazardous materials.

5895 1993

Source : CHEMICAL HAZARDS IN INDUSTRY, 1993, DEC.
Location : , GERMANY

Injured : 0 **Dead :** 0

Abstract

Rupture of dinitrobenzene tank. During cleaning of a tank at 130 degrees C, the tank split and fractured pipework. It was thought that picric acid and styphnic acid had become enriched in the residue through insufficient washing on previous occassions.
[cleaning inadequate]

Lessons

[None Reported]

5843 03 November 1992

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

A dust explosion occurred in a bag filter of a polymer plant and vented through explosion panels. A fire subsequently occurred in the bag filter dust collector. It was determined that the polymer accumulation inside the filter bag had degraded and autoignited due to long time at elevated temperature.
[autoignition, fire - consequence, processing]

Lessons

In future plant to have increased inspection and cleaning of bags. Improved bag design being considered.

1200912 May 1992

Source : ICHEME
Location : ,
Injured : 0 **Dead :** 0

Abstract

On May 11, an operator charged makeup DIB and xylene to a batch of maleic anhydride. Some time later he charged the styrene chaser and tried but had difficulty getting the xylene flush charged. Another operator found and closed a DIB charging block valve which was in the open position. Once this valve was closed the xylene flush was completed smoothly. The batch processed to completion without incident.
On May 12, raw material charging on the next batch proceeded normally. The mix was warmed to 114 degrees C and the first catalyst shot made. As the exotherm began, the normal cooling was applied. Upon observing that the temperature rise was not abating, full cooling was applied. The exotherm continued and the operator realised he was not able to control it. The pressure began to increase and the operator opened the 3 inch vent line to an attached vessel but the pressure increase continued. The operator opened the normal vent to the roof through the condenser and vacated the area. The reactor pressure increased to a reported 40 - 50 psig. The pressure blew out the reactor agitator seal O-ring and spewed a heavy concentration of vapours into the department. A 35 psig relief valve did unseat but the 50 psig rupture disc did not burst. The Plant had experienced an uncontrolled runaway polymerisation in the reactor while manufacturing crude polymer.
[maleic anhydride, styrene, xylene, processing, reaction, reactors and reaction equipment, agitator, non-return valve, environmental, runaway reaction, valve failure, inadequate engineering, design or procedure error]

Lessons

The runaway reaction was a direct result of styrene backflowing into the DIB charging line via the open block valve and a faulty antiquated check valve during the first batch. During the second batch, the normal DIB charge in fact included the styrene. The styrene/maleic copolymerisation reacted much more rapidly than the normal DIB/maleic reaction and exothermed uncontrollably.
Some key contributing factors were:
1. Operator not closing shutoff/charging valve after completion of charge, or opening wrong valve and leaving it open, or not checking valve alignment.
2. Antiquated/faulty check valve in DIB line.
3. Agitator seal pressure design insufficient to hold pressure at the rupture disc setting.
4. No easy means to source emergency quench water, nor a clear criteria for when to inject quench water.
5. Failure of operator(s) and Team Manager to realise potential consequences of the abnormal valve arrangement when it was discovered.
6. Actuator for the department evacuation signal required someone holding it to keep it activated/actuated (was in the locale of the vapour cloud around the reactor).
The actions taken as a result of this incident were:
1. Agitator seal replaced with one of split design and rated for 100 psig.
2. Header charginmg valves modified to allow only one valve open at a time (to charge the wrong material would now take 4 separate sequential incorrect actions). Used and cumbersome piping was removed and replaced with very direct/simple piping to minimise the potential of material going anywhere but to the meter centre.
3. Antiquated non-return (check) valves on raw material charging lines have been removed and new ones installed within the modified piping outlined in 2 above.
4. All other charging lines have been surveyed and non-return valves have been installed as appropriate.
5. An easily installed and highly visible means of sourcing emergency quench water has been installed and will be accompanied by special instructions in the SOP and on the floor.
6. The knock-out pot has been installed on the normal vent line off the condenser to forewarn of a heavy/condensible vapour flow past the condenser and/or prevent minor upsets from purging small liquid quantities to the outside environment.
7. The department evacuation actuator will have latching mechanism installed.

7433 May 1992

Source : LOSS PREVENTION BULLETIN, 110, 25-26.
Location : ,

Injured : 6 **Dead :** 0

Abstract

A plant experienced an uncontrolled ("runaway") polymerisation in the reactor which produced a maleic co-polymer. This resulted in a pressure build up and discharged vapours finding their way in to the work area. Six employees were treated for respiratory irritation.
On the day in question, charging the batch proceeded normally. The reactor was heated to 114 degrees C, when the first catalyst addition was made. As the exotherm developed, the reactor was put on normal cooling. The exotherm did not abate and the reactor was put on full cooling. The operator realised then he was not able to control the reaction. The pressure rose and the operator opened a 3 inch vent line to an adjacent vessel, but the pressure continued to rise. He then opened the vent line to the roof through a condenser and evacuated the plant.
The pressure in the reactor rose to an estimated 40-50 psi. A 35 psig relief valve lifted but the 50 psig bursting disc did not burst. However, the agitator seal O-ring blew out and a heavy concentration of vapours were released into the area.
After investingations it was found that:
The reaction runaway was due to styrene back flowing into the other monomer line via the left open block valve. An old non-return valve failed to prevent this. The second batch contained this styrene in the initial charge. The maleic/styrene co-polymerisation is much more vigorous than the maleic/monomer co-polymerisation and consequently exceeded the reactor control.
[runaway reaction, gas / vapour release, high pressure]

Lessons

[None Reported]

7581 09 January 1992

Source : LOSS PREVENTION BULLETIN, 107, 17-20.
Location : ,
Injured : 0 **Dead :** 0

Abstract

An incident occurred in the regenerator section of a Fluid Catalytic Cracker Unit (FCCU) 50 hours after a unit shutdown. The shutdown was not planned and was caused by mechanical failure of the regenerator airblower.
FCCU regenerators are large vessels containing beds of fluidised catalyst in which air is used to burn off both carbon, referred to as coke, and hydrogen based material trapped in and on aluminium silicate catalyst which has a porous structure. The air flows into the regenerator through a two, tier air grid system from an airblower.
Two days before the incident, the airblower tripped out due to activation of the airblower vibration shutdown monitoring equipment. The vibration was caused by a mechanical failure of one of the air blower rotor discs.
This initiated automatic shutdown of the unit. As a result the regenerator fluidised bed slumped and steam was automatically injected into the catalyst bed.
The air blower rotor assembly was inspected through a small manway inspection door, visually confirming that the rotor was damaged and would have to be repaired. At the same time the decision was taken to enter the regenerator/riser/reactor circuit to undertake other necessary repair work.
Over the subsequent 2 days operations staff prepared the regenerator for manway removal. It was recognised that catalyst temperature would be higher than usual. Previously when the air blower had tripped and the manways to the regenerator, riser/reactor and ductwork, including the waste heat boiler (known as the cat circuit) had been opened, the equipment had been gas tested and entered without incident. During the preparations a large butterfly valve and a critical flow nozzle were removed from the ductwork to the flue. These were normal procedures in preparing the cat circuit for entry. The removal of these items reduced the draught of the flue on the regenerator and would have contributed to an oxygen deficiency in the regenerator.
After all the necessary blinds had been inserted, operational procedures permitted the regenerator manways to be removed to allow the final vacuum truck removal of remaining catalyst.
On the day of the incident, work commenced to remove one of two manways on the regenerator, at the base about 9 m above ground level. A small manway was opened first to ensure that there was not a residual mound of hot catalyst resting against the large manway door that might have slumped onto those on the access platform. This manway was opened as the system was considered to be an air system open to atmosphere by virtue of the flue connection.
Work then proceeded to open the large 1.5 m manway. With one bolt remaining on the large manway, some witnesses reported a rumbling noise inside the regenerator. It was immediately followed by an orange-red flash which came out of the left side of the manway, from where the penultimate bolt had been taken.
Simultaneously a flame front and hot particles exited from the small manhole on the other side of the regenerator platform.
The flame and pressure front passed through the regenerator into the downstream flue ductwork. Where the duct was broken and plant items removed flame fronts and hot catalyst exited.
After a period of a few seconds, there was a louder secondary noise which emanated from the waste heat boiler and associated flues which sustained structural damage.
The following conclusions were made:
This unique incident was due to the ignition of hydrogen, light hydrocarbon gases and carbon monoxide. These gases were generated by contact of unregenerated catalyst with steam in an oxygen deficient atmosphere. Removal of a manway to allow access for vacuum truck removal of catalyst allowed oxygen re-enrichment of the internal atmosphere and the re-establishment of conditions that permitted ignition. Lighter-than-air combustible gases were trapped in a reservoir created by the internal configuration of the plant. The opening of the manway caused some gases to be dispersed into the ductwork prior to the ignition.
[catalytic cracker, blower failure, fire - consequence, oxygen enrichment, fluid cracker]

Lessons

[None Reported]

7872 January 1992

Source : LOSS PREVENTION BULLETIN, 109, 7-10.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A centrifuge feed tank, of 30 m3 capacity, manufactured of rubber lined carbon steel and containing an aqueous slurry of iminobaisacetonitrile (IBA), ruptured due to overpressurisation caused by decomposition reactions during a cleaning operation. Although personnel injuries were minor, there was extensive damage to plant facilities. The cost of plant rebuilding and the business interruption loss amounted to the equivalent of well over £10 million (1992).
On the day of the incident a large build-up of solids was noticed on the internal coil and in the tank headspace, and level instrumentation problems were experienced. Further investigation revealed that the tank vent was blocked and causing the level transmission errors by allowing a vacuum in the tank. Realising that tank clean out was necessary, operational staff stopped transfers into the tank and continued feeding forward to the centrifuge via a side outlet. When the level dropped to this outlet, an attempt to empty the heel of slurry to the centrifuge through the tank bottom was made, but the connection was blocked. The blockage was cleared but the heel was not emptied.
The tank was then filled with process water until the level reached the upper tangent line of the top head, as observed through a sightglass. At 1615 hours circulation was started and steam was turned on to the coil, with the objective of heating the contents to 70 degrees C and then allowing circulation of the hot water for a further 30 minutes. Soon after the steam flow was started the level indicator reading returned to normal, suggesting that the tank vent was at least partially open.
At 1640 hours the tank contents reached 40 degrees C, the upper limit of the installed temperature indicator. Subsequently, temperature measurements were made using a portable surface-reading pyrometer on the circulation pump suction piping. At 1740 the temperature was 55 degrees C and at 1835 it had reached 74 degrees C. Steam was then shut-off from the coil, the circulation was stopped, and an operator tried to empty the tank contents via a gravity drain line.
Draining was unsuccessful due to a blockage in the pipe, a flexible hose to a drain valve on the discharge of the pump. At 1910 hours draining was started via the hose to a floor drain. The operator looked through the tank sightglass to confirm that the level had started to decrease before returning to the control room.
At about 1920 hours two field operators responded to what sounded like a high pressure steam leak in the feed tank area of the plant. Almost immediately they came within view of the tank, at a distance of about 12 metres, it violently ruptured. They were blown backwards and sprayed with a black residue, but returned to the control room unaided and sustained only minor injuries.
The tank overpressurisation was caused by the steam pressure that was generated by the heat of chemical reactions. Initially the IBA started to decompose due to overheating during the cleaning operation. The hydrogen cyanide (HCN) formed then polymerised, significantly augmenting the heat evolution, and provided the heat essential for vessel rupture.
The chemical reactions were initiated by the use of a tank cleaning operation which was unsuitable for the process material, particularly in respect of heating medium, water quality and procedure.
[vent blocked, solids deposition]

Lessons

As a result of the investigation a series of preventative recommendations were made:
1. Reduction in IBA build-up.
Consider the impact of upstream equipment performance and operations on solids build-up in the feed tank.
Consider the installation of nozzle inserts in the feed tank entry and re-circulation piping to minimise splashing and run-down on the head.
Consider operating the feed tank through the bottom outlet only and decide on the need for a side outlet.
2. Reduction in IBA quantity at clean out.
Establish clear guidance on the planning and minimum frequency of feed tank clean outs.
Enssure that cleaning is carried out before the build-up is too large, and only after the feed tank is fully drained.
3. Reduction in temperature to safe level below IBA decomposition.
Enssure that steam is not used for cleaning the feed tank and for unblocking/decontaminating associated piping. Remove steam connections to the coil.
Develop a safe temperature controlled method for cleaning the feed tank and associated piping, provide the necessary facilities to support the method, and establish formal instructions for clean out.
Enssure that steam is not used for cleaning all other vessels where IBA is present and for unblocking/decontaminating associated piping. Provide for temperature controlled cleaning as above. Where steam heating is employed as part of normal operation, evaluate the use of tempered water or gain formal approval of continued use of steam.
4. Reduction in IBA exposure time to heat.
Provide for specified time limits as part of new cleaning procedures.
5. Prevention of contact with alkaline solutions.
Connect only non-basic pH controlled water to the feed tank.
Connect only non-basic pH controlled water to other vessels containing IBA and/or HCN .
6. Improvement in process instrumentation.
Provide an improved temperature measuring system on the feed tank to reliably monitor both normal and clean out temperature ranges.
Provide a high temperature alarm, high temperature interlock, and high rate of temperature rise interlock on the feedtank. Either interlock should discontinue cleaning operations and initiate corrective actions.
Provide a high temperature alarm, high temperature interlock, and high rate of temperature rise interlock on other vessels containing IBA and/or HCN. Either interlock to be discontinue normal operations and cleaning operations, and initiate corrective actions.
Provide an improved level measuring system on the feed tank to operate reliably independently of vessel pressure.
7. Improvement facilities in emergency.
Consider the provision of quench systems to terminate a reaction if started in the feed tank and other vessels containing IBA. Ensure that the feed tank and other vessels containing IBA are provided with vent systems of adequate size which can be monitored and maintained operational.
8. Improvement in process knowledge and documentation.
Enssure that all process documentation is updated to effectively emphasise the reactivity and thermal stability characteristics of IBA. Establish a procedure to review, incorporate and communicate changes or new information impacting process safety at least annually. Educate all personnel on the hazards of IBA reactivity, particularly in respect to the revised operating and cleaning procedures introduced.
9. Additional hazard assessment.
Conduct HAZOP studies on designated IBA/HCN containing vessels throughout the manufacturing process.

1333 1992

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

An operator attempted to clear a blockage caused by caustic soda in the drain line at the bottom of a depropanizer reboiler. The operator dismantled the drain line leaving a 50mm gate valve in place. This was found to be blocked but was eventually cleared using steam. A mixture of butane and butylene at 17 bar pressure then started to escape from the valve.
This valve was closed by operators using breathing apparatus in accordance with the emergency procedures, but not before the depressuring valve was opened. A decision was taken to reduce pressure in both the depropanizer and an associated propane/propylene splitter. Gas was diverted into the flare line via a 400mm ball valve. Just upstream of the point where the flare line met the flare header were a 250mm diameter sump and a drain line.
The sump and drain line were blocked by a mixture of scale and discarded welding rods which, according to the company, were probably left by contractors who worked on the plant in 1988. The blockage had allowed 30m3 of liquid to collect in the flare line.
When the diverted gas hit this huge slug of liquid, the vibration dislodged about 100m of the flare line, which fell 10m to the ground and buckled on impact in the area of contact.
The buckling of the pipe was typical of that seen in ductile collapse of steel pipe, where the walls of the pipe fold inwards to form uniform lobes on the inside of the pipe. At the trough between two of the lobes there was a series of long open-mouthed cracks. The region of cracking extended over a total length of approximately 170mm. The cracks were found to have propagated to a depth of 7.7mm in one place, leaving 2.3mm of metal remaining from a nominal thickness of 10mm. The length of the damaged pipe was quite small.
The view of the inspector was that the incident could have been a major disaster in that their calculations showed that, if there had been a leak followed by a vapour cloud explosion, there would have been total destruction of plant and equipment within a 60m radius and collapsed buildings within 240m.
Since the incident several hundred thousand pounds have been spent on improving the flare system.
[processing, flow restriction, corrosion, solids deposition, gas / vapour release]

Lessons

The above incident provides a reminder of problems which can be experienced with corrosion and deposition in flare pipeline systems. Unfortunately, blockage and corrosion is probably most likely to occur at the low drain points provided specifically to remove liquid condensation.
Finding problem points is not easy. In the past blockages have been looked for by pipeline radiography with some success, followed by selected cleaning of sections, such as bends, crossovers, and expansion loops.
The use of higher grade steels and purging at dead ends of the flare line systems are methods used at some sites to reduce problems.

1194415 October 1991

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

A non-vital nitrogen reticulation was contaminated with 300 litres of an ethyl aluminium dichloride (EADC)/ heptane mixture. Some of this was released to atmosphere when the EADC reacted with moisture to release hydrogen chloride vapour.The flame arrestor on the vent line of a catalyst blowdown drum had blocked and the drum became pressurised by a vital nitrogen purge. The blockage mechanism was catalyst vapour reacting with water in the flame arrestor to form solid aluminium hydroxide. After the non-vital nitrogen system was isolated for maintenance, the non-vital nitrogen header pressure dropped through leaks. The bursting disc connecting this to the drum pressured in the reverse direction and burst. The pressure pushed liquid up into the non-vital nitrogen system.The vital nitrogen to the drum had a low flow alarm; insufficient attention was paid to this.
[unwanted chemical reaction, gas / vapour release, flow restriction, preparation for maintenance, flame arrestor, additional chemical present, cleaning inadequate]

Lessons

Root cause analysis identified the following:
1. Immediate causes:·
Over-riding/ ignoring safety devices: sounding of low flow alarm was not adequately investigated.
Defective equipment: blockage in flame arrestor.
Inadequate procedures: actions in the event of the alarm sounding not defined.
2. Basic causes:·
Inadequate maintenance: no programme for checking for blockage in the flame arrestor·Inadequate engineering: design of system did not fully take into account the potential for cross contamination of the nitrogen system arising from overpressure of the blowdown drum and failure of the bursting disc.
Inadequate work standards: procedures not adequate to arrive at correct interpretation of the cause of the alarm sounding.Lack of knowledge: causes and consequences of sounding low flow alarm were not appreciated.

1047902 August 1991

Source : ICHEME

Location : , UK

Injured : 1 **Dead :** 0

Abstract

A fire broke out in a building used for the storage and packaging of 'friction dust' (a phenolic resin material). One fire fighter sustained slight eye injuries. The emergency response plan was triggered and local residents alerted.

A detailed report of the mechanism which caused the fire is not given - however it is summarised as follows:

"The cause of the fire was self heating and subsequent combustion of a process by-product formed during a production trial. The self heating was the combination of the chemical nature of the material plus the way it had been stored in the building".

The fire occurred during a shutdown period, when there was a very low level of manning (and routine inspection) on the site.

[resins, storage equipment, fire - consequence, decomposition, spontaneous combustion, design or procedure error, injury]

Lessons

A very large list of recommendations was made. The most important of these appear to be:

· better control of experimental manufacturing

· tighter control of storage methods for 'friction dust' materials

· more frequent area monitoring during shutdown periods

1049729 July 1991

Source : ICHEME
Location : , USA

Injured : 0 **Dead :** 0

Abstract

A fire occurred on a solids processing plant - no serious damage resulted.
The fire was in a pit housing a drive motor, and it seems that a faulty fluorescent light fitting caused ignition of resin dust (and possibly peroxide) on the wall of the pit. A sprinkler system had recently been installed, and this extinguished the fire.
Some shortcomings in the emergency response were identified.
[polymer, solids processing equipment, fire - consequence, electrical equipment failure, cleaning inadequate]

Lessons

The following recommendations were made:
· old fluorescent light fittings to be replaced by vapour-tight units
· improve standards of cleanliness in pits
· update fire water distribution drawing
· update emergency response phone numbers

5391 26 July 1991

Source : WASHINGTON POST, 1991, 24 JUL.
Location : Lorton; Fairfax County; Maryland, USA

Injured : 0 **Dead :** 0

Abstract

A road transportation incident. A road vehicle carrying toxic chemicals caught fire. An aluminium powder waste from a tear gas factory ignited spontaneously.
Other substance involved: methylene chloride and lindane
[autoignition, fire - consequence]

Lessons

[None Reported]

7920 24 July 1991

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

A transfer pump was hooked up to the water draw off connection of tank A, and the last 4' of product was transferred to tank B (11th July 1991). This was completed on the 17th July. Tank transfer line blinds were inserted on the 18/19th and arrangements were made to start cleaning the tank as soon as the manways were opened. This was the same procedure used for sister tanks B and C in 1990/91.
On the 24th July the manways on the north and south side of tank 68 were removed by fitters, who reported that the tank was open shortly after 11.00 hours.
At approximately 11.30 hours the Area Supervisor arrived at the tank to verify that the tank was open and to assess the amount of material to be removed. As he approached the bundwall to walk around the tank, a fire erupted inside the tank with flames initially shooting out of the manway.
No one else was in the vicinity of the tank at the time and there were no injuries.
The supervisor immediately activated the Emergency Response Team, and they controlled the fire by cooling the tank shell and injecting foam into the open manway on the north side of the tank.
The fire was finally extinguished by 13.30 hours.
The most probable cause of the fire was from pyrophoric scale which ignited residual naphtha in the tank.
Between the tank being emptied on the 17th July and when it was opened on the 24th, there had been extremely high ambient temperatures (95 degrees F), which had most likely dried out the scale in the tank.
The introduction of air by opening the manways and the continuing high ambient temperatures completed the drying out of the scale and led to the fire incident.
[material transfer, fire - consequence, spontaneous combustion, hot weather]

Lessons

The following recommendations were made:
1. Flooding the tank with at least 4' of water immediately after the connection blinds are installed, and maintaining this water level in the tank until the manpower is available to remove the manways and begin cleaning the tank.
2. The cleaning process to begin immediately after the tank is opened.
3. The incident clearly shows how rapidly pyrophoric scale can react following a drying out period and then exposure to the air. Refineries must pay particular attention to this aspect when tanks are known or suspected to have been on 'sour duties' and adjust their procedures accordingly, for example cross flows of air (i.e. opposite manholes open) should be avoided at the early stage, keeping deposits well wetted down with water.

1265623 August 1990

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

A fire occurred on a methanator. The vessel was found to be deformed and had a 3-4 inch rupture at a position corresponding to the top of the catalyst bed.
It is though that the incident was caused by ethylene entering the methanator. The ethylene reacted with hydrogen on the nickel catalyst, resulting in a very rapid release of energy.
The corresponding temperature rise was sufficient to cause a ductile failure of the vessel.
The proposed mechanism for the reaction is that ethylene vapour entered the methanator via the cold box where there was a low pressure/high temperature following the trip. On repressuring, the ethylene was carried forward through the 90% hydrogen line to the methanator.
[runaway reaction, fire - consequence, reactors and reaction equipment]

Lessons

[None Reported]

5053 17 July 1990

Source : THE WASHINGTON TIMES, 1990, 18 JUL.
Location : Glenelg; Baltimore; Maryland, USA

Injured : 17 **Dead :** 0

Abstract

A chlorine gas cloud formed at a swimming pool when hydrochloric acid was accidentally mixed with chlorine. A correct label had fallen off or been removed from the can of hydrochloric acid and a hand written label that remained indicated the can contained chlorine.
[gas / vapour release, accidental mixing, labelling incorrect, operator error, containers]

Lessons

[None Reported]

1293905 July 1990

Source : ICHEME
Location : ,

Injured : 1 **Dead :** 0

Abstract

A small flash fire occurred in the cell of a plant as an operator was emptying a process vessel of a molecular sieve laden with organic peroxide into a water bath. The operator sustained minor burns.
An investigation into the incident found that the operator had not followed the procedure and created a ration of molecular sieve to water, which caused excessive heat generation and vaporisation of organic peroxide. It is thought that somewhere within the molecular sieve a local temperature hot spot was generated sufficient enough to cause autoignition of the flammable vapour.
[fire - consequence, processing, design or procedure error, injury]

Lessons

The following recommendations were made:
The water bath is to be earthed to remove the possibility of static electricity as an ignition source, and a temperature indicator installed in the bath to provide a criteria by which the sieve emptying operation can be controlled.

7489 30 May 1990

Source : LOSS PREVENTION BULLETIN, 094, 30.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A transportation incident. A runaway chemical reaction on a tanker triggered the evacuation of 2000.
[runaway reaction]

Lessons

[None Reported]

4998 29 May 1990

Source : HAZARDOUS CARGO BULLETIN INCIDENT LOG, 1990, AUG.; TOXIC MATERIALS NEWS, 1990, 6 JUN.
Location : Freeport; Texas, USA

Injured : 0 **Dead :** 0

Abstract

Error at chemical plant caused addition of dichloropropane to the tank of a marine chemical tanker containing 2-(2-aminoethylamino) ethanol. Gas containing ammonia and hydrogen chloride released causing the evacuation of 2000 people and closure of the waterway.
[gas / vapour release, contamination, accidental mixing, marine tanker, transportation]

Lessons

[None Reported]

4983 14 May 1990

Source : SEDGWICK LOSS CONTROL NEWSLETTER, 2ND QUARTER, 1990.
Location : Tomsk; Siberia, USSR

Injured : 0 **Dead :** 0

Abstract

An explosion occurred in a new 300,000 tonnes per year ethylene cracker, one of four production lines. Major fire around fractionation area. The incident was caused by failure of a separation column where incorrect steels had been specified during the design phase.
[incorrect material of construction, mechanical equipment failure, fire - consequence, separation equipment, design fault, cracking]

Lessons

[None Reported]

4937 20 March 1990

Source : LLOYDS LIST, 1990, 21 MAR.; HAZARDOUS CARGO BULLETIN, 1990, MAY; THE GUARDIAN. 1990, 21 MAR.; CATES A.T, FLUORAROMATICS EXPLOSION 20 MARCH 1990 ASSESSMENT OF THE EXPLOSION AND OF BLAST DAMAGE, JOURNAL OF HAZARDOUS MATERIAL 1992, 32, 1-39; MOONEY D.G, AN OVERVIEW OF THE SHELL FLUOROAROMATICS PLANT EXPLOSION, HAZARDS XI SYMPOSIUM, UMIST,MANCHESTER, 16-18 APRIL 1991, ICHEME NORTH WESTERN BRANCH, 1991; LOSS PREVENTION BULLETIN, 100, 21-25.

Location : Stanlow; Cheshire, UK

Injured : 5 **Dead :** 1

Abstract

A runaway reaction caused vessel rupture and congested fire ball in a chlorofluoroaniline production unit. 95% of the plant was destroyed and debris was projected up to 300 meters away. The reactor vessel was used for the manufacture of 2,4-difluoronitrobenzene (DFNB) from 2,4-dichloronitrobenzene (DCNB) by reaction with potassium fluoride in the presence of dimethylacetamide (DMAC) as solvent.

The most likely description of events is as follows:

1. There was a runaway reaction in the reactor vessel, evolving some gas (almost certainly ketene and carbon dioxide), which caused the pressure to rise rapidly once the vessel approached its process temperature.
2. As the pressure rose, the safety valve blew. A flange (or similar) failed above the vessel and gave rise to a fire. The jet fire carried on burning for at least 30s before vessel failure.
3. The vessel burst, at a pressure of around 60-80 bar. The vessel fragments tore into two major and several minor fragments. The vessel fragments, and many surrounding pieces of plant work, were turned into energetic missiles, which flew up to 500 m away. The contents of the vessel did not denote.
4. As the vessel failed, the vessel contents continued to release energy, entrained air and rapidly ignited. The entrainment of air and combustion were greatly speeded up by the highly congested environment in which the vessel failure took place. The blast wind from this combustive event probably increased the number and severity of the missiles.
5. A large fire ball extending outside the structure occurred. A secondary fire started, which quickly involved the inventory of some nearby xylene storage vessels.

After the explosion, substantial amounts of acetic acid were found in various vessels and in the solvent recovered for recycling to the reactor. Laboratory-scale trials then showed that acetic acid would react vigorously with DCNB, heating the reaction mixture to about 240 degrees C, at this temperature a second exotherm started leading to an explosive decomposition. The problem facing the investigation was how did acetic acid come to be present in significant amounts?

They knew or had established the following:

1. Eighteen days before the explosion a holding tank for the reaction product and a filter had been washed out with water and some of the water passed through two leaking valves into the vessel in which the reaction product was stored before distillation.
2. Water reacts with DMAC forming acetic acid.
3. An azeotrope of DMAC and acetic acid has a similar boiling point to DMAC so it was recycled to the reactor with the recovered DMAC.

Water contamination had occurred before without causing any problems and any water present was normally removed at the start of the batch distillation. On this occasion there was so much water present that, unknown to the operators, it formed a separate, upper layer in the distillation column feed vessel. This layer was pumped into the distillation column during the later, high temperature stages of the distillation when the operators thought that all the water had been removed, acetic acid was formed, distilled off with the DMAC and recycled to the reactor.

[reaction vessel, fire - consequence, fatality, batch reaction, injury]

Lessons

1. All processes to be looked at again after a number of years to see if, in the light of new knowledge and new techniques, they present any hazards.
2. When a new process is being developed (or old one re-examined) all impurities which could plausibly be present should be identified.
3. Similarly, when a new process is being examined (or an old one re-examined) possible deviations from flowsheet conditions must be examined to see if they reduce safety margins, particularly the gap between operating and runaway temperatures.
4. Follow up unusual observation.
5. Any sudden change in pressure or temperature on a batch reactor will trigger an alarm.
6. Data that might be needed for investigation must be recorded in a way that will survive fire and explosions. The source of a problem may be far in distance or time from its effects.
7. Alternative processes are said to be uneconomic but perhaps they justify further study.

4738 06 October 1989

Source : DAILY TELEGRAPH, 1989, 7 OCT.
Location : Whiston, UK

Injured : 0 **Dead :** 0

Abstract

A polyol and isocyanate were accidentally mixed causing a mile long gas cloud, resulting in the evacuation of people.
[accidental mixing, gas / vapour release]

Lessons

[None Reported]

4639 10 July 1989

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

An explosion and fire occurred in a storage tank of ethyl acrylate resulting in the roof being blown off. It is believed that the temperature inside the tank rose during the summer and polymerisation occurred.
[fire - consequence]

Lessons

[None Reported]

1313619 May 1989

Source : ICHEME

Location : ,

Injured : 0 **Dead :** 0

Abstract

Reaction products for an agrochemical product were charged to a 2,000 litre glass lined batch reactor one Friday evening. According to the process instructions, the reaction should have been started only after the addition of caustic soda on Monday morning. The reactants were left in the vessel at ambient temperature, without agitation or supervision, over the weekend. The thermal behaviour of the reaction mixture (without caustic soda) had not been investigated.

Contrary to previous weekends when a similar procedure had been followed, the reactants started to self-heat and a runaway reaction occurred after about 45 hours. Part of the batch was blown out of the reactor.

[batch reaction, storage, product loss, gas / vapour release, safety procedures inadequate, reactors and reaction equipment, uncontrolled reaction, overheating]

Lessons

Laboratory analysis revealed a high reaction and decomposition energy (potential adiabatic temperature rise 700 degrees C). Simulations based on this data showed a 'temperature runaway curve' similar to that shown in the incident, for a starting temperature of 28 degrees C - roughly in line with the ambient temperature over that weekend. Ambient temperatures for previous batches left in this way without overheating had been somewhat lower.

The following recommendations were made:

1. Process instructions must indicate at which steps the process may be interrupted without risk
2. Thermal behaviour of the reaction mixture must be measured and hazard analysis carried out.

1304509 May 1989

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

Reaction products for an agrochemical product were charged to a 2,000 litre glass lined batch reactor one Friday evening. According to the process instructions, the reaction should have been started only after the addition of caustic soda on Monday morning. The reactants were left in the vessel at ambient temperature, without agitation or supervision, over the weekend. The thermal behaviour of the reaction mixture (without caustic soda) had not been investigated.
Contrary to previous weekends when a similar procedure had been followed, the reactants started to self-heat and a runaway reaction occurred after about 45 hours. Part of the batch was blown out of the reactor.
[batch reaction, storage, product loss, gas / vapour release, safety procedures inadequate, uncontrolled reaction, overheating, batch reactor]

Lessons

Laboratory analysis revealed a high reaction and decomposition energy (potential adiabatic temperature rise 700 degrees C). Simulations based on this data showed a 'temperature runaway curve' similar to that shown in the incident, for a starting temperature of 28 degrees C - roughly in line with the ambient temperature over that weekend. Ambient temperatures for previous batches left in this way without overheating had been somewhat lower.
It was recommended that:
1. Process instructions must indicate at which steps the process may be interrupted without risk.
2. Thermal behaviour of the reaction mixture must be measured and hazard analysis carried out.

4531 04 April 1989

Source : THE WASHINGTON POST, 1989, 5 APR.
Location : Fairfax County, USA

Injured : 0 **Dead :** 0

Abstract

50 to 100 people evacuated when it was feared that two chemicals were mixed that would produce hydrogen cyanide.
[accidental mixing, evacuation]

Lessons

[None Reported]

4490 06 March 1989

Source : ICHEME
Location : , JAPAN

Injured : 3 **Dead :** 0

Abstract

Corrosion inside one of the outlet headers of an air fin fan cooler was caused by iron sulphide scale deposits accelerated by increased chloride content of fluid which itself was caused by a process modification which had resulted in decreased flow rate. Corrosion caused release of hydrogen rich gas with oil which ignited giving an explosion which caused 800 window glass damage.
[solids deposition, modification procedures inadequate]

Lessons

There is a technical lesson to be learnt about the corrosion of carbon steel under iron sulphide scale deposit in fluid containing hydrogen sulphide, ammonia and water.
1. Corrosion is fairly accelerated by iron sulphide scale deposits.
2. Corrosion is accelerated by chlorides which are concentrated in the scale.
3. Corrosion speed increases under tensile stress.

Safety management system
1. For such desulphurisation plant, management system of operation and equipment should be intensified to discover early and to measure any abnormal condition such as local corrosion.
2. Safety examination system should be reinforced for modification or new installation facilities.

4488 03 March 1989

Source : HAZARDOUS CARGO BULLETIN INCIDENT LOG, 1989, APR.; LLOYDS LIST, 1989, 4 MAR.; FIRE PREVENTION, NUMBER 222, 1989, SEP.
Location : Istanbul, TURKEY

Injured : 31 **Dead :** 11

Abstract

11 killed and 31 injured after an explosion and fire at a paint factory. Cause given as a chemical reaction. Fatality.
[runaway reaction, fire - consequence, processing, injury]

Lessons

[None Reported]

7617 30 January 1989

Source : LOSS PREVENTION BULLETIN, 129, 14.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A fire occurred near a quench tower in the reactor area of this synthetic fuels plant. The main process equipment, such as the quench tower and associated heat exchangers, was not seriously damaged by the fire, however, the piping, instrumentation and electrical equipment in the process area experienced substantial damage. The tower skirts and pipe rack supports were protected by three to four hour rated fireproofing, which prevented the failure of these structures and limited the amount of property damage.
The fire resulted when a 6-inch carbon steel pipe, which is the return line of the recycle system for the quench tower that cools and separates the synthol reactor product stream, failed as a result of corrosion/erosion. Iron particles in the oil stream, subjected to a zone of turbulence, were a contributing factor in the pipe failure. The failure of the pipe caused a release of hydrocarbon product that spontaneously ignited under the high pressure and high temperature operating conditions.
[spontaneous combustion, fire - consequence, pipeline failure, processing, damage to equipment]

Lessons

[None Reported]

2762 1989

Source : COMMUNITY DOCUMENTATION CENTRE ON INDUSTRIAL RISK, MAJOR ACCIDENT REPORTING SYSTEM LESSONS LEARNT FROM ACCIDENTS NOTIFIED, INSTITUTE FOR SYSTEMS ENGINEERING AND INFORMATICS, COMMISSION OF THE EUROPEAN COMMUNITIES JOIN RESEARCH CENTRE, 1991, ISBN 9282622894.

Location : ,

Injured : 0 **Dead :** 0

Abstract

Production of PVC proceeded without adequate ammonia addition. Hence, the excess of HCl produced caused coagulation of the latex. The mixer failed but there was no indication of it. Consequently, a local overheating was caused since steam of 165-175 degrees C was used (latex starts decomposition at 140 degrees C), but this was not detected. An expansion of coagulated latex clogged all the piping including the inlet to the safety valve. Not compensated HCl started to react with the reactor material. Though the steam supply had been stopped and external cooling started, the vessel burst because the wall thickness had been reduced from 9.8 mm to 2 mm. Activation of the sprinkler system enhanced reactor cooling and diluted HCl vapours.
[mixing, runaway reaction, design or procedure error, damage to equipment]

Lessons

1. A substitution of the plasticising agent and use of steam with a maximum temperature of 127 degrees C (latex starts decomposing at 140 degrees C).
2. Installation of a double signalling device on the mixer for the detection of malfunctions.
3. Interlock of the steam supply to the mixer so that steam supply will be automatically shut off in the case of agitator failure.
4. Installation of 2 independent temperature sensors. The steam supply will be automatically shut off in case any of the sensors indicates a temperature above 100 degrees C or when there is a substantial difference in the indications of the 2 sensors.
5. Installation of a level switch which will automatically shut down the steam supply when a high level in the reactor is reached.
6. All these steam shut-off actions will be coupled to an alarm indication in the control room. Batch control on quality, pH and persulphate content will be introduced.
7. During the process the pH will be monitored through regular sampling; the possibility of continuous pH-monitoring will be investigated.

2864 1989

Source : COMMUNITY DOCUMENTATION CENTRE ON INDUSTRIAL RISK, MAJOR ACCIDENT REPORTING SYSTEM LESSONS LEARNT FROM ACCIDENTS NOTIFIED, INSTITUTE FOR SYSTEMS ENGINEERING AND INFORMATICS, COMMISSION OF THE EUROPEAN COMMUNITIES JOIN RESEARCH CENTRE, 1991, ISBN 9282622894.

Location : ,

Injured : 2 **Dead :** 0

Abstract

Laboratory trials had shown that distillation of a crude 2-nitroimidazole compound at 100 degrees C under vacuum yields a pure product. This operation was repeated at pilot-plant scale in a 450 1 glass-lined reactor. As soon as the substance was dissolved and the reactor agitator was turned on, a yellow fume began to emerge from the closed manway. The pilot plant operator left the place and within seconds 2 successive explosions (blast 2.5 kg TNT equivalent approximately) were heard. The process plant was severely damaged, windows broke in a radius of 30 m, while windows of houses in the town 2 km away shook, 2 operators were slightly injured. Though danager of an explosion for this substance was suspected, no relevant data had yet been experimentally obtained. This was planned before the substance was to be used at production scale. The local police evacuated 2 nearby (100 m away) factories (300 people evacuated). The fire was already under control when the local fire brigade arrived on the scene. The smoke from the fire and the explosion drifted slowly (calm day) towards a nearby town, causing public concern. The manufacturer alleviated the public's fears by stating on national radio and TV that the smoke was not toxic.
[reactors and reaction equipment, evacuation, fire - consequence, damage to equipment, laboratory work, runaway reaction, safety procedures inadequate, injury]

Lessons

4234 22 July 1988

Source : LOSS PREVENTION BULLETIN 101, 1-2; SAFE USE OF CHEMICAL ADDITIVES, ICHEME, SAFETY TRAINING PACKAGE, 018, 3.6.
Location : Houston; Texas, USA

Injured : 0   **Dead :** 0

Abstract

A rail transportation incident. A stainless steel rail tanker carrying acid-washed methacrylic acid was in a plant siding when it was noticed that a pressure-relief valve was lifting. The area was secured and a remote fire monitor was set up to knock down the vapours. Several hours later the relief valve stopped lifting. An explosion of the tanker occurred approximately 20 hours after this incident. This was one of five tankers filled with acid-washed methacrylic acid. Previously this substance was loaded into tank cars lined with a phenolic resin material and this was the first time stainless steel had been used. The most likely cause was polymerisation of the methacrylic acid and failure of the relief valve on the tanker due to it being blocked with polymer. The polymerisation was caused by a combination of iron contamination from corrosion of the stainless steel by the lower acid layer normally present in acid-washed methacrylic acid and the hydroquinone inhibitor level being lower than the target specified for shipment.
[safety relief valve failure, incorrect material of construction, lack of stabiliser/inhibitor, modification procedures inadequate]

Lessons

The following recommendations were made:
1. The rail tankers normally used were coated with phenolic resin, this was the first time that a stainless tanker had been used.
2. The modification to the process should have been assessed to establish whether there was any hazard involved in the use of the stainless steel. In this case there was a hazard which had not been identified.

1078506 July 1988

Source : ICHEME
Location : , UK

Injured : - **Dead :** -

Abstract

This incident concerns the contamination of the public water supply from a water treatment works. This was caused by a supply of aluminium sulphate solution being discharged into the wrong tank.
A relief driver arrived to discharge his road tanker of aluminium sulphate solution at the water treatment works (which was, at the time unmanned). The regular driver had given him a key to obtain access, and verbal instructions as to where to discharge the solution. Once inside the works, the relief driver found what he thought was the correct storage tank to accept the load, and opened the cover using the same key. He then discharged the load and left (without any contact with water works staff).
The aluminium sulphate had in fact been discharge into the 'contact tank' (which fed treated water directly into the reservoir) instead of into the aluminium sulphate storage tank. Thus relatively high levels of aluminium were present in water supplies to a large number of consumers.
Complaints from consumers started later that day, however diagnosis of the real problem was delayed and confused by coincidental problems with lime dosing pumps, also causing low pH levels in the treated water. It was not until two days later that the true reason for the incident was discovered.
The contaminated water caused widespread alarm and discomfort amongst consumers (although probably little long-term health effects). Flushing of the contaminated water into rivers (to clear the distribution system) led to substantial fish kills.
[material transfer, unloading, pollution, poisoning, ecological damage, incorrect chemical concentration, chemicals added incorrectly, driver error, safety procedures inadequate, storage tanks, contamination]

Lessons

A detailed enquiry and report was produced: this recommended a number of improvements:
1. More rigorous control of key security.
2. More rigorous systems for receiving goods.
3. Improved monitoring instruments for final treated water quality.
4. Better labelling of installations.
5. Improved emergency procedures, both in terms of response to the incident and to communications with the public.
6. Adoption of the Hazard Study technique.

7515 28 June 1988

Source : LOSS PREVENTION BULLETIN, 122, 9-10.
Location : ,
Injured : 0 **Dead :** 5

Abstract

The accident occurred in a plant making dyes and a chromate dip for electroplated products. These products were treated in a series of open-topped tanks located in a sub-basement, known as the zinc-plating room, which contained two parallel rows of tanks separated by a grated walkway. A concrete drainage pit lay beneath the walkway. Ventilation in the zinc-plating room was provided by two ceiling exhaust fans, five windows and the door to the room were closed at the time of the accident.
The last tank in the series, where the accident occurred, was used for drying parts after they had been electroplated. The tank measured 1.5 x 1.2 x 1.5 metres. The parts were suspended above the tank, and excess zinc cyanide solution dripped into the tank. Waste zinc cyanide was pumped from the tank once each year.
On the day before the accident, an industrial cleaning and hauling company pumped the waste from the tank, leaving a layer of zinc cyanide sludge in the bottom. On the day of the accident the night shift leader began preparations to clean the remaining sludge by spraying 1 or 2 gallons of hydrochloric acid into the drying tank.
After investigation it was concluded that the night shift leader unknowingly created hydrogen cyanide, a highly toxic compound, by combining sulphuric acid and zinc cyanide, two commonly used industrial chemicals. Hydrogen cyanide acts to block absorption of oxygen by the lungs and can cause death.
After adding the sulphuric acid, the night shift leader, who worked alone and wore no respirator, climbed a ladder and descended into the tank. He did not test or ventilate the tank before entering. After several minutes, co-workers saw him struggling to climb out of the tank.
Four other workers attempted to help and were quickly overcome. Two were forced back by the vapours. The other two collapsed, one inside the tank and the other with his head hanging over the edge. Fatality.
[accidental mixing, testing inadequate, entry into confined space, safety procedures inadequate]

Lessons

Chemical safety.
Ensure that good chemical safety practices are followed in the workplace:
1. Chemicals must be clearly labelled. Labels must be legible and in English. Warnings to be provided in other languages, as necessary.
2. More emphasis must be placed on dangers that can result from combining chemicals. Workers to be trained to recognise and anticipate hazardous chemical reactions.
3. Materials safety data sheets must provide necessary warnings as well as other important information on chemical hazards.
Ensure that confined spaces are clearly identified and that workers can perform tasks safely within these areas.
1. Workers must be trained to recognise confined spaces, and management must take appropriate precautions to ensure that work is performed safely.
2. A confined-space work plan must include a method or plan for rescue. The safest methods for confined-space rescue do not require that rescuers enter these hazardous areas. Body harnesses, safety lines, and reliance on the buddy system can prevent unnecessary risks.
3. Entry permit systems are a must, and issue of these is likely to be subject to environmental analysis for toxic or flammable gases, and oxygen content.
Ensure that all personnel know what to do in the event of an emergency.
1. Notify authorities immediately when an emergency occurs. Workers or supervisors who are likely to witness or discover an injured or collapsed co-worker should be trained to initiate an emergency response sequence.
2. Ensure that workers (first responders at the operations level) are training to take appropriate actions and precautions. Workers must never enter a confined space for the purpose of rescue without suitable breathing apparatus.
3. Ensure that all emergency response personnel are properly informed and trained. In this instance, emergency response crews were initially unaware that hydrogen cyanide was involved.

4211 28 June 1988

Source : THE SUN BALTIMORE, 1988, 29 JUN.; HAZARDOUS CARGO BULLETIN INCIDENT LOG, 1988, SEP.
Location : Auburn; Indiana, USA

Injured : 14 **Dead :** 4

Abstract

Two incompatible chemicals mixed to produce cyanide gas at a metal plating plant. No explosion. Fatality.
[accidental mixing, hydrogen cyanide]

Lessons

[None Reported]

4192 15 June 1988

Source : HAZARDOUS CARGO BULLETIN INCIDENT LOG, 1988, SEP.
Location : Akita, JAPAN

Injured : 0 **Dead :** 0

Abstract

A marine transportation incident. Spontaneous combustion in hold with fishmeal. 10000 kg carbon dioxide injected to quell fire.
[fire - consequence]

Lessons

[None Reported]

4012 04 November 1987

Source : LLOYDS LIST
Location : Oran, ALGERIA

Injured : 0 **Dead :** 0

Abstract

A marine transportation incident. Fire in hold of marine vessel carrying Peruvian fishmeal due to spontaneous combustion.
[fire - consequence]

Lessons

[None Reported]

1018601 November 1987

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

A fire occurred in and around the hot loop separator of the acrylates distillation unit. Prior to the fire, the unit had been processing a liquid monomer, HEMA (hydroxy ethyl methacrylate). Being a monomer, this liquid has the propensity to polymerise and in doing so form a solid. The formation of this solid in the separator is the most frequent cause of process failure. The day before, the process failed due to a bulk polymerisation in the separator. The unit was left drained and vented overnight.
The separator lid was removed the day after and it was commented that the separator was remarkably fume free. The inside of the vessel was inspected and some large lumps of polymer were removed from the top and placed on the open grid flooring adjacent. The fumes were quite bad by this time. An air hose was introduced to disperse the fumes. To effectively clear such a polymer build-up, a process operator returned to the acrylates structure to start water washing 20 minutes later. Fires on the lower floors were spotted (caused by falling burning debris or polymer igniting the cable trays and other material) and extinguished and the fire alarm was raised. The operator reached the top floor and flames were rising to a height of 2-3 feet from the separator.
[distillation, separator, fire - consequence, spontaneous combustion, polymerisation]

Lessons

Since a fitter is required in order to remove any item of plant, water flushing can only be carried out when maintenance personnel are available. The polymer may then be left in the separator at elevated temperatures for a prolonged period before the separator lid is removed. HEMA polymer now removed from the separator is then still hot and may still be reactive.
Putting large lumps of hot polymer onto the open grating must be regarded as placing the material in a 'forced draught' since the structure is largely open with only the top floor enclosed. The introduction of an air hose must also be considered 'forced draught'. Both locations experienced similar conditions - hot hydrocarbon exposed to excessive fresh oxygen supply which must be regarded as hazardous.
It is the opinion of the incident investigation team that the hot HEMA polymer exposed to a forced draught had spontaneously ignited. The following was recommended:

1. A detailed operating procedure for removal of polymer must be devised and adhered to i.e. copious water dousing, breaking down large growths into small lumps, polymer removal in sealed containers, complete isolation from ventilated environments.
2. Other divisions should be made aware of the incident
3. Further laboratory investigation should be undertaken to gather appropriate data and to assist in understanding the mechanisms of the incident.
4. Mechanical inspection of the separator should be undertaken following six months of operation
5. Re-iteration of the emergency procedures should be undertaken with the site fire teams in the light of experience gained from this incident.
6. The importance of good housekeeping must be made plain to the production and project departments with respect to contract labour.

7933 22 August 1987

Source : ICHEME
Location : ,

Injured : 0   **Dead :** 0

Abstract

The failure of a plug on a hot wax pump allowed product which was above autoignition temperature to be released. This resulted in a major fire on a vacuum unit.
Nobody was injured but fire damage was estimated at £200,000 (1987). The electrically driven heavy-wax take-off pump was running at the time of the incident. When the fire was extinguished it was discovered that a plug from the pump casing was missing.
This was found near the pump. Product had been released above auto-ignition temperature through this hole.
The heavy wax off-take temperature was 385 degrees C.
After investigation, it was clear that the plug was in carbon steel instead of in a chromium alloy similar to the material of the casing of the pump (13% chromium). The plug was not sealwelded.
It was judged that over the years the plug material inside the pump casing had been corroded by the heavy wax. It had corroded to such an extent that finally the plug had blown out and caused the incident.
This theory was confirmed by further investigation. The threaded part of the 3/4" plug was only 10mm long where it should be minimum 16mm, according to the ANSI B16.11. The difference corresponds to the corrosion rate found on carbon piping in this service.
Three other plugs on the same pump were retained only by 1 or 2 threads and corroded in the same way as the plug that had blown out.
During the emergency shut down of the vacuum unit the materials of the plugs and piping on hot pumps were checked and changed out as necessary. All plugs were sealwelded.
An inspection programme was set up to check hot pumps on other units. Also the system for the issuing of spare plugs from the stores is to be modified.
[pump failure, fire - consequence, incorrect material of construction]

Lessons

It is not known when the four plugs on this pump were last changed or whether they were the original plugs. If they had been changed at some time in the past this incident clearly shows the importance of ensuring that only correct spares or replacement parts are used and full regard must be given to manufacturers' drawings and specifications. Also it highlights the need for proper inspection of equipment by maintenance engineers on completion of maintenance but prior to recommissioning.

1048022 June 1987

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

A fire started during a venting operation at the base of a reactor used for processing hydrocarbons on Monday 22 June 1987 at 1955 hours. It was fierce, but quickly extinguished by the sire fire service. There were no injuries. Damage was local and confined to instrument boxes and piping, cables and valve packing.
The reactor was being prepared for engineering work. In order to clear the contents and inert the vessel it was pressurised with nitrogen to 6 bar gauge and then vented to flare six time. The reactor was left sitting at 6 bar gauge pressure, and it was then decided to vent it again using a blanked off vent valve near the base. On opening the valve a small quantity of liquid emerged. The operator attempted to hose the spillage away. On contact with the water there was an immediate ignition.
Investigations suggested that a dead leg leading to the vent contained liquid hydrocarbon residues and fines of catalyst, which was metallic sodium. The water and sodium reacted violently and ignited the hydrocarbon.
[processing, maintenance, cleaning, reaction vessel, venting, vent, fire - consequence, sodium, water, hydrocarbon, catalyst, spill, cleaning procedure incorrect, cleaning inadequate, additional chemical present, competency lacking]

Lessons

1. Even apparently thorough purging of the reactor, hazardous materials can remain in dead spots within the reactor. The operators were to be reminded of this.
2. Venting to atmosphere of streams containing catalyst is always going to be a potentially hazardous operation. In future this should be done to open areas, and the vent line exit submerged in water to deactivate the catalyst.
3. Ways should be investigated for venting hazardous streams to a closed vessel.

3925 10 June 1987

Source : REUTERS
Location : Schweizerhalle; Basle, SWITZERLAND

Injured : 0 **Dead :** 0

Abstract

A cloud of 15 kg of pyridine gas was released after a runaway reaction.
[gas / vapour release]

Lessons

[None Reported]

3901 29 April 1987

Source : INTERNATIONAL HERALD TRIBUNE, 1987, 30 APR.
Location : Basle, SWITZERLAND

Injured : 0 **Dead :** 0

Abstract

An accidental mix of two chemicals for textile dyes in a water treatment plant turned a river red.
[pollution, accidental mixing, drains & sewers]

Lessons

[None Reported]

3875 20 March 1987

Source : LLOYDS LIST, 1987, 23 MAR.; GAZETTA DEL SUD, 1987, 21 MAR.; LA REPUBLICA, 1987, 21 MAR.
Location : Augusta; Sicily, ITALY

Injured : 6 **Dead :** 0

Abstract

A marine transportation incident. A marine tanker arrived to collect a load of aviation gasoline but inspector said the tank was not clean. The tank was cleaned using toluene and steam combined with caustic soda. An explosion occurred.
[cleaning, aviation fuel, cleaning inadequate, gasoline]

Lessons

[None Reported]

11109December 1986

Source : HAZARDOUS CARGO BULLETIN, DECEMBER 1986

Location : , SPAIN

Injured : 0 **Dead :** 0

Abstract

A marine transportation incident. A cargo of methyl methacrylate monomer was being transported by sea, a five day trip. Samples were taken on loading and these accompanied the cargo. Some of the sample bottles exploded during the voyage and on arrival at a port, it was found that some of the cargo had polymerised. The reaction was not completed and the cargo was capable of being pumped ashore.
[polymerisation, explosion]

Lessons

This incident proves that it pays to monitor every possible indicator of how a cargo might be behaving throughout the voyage.

3789 20 November 1986

Source : INDEPENDENT, 1986, 21 NOV.
Location : Basle, SWITZERLAND

Injured : 0   **Dead :** 0

Abstract

Release of phenol after vessel overfilled leading to uncontrolled reaction. Leak.
[overflow, unwanted chemical reaction]

Lessons

[None Reported]

7972 09 September 1986

Source : ICHEME

Location : ,

Injured : 1 **Dead :** 2

Abstract

Two contractor employees were killed, and one other suffered a broken ankle, whilst cleaning out a crude oil rail tanker car on the premises of a specialist cleaning contractor.
No mechanical damage to the rail car or associated equipment was reported.
Rail cars that had been used for carrying crude oil were delivered to a specialist cleaning contractor for the removal of sludge deposits. Due to the limited information available it is not possible to confirm the details of the gas freeing and cleaning techniques adopted by the specialist cleaning contractor. However, it is known that one stage of the operations did involve the entry of two contractors into the rail car to clean out the residual sludge. During this manual sludge removal operation it was noticed that the sludge discharge chute was not fitting correctly at its point of contact with the disposal skip. As a result one of the two contractors positioned around the skip decided to solve the problem by grinding off a section of the chute. The resulting sparks from the grinding operation ignited the sludge in the chute causing a flashback into the top rail car.
There was a short duration fire which killed the two men inside the rail car. The man at the top of the rail car jumped to safety, but in doing so broke his ankle in the fall.
An investigation into the incident revealed that the cause was due to the ignition of a flammable mixture in the discharge chute by sparks from the grinding operation. Fatality.
[solids deposition, hot work, entry into confined space, fire - consequence]

Lessons

[None Reported]

3674 15 July 1986

Source : THE EVENING SUN, 1986, 15 JUL.
Location : Anne Arundel County; Baltimore, USA

Injured : 4 **Dead :** 0

Abstract

Chlorine and hydrochloric acid mixed at swimming pool.
[accidental mixing]

Lessons

[None Reported]

1110810 June 1986

Source : FIRE PREVENTION NO. 195, DECEMBER, 1986.
Location : , UK

Injured : 0 **Dead :** 0

Abstract

Three adjacent 19th century buildings had been converted into office use but the continuous rood void was retained.
A workman was stripping paint from the facia of one of the buildings at a place where a cavity wall existed between two buildings. A fire started in the cavity and spread to the roof where large volumes of paper and files were stored. These fed the fire which damaged two of the three buildings, causing a £250,000 (1986) loss.
The workman thought that he had put out the original cavity all fire, but alerted the fire-brigade anyway, which was fortunate.
[fire - consequence, damage to equipment, storage, hot work, polymerisation]

Lessons

[None Reported]

3637 03 June 1986

Source : INDEPENDENT LOCAL RADIO NEWS, 1986, 3 JUN.
Location : Clwyd; Wales, UK

Injured : 0 **Dead :** 0

Abstract

An explosion following accidental mixing of unknown chemicals in a tannery.

Lessons

[None Reported]

11269June 1986

Source : CHEMISTRY AND INDUSTRY, 3, NOV, 1986.
Location : , UK

Injured : 4 **Dead :** 0

Abstract

A runaway reaction at a chemical plant led to the discharge into the atmosphere of some 600 gallons of concentrated acid. A jet of acid droplets from a ruptured bursting disc reached a height of 50-100 feet. Thirty local residents complained of eye and skin irritation after being showered by the falling acid. Four required hospital treatment.
The chemical plant makes mono-nitroxylene (used in dyestuffs manufacture) in the reactor that burst. Normally xylene in the tank is nitrated by the slow dropwise addition of mixture of concentrated sulphuric acid and concentrated nitric acid. 14 of 15 batches required had been made without any problems. An operator sought xylene from another part of the factory to complete the final batch. Unknown to the operator a 45 gallon drum labelled as xylene actually contained methanol.
When the acid mixture was added to the methanol a violent exothermic reaction followed. Plant operators struggled to control the reaction which caused a sharp increase in pressure within the tank. Eventually the tank ruptured via a bursting disc.
The company was prosecuted and sections 2 and 3 of the Health and Safety at Work Act
[gas / vapour release, bursting disc failure, reactors and reaction equipment, accidental mixing, reaction, labelling incorrect, injury]

Lessons

All chemical must be stored in correctly labelled containers.

1211512 April 1986

Source : FPA CASEBOOK OF FIRES, APRIL 1986.
Location : , WEST GERMANY

Injured : 0 **Dead :** 0

Abstract

A fire occurred which destroyed two textile warehouses and caused approximately £1.5 million (1986) damage. The fire is thought to have been caused by a cigarette or from spontaneous combustion inside a container of textiles and was not the result of arson.
[fire - consequence, damage to equipment]

Lessons

[None Reported]

7948 19 March 1986

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

A 180/200 pen bitumen tank which was known to be in poor condition with holes appearing in shell plates, was seen to be on fire during a transfer to a coastal vessel.
The tank was heated by electrical heaters, these being switched off at the 1m level, and the tank continued lowering to 0.2m level when smoke was noticed coming out of the tank.
The tank shell was cooled with water and initial attempts made to extinguish the fire with dry powder. This was called off as it was difficult to get access, and eventually the fire was extinguished by injecting nitrogen into the tank via a temporary 1/2" supply line.
The primary cause of the fire is thought to have been due to the long time that the tank had been in service, and with air drawn through various holes, during the lowering of the bitumen level, causing pyrophoric material on the underside of the roof to become incandescent and fall off onto the bitumen.
[fire - consequence, spontaneous combustion, material transfer]

Lessons

[None Reported]

7950 March 1986

Source : ICHEME
Location : ,

Injured : 0   **Dead :** 0

Abstract

Heat transfer oil leaked from the heating coil into the bitumen tank. The oxidised bitumen transfer temperature to storage was above that recommended in the IP Bitumen Safety Code (230 degrees C maximum), and it is probable that due to earlier degradation of the heat transfer oil the latter auto-ignited.
[autoignition]

Lessons

[None Reported]

102601986

Source : ICHEME
Location : , NETHERLANDS

Injured : 0 **Dead :** 0

Abstract

A marine transportation incident. An incident occurred on a chemical carrier loaded with methyl methacrylate monomer. During a five day trip, bottled samples taken from the vessel's tanks exploded.
On arrival at the port, arrangements were made to discharge the parcel of methyl methacrylate monomer first but, in spit of this, some polymerisation had occurred in the tank before the discharge was finished. However, it is possible to remove polymerised cargo mechanically from the tanks as well as from the pipes and pumps.
[explosion]

Lessons

There is no doubt that the comparatively short journey helped to avoid far greater problems. If the trip had been twice as long, the polymerisation would most probably have resulted in widespread solidification of the cargo and damages to the ship.
The obvious lessons learnt here is that it pays to be alert for possible reactions in the cargo if it is observed that samples kept onboard are themselves undergoing change during the voyage.

127311986

Source : COMMUNITY DOCUMENTATION CENTRE ON INDUSTRIAL RISK, MAJOR ACCIDENT REPORTING SYSTEM, LESSONS LEARNED FROM ACCIDENTS NOTIFIED, EUR 13385 EN.

Location : ,

Injured : 1 **Dead :** 0

Abstract

An explosion occurred in the condenser of a reactor due to a runaway reaction. The incident occurred due to an accidental error in the order of introducing acids causing the formation of methyl nitrate, which in turn caused a runaway reaction. A worker was injured in the incident and damage to equipment occurred.

Chemicals involved: sulphuric acid, nitric acid.

[reactors and reaction equipment, operator error, injury]

Lessons

[None Reported]

127321986

Source : COMMUNITY DOCUMENTATION CENTRE ON INDUSTRIAL RISK, MAJOR ACCIDENT REPORTING SYSTEM, LESSONS LEARNED FROM ACCIDENTS NOTIFIED, EUR 13385 EN.

Location : ,

Injured : 30 **Dead :** 0

Abstract

An uncontrolled exothermic polymerisation occurred due to a loss of power supply. The condenser could not be started. The injection of ethyl benzene to limit the polymerisation was unsuccessful. The pressure in the reactors rose causing the rupture of the bursting disks and release of the reactor's content. A false indication in the control room probably cased a delay in taking action.
Thirty people were injured in the incident.
[uncontrolled reaction, electrical equipment failure, injury]jury]it created concern. Then a rapid exothermic reaction occurred within the

Lessons

Following the incident, a redundant bank of the condenser and redundant sensor to follow the evolution of polymerisation has been installed.

126801986

Source : ENDS REPORT 151, AUGUST 1987.
Location : Yorkshire, UK

Injured : - **Dead :** 0

Abstract

Sulphuric acid and nitric acid sprayed from a plant. The incident occurred due to the mislabelling of a storage tank resulting in a drum of methanol, instead of xylene, being fed to a nitration reactor. Several people were affected.
The company was fined £2,000 (1986).
[gas / vapour release, labelling incorrect, storage tanks, accidental mixing, material transfer, drums, reactors and reaction equipment]

Lessons

8028 02 November 1985

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

During a unit shutdown a fire was discovered inside the visbreaker fractionator tower.
The fire was brought under control although minor pockets of burning continued until eventually burning out. The fire severely damaged the vessel and caused buckling in trays 19-21. No personnel were injured. Major repairs, at a cost of about £180,000 (1985), on the column were necessary before it was brought back on line some 87 days after the incident.
Investigation concluded that the incident was caused by autoignition of pyrophoric material which in turn ignited extensive coke deposits on the region of trays 19-21. With four out of the five manways open adequate draft was available to fan the flames and produce intense heat which eventually led to the tower buckling in that region.
[cracking equipment, separation equipment, fire - consequence, damage to equipment]

Lessons

The following recommendations were made:
1. All operators made aware that pyrophoric materials may be present which can ignite even though the column/vessel has been gas freed. The need for vigilance in this respect be over-emphasised because no matter how good the shutdown procedure, it is only by close observation of the equipment that occurrences of this sort can be avoided.
2. Consideration should be given to re-instituting the practice of water or dilute sodium carbonate washing depending on the equipment materials of construction (e.g. alloy linings in vessels makes water washing a problem due to chloride attack).
3. Adequate means of dealing with coke ignition should be made available at site should such an incident occur. One method that could be used is the exclusion of air by rapidly replacing the manhole covers and the introduction of steam or nitrogen into the column.
4. A ready supply of water should be made available to dampen down any pyrophoric "coke" material to prevent re-ignition.
5. The coking of visbreaker fractionators above the flash zone results from low liquid loadings on the trays in this section caused by such factors are:
· The maximising of gas oil offtake during operation.
· The use of residue quench as opposed to quench distillate.
· Poor feedstock quality causing low conversion rates with an associated low liquid loading in the column It is therefore important to set up a system to monitor the column's performance so as to highlight those occasions when the liquid loadings in the flash zone are too low and enable corrective measures to be taken.
6. Consideration to be given to modifying column internals.

3435 02 November 1985

Source : SEDGWICK LOSS CONTROL NEWSLETTER
Location : Jurong, SINGAPORE

Injured : 0 **Dead :** 0

Abstract

Deposits of coke on trays in distillation column ignited by spontaneous combustion of iron sulphide causing fire. Carbon.
[fire - consequence]

Lessons

[None Reported]

1192823 September 1985

Source : FPA CASEBOOK OF FIRES.
Location : , UK

Injured : 0 **Dead :** 0

Abstract

A fire occurred in the caustic chlorine section of a large chemical manufacturing complex. The incident was the result of a defective non-return valve allowing hydrogen to leak into a chlorine pipeline. Spontaneous combustion with two minor explosions ensued. The works fire brigade responded immediately, followed within 5 minutes by the county fire crews. Breathing apparatus and protective clothing was used to protect against the released chlorine. The fire was intense and the mains water supply had to be supplemented from a fire sump some 400 metres away. After 100 minutes the fire was brought under control. The estimated cost of the damage was £375,000 (1985).
[fire - consequence, hydrogen, damage to equipment, valve failure]

Lessons

Chlorine is normally produced by electrolysis of an aqueous solution of NaCl. Chlorine is liberated at the graphite anode of the electrolytic cell with sodium at the mercury cathode. The Na forms an amalgam with the mercury, which then flows into a second cell where it reacts with water to form hydrogen and a solution of sodium hydroxide.

3362 31 July 1985

Source : INTERNATIONAL PETROLEUM REPORTER, 1985, 1 AUG.; ICHEME.
Location : Dunkirk, FRANCE

Injured : 0 **Dead :** 0

Abstract

A flash explosion occurred during the start-up of an ethylene cracker following a maintenance shutdown. Various drainage operations involving hot fluids had been carried out during this time, into the sewers. The sewer network was made up of horizontal gathering lines with a hydraulic guard, studded with drain sumps either leading to the open air (protected by metal grating) or sealed off by a reinforced concrete plug. Some plugged drain sumps were equipped with vent pipes leading to the atmosphere, ending in a 180 degree bend. On the day of the fire the hydrocarbons blocked off by the hydraulic guard system, became heated up and degassed. A slight wind entrained the cloud of gas toward a burner. The fire was limited to two drain sumps, but it was sufficient to ignite the gas issuing from a vent. Passing underneath this vent equipped with a crosshead were some cables which caught fire.
[fire - consequence, damage to equipment, cracking, solids deposition]

Lessons

Solutions proposed
1. Systematic cleaning of the sewer line (hydrocarbon deposits).
2. Change in the vent outlet.

8018 01 July 1985

Source : ICHEME
Location : , GERMANY

Injured : 0 **Dead :** 0

Abstract

A heavy fuel oil line was taken out of service prior to being transferred to an alternative duty. The line was to be cleaned by filling with hot boiler feedwater (110 degrees C) and the line contents then discharged with a pig driven by cold hydrant water. The hot effluent from the line was transferred into the oily waste water system.
After the first cycle the line was not cleaned to an acceptable degree so it was decided to repeat the operation. During the second cleaning operation, process personnel observed vibrations on some of the drain covers of the oily waste water drain system followed by the emission of vapour and liquid from these drains. The cleaning operation was immediately halted and cold hydrant water fed into the oily waste water drains.
However, before this achieved the desired effect the contents of the latter were blown out through the drain covers in this area.
An explosion then occurred in the nearby AS and emergency power unit building blowing open its doors and igniting the gas cloud and pools of liquid between the platform II and the station.
The result was a small fire which was quickly put out by the site fire brigade.
Apart from superficial damage to the power building, there was no other damage to equipment and no one was injured.
Cause of the Incident:
The subsequent incident investigation concluded that heating by near boiling water led to spontaneous vaporisation of hydrocarbons. This caused a pressure build-up in the drain system which culminated in the contents being blown to atmosphere. The resulting vapour cloud formed a flammable mixture which then entered the power unit building via the forced ventilation system.
It is believed that the associated electrical switch relay situated inside the building and immediately beneath the air inlet louvres ignited the vapour.
[cleaning inadequate, spill, gas / vapour release, fire - consequence, damage to equipment]

Lessons

The following recommendations were made:
1. To review oily waste water facilities to ensure where possible that draining near boiling liquids and light hydrocarbons into the system is avoided.
2. To modify site procedures and instructions to ensure that when the draining of such liquids is unavoidable all aspects of the hazards and risks involved have been fully addressed and the appropriate precautions taken.
3. To ensure that all site operating and maintenance personnel (employees and contractors) and in particular their supervisors are fully aware of the hazards involved in allowing hot water or near boiling liquids to enter an oily waste water drainage system. The refinery should ensure that when contractors under their control are entrusted to carry out such work that they are fully satisfied with the competence of such contract personnel and their ability to carry out the agreed work programme safely.

3262 21 March 1985

Source : ICHEME

Location : ,

Injured : 0 **Dead :** 0

Abstract

A fire and explosion occurred on a reactor involving ethylene on a petrochemical polyethylene plant caused by auto decomposition.
[fire - consequence, reactors and reaction equipment, processing]

Lessons

[None Reported]

7959 21 January 1985

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

A leak developed from an eductor pressure gauge during a tetramethyl lead (TML)/gasoline blending operation.
Investigation of the shutdown system, revealed that the leak resulted from hairline cracking on the bourdon tube of the pressure gauge.
Two technicians were assigned to the TML blending operation at 0300 hrs. The operating steps taken were correctly carried out according to detailed instructions.
Vibrations of the eductor and associated piping/gauges had been observed at every TML blending when throttling down the bypass valve of the eductor. This is because of cavitation in the gasoline stream which caused rapid pressure fluctuations leading to the mechanical vibrations.
At 0555 hrs., one of the technicians returned to the TML blending area. He did not notice or smell anything abnormal initially because he had a cold, however, he subsequently saw a leaking pressure gauge downstream of the eductor. He radioed control room about the leakage and hurriedly left the area.
On instructions from the Acting Supervisor, two technicians, carrying canister respirators from the control room, returned to the site, and proceeded to shut down the system.
Under cover of water spray protection and using canister respirators, the two technicians isolated the ball valve of the leaking pressure gauge. They continued washing the piping, valves, surroundings, etc. with water for the next 20-30 minutes. The spillage was confined within the bunded area of the TML Meter Package Unit and flushed to the leaded slop pit.
The Shift Superintendent was informed and the Acting Supervisor came to the site. He detected the smell from a distance and did not go nearer.
By 0630 hrs., the situation was under control. The three personnel at the scene of leakage were advised by the Shift Superintendent to have medical check ups.
Cause of Incident:
Dye penetrant checks on both failed bourdon tubes revealed hairline cracks at similar locations with similar configurations. Subsequently, one of them was sent for metallurgical examination, and this pointed to stress corrosion cracking characteristic of austenitic stainless steel.,
Based on this information, the most likely theoretical cause of the stress corrosion cracking is the presence of moisture and organic chlorides environment.
The moisture most probably came from the gasoline circulation line while the organic chlorides are present in TML as 18.8% of EDC.
The secondary contributing factor is the mechanical vibration and pressure surge of the gasoline which aggravate the stress on the bourdon tubes.
[pressure meter/control, excessive vibration, tube failure, incorrect material of construction, processing]

Lessons

The following recommendations were made:
1. Modifications to be made to drain as much water from the blending components as possible.
2. The original specification of phosphor bronze bourdon tube pressure gauge to be reinstated. If for any reason not possible, then monel, inconel or ferritic stainless steel tubes can be used to avoid stress corrosion.
3. To reduce vibration, separate the gauge mounting from the eductor mounting using an impulse line with one or two anti-vibration loops. The material used will be compatible with the piping and gauge.
4. Compressed air breathing apparatus will be provided to deal with leakage, because the duration of leakage and concentration of the toxic leaded vapours is not predetermined and canister masks can be saturated even in an open ventilated area.
5. Whenever possible a technician should stay at site during the additive blending operations. If not possible, regular checks to be made of the area, to ensure the earliest warning is obtained should an emergency arise.
6. At least two complete sets of protective equipment to be readily available kept in UNLO.

110841985

Source : LLOYDS LIST, 25 JUN, 1985, 1 JUL, 1985, GUARDIAN, 1 JUL 1985.
Location : Los Angelese, USA

Injured : 0 **Dead :** 50

Abstract

An outbreak of the bacterial disease listeriosis was linked to contaminated cheese produced at a factory where raw milk had been mixed with pasteurised milk to increase production. Fatalities were concentrated among newborn or still born infants and the elderly and infirm.
[fatality, people, processing, safety procedures inadequate, contamination, accidental mixing, toxic chemical]

Lessons

[None Reported]

9895 1985

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

The chloride activated catalyst in a naphtha reforming unit has to be regarded by burning off coke. Shortly after coming back on stream after a regeneration, a leak development in the reactor effluent air cooler. During regeneration a bicarbonate solution was injected to the inlet of this cooler to prevent hydrochloric acid corrosion. It was found that the control for maintaining the composition of this solution for the whole regeneration period were inadequate. This was corrected and the injection point was modified to improve distribution of the solution.
[hydrochloric acid, start-up, fin fan cooler, blowout, cleaning inadequate, inspection inadequate]

Lessons

[None Reported]

8766 1985

Source : COMMUNITY DOCUMENTATION CENTRE ON INDUSTRIAL RISK, MAJOR ACCIDENT REPORTING SYSTEM LESSONS LEARNT FROM ACCIDENTS NOTIFIED, INSTITUTE FOR SYSTEMS ENGINEERING AND INFORMATICS, COMMISSION OF THE EUROPEAN COMMUNITIES JOIN RESEARCH CENTRE, 1991, ISBN 9282622894.

Location : ,

Injured : 0 **Dead :** 0

Abstract

After a reaction, in which raney nickel was used as a catalyst, had been completed, the reactor was to be flushed out by ethanol decanted from an 8 m3 capacity vessel. When the reactor was full, the manway was closed and heating started. After a certain period of time, the control room operator discovered that the temperature was 87 degrees C, well above the pre-set level of 70 degrees C. He shut off the heating but shortly afterwards the fire alarm in the area and the sprinkler system were activated. The flash fire was extinguished by the sprinklers system.
Post-accident investigation showed that the temperature control loop failed (controller output failed to update control valve position) and that the reactor manhole clamps were not fully tightened.
In addition, an examination of the remaining content in the ethanol vessel showed that the reactor was slightly overfilled. Consequently, ethanol vapours must have been emitted through the loose reactor manhole. The most probable ignition source could have been pyrophoric nickel material forced out of the reactor by the boiling ethanol at the partially closed manhole (the investigation revealed that all electric equipment in the area was functioning correctly).
[reactors and reaction equipment, fire - consequence, operator error, runaway reaction]

Lessons

1. Provide that the post-campaign flush-out batch sheet gives a warning of potential overfilling of the reactor;
2. Introduce proper manhole bolting practices;
3. Ensure that control room attendants carefully review all non-standard operations with local operators;
4. Update preventive maintenance plans to ensure that steam control valves and associated control loops are regularly checked.

3182 1985

Source : ICHEME

Location : , ITALY

Injured : 2 **Dead :** 0

Abstract

A reactor was charged with toluene diisocyanate and methylene diisocyanate followed by a mixed polyol and maintained at 80 degrees C for 2 hours. Shortly after a foam stabilizer and a flame retardant had been added there was a sudden temperature rise. Pressure rose and sheared the reactor top bolts and the cover was projected 2 meters. Investigation showed that one drum of the polyol was an amine polyol which should not have been added.
[charging reactor, reactors and reaction equipment, chemicals added incorrectly, contamination, damage to equipment]

Lessons

[None Reported]

3152 03 December 1984

Source : CONTROL OF EXOTHERMIC CHEMICAL REACTIONS, ICHEME TRAINING PACKAGE, 023; LEES, F.P, LOSS PREVENTION IN THE PROCESS INDUSTRIES, VOL 3, 2ND. ED., BUTTERWORTH HEINEMANN, 1996, ISBN, 0750615478; MANY NEWSPAPER REPORTS.

Location : Bhopal, INDIA

Injured : 200,0(**Dead :** 2000+

Abstract

The incident involved the release of 36 tonnes of methyl isocyanate (MIC) from storage tanks during the night.
MIC was an intermediate in the production of Carbamoyl, the active agent in the pesticide Sevin. The MIC was stored in two refrigerated underground tanks, due to MIC being unstable. A third tank was in place to take off-specification MIC. Originally the plant was designed to receive Carbamoyl and process it into Sevin.
During the 1970s local Carbamoyl production commenced, involving the production and storage of MIC. In the 1980s demand for pesticides diminished rapidly, the plant was mothballed and staff were made redundant.
There was a common line to the Carbamoyl reactor on which a relief vent header was placed. Rejected MIC was recycled to the tanks and contaminated MIC passed to a vent gas scrubber (VGS) for neutralisation. Each MIC tank had local and control room temperature and pressure instrumentation, a local level indicator and an alarm. Other safety items included a limited capacity flare system, fixed water monitors and refrigeration units on the MIC tanks. The flare could be used in combination with the VGS for larger releases. The refrigeration system which cooled the MIC in the refrigerated tanks was taken out of service in June 1984 and its refrigerant removed.
On 2 December 1984 the second-shift production superintendent ordered the MIC plant supervisor to flush out the pipework with water. Isolation that should have preceded the operation was neglected, allegedly due to redundancies in the maintenance department a few days earlier. Amongst other possibilities the water used for flushing may have found a sneak path to one tank.
At 23:30 operators noticed MIC and dirty water being released from the downstream side of the MIC tanks. By 00:15 the pressure in the tank had risen to 30 psi, minutes later it read 55 psi, the top of the scale. In the control room an attempt was made to start the VGS and the plant superintendent was called. On arrival he ordered the shutdown of the plant. The water sprays were turned on but only reached 15 m in height. The MIC was released at 33 m. An attempt was made to start the refrigeration system; this failed due to the lack of coolant. The toxic gas alarm was sounded to warn the local community. This was turned off a few minutes later, however, leaving only the plant siren to warn workers. It was reported that the earlier siren caused confusion among the people because those living in the neighbourhood rushed into the streets intending to put out what they thought to be a fire in the plant. The workers fled in the opposite direction to the toxic cloud.
The relief valve remained open for two hours. A tri-phase mixture of gas, entrained liquids and solids was released at a temperature of over 200 degrees C and pressure of over 180 psi.
[mechanical equipment failure, leak, underground storage, management system inadequate, fatality]

Lessons

1. Poor isolation of storage tanks and no valve position indicators fitted.
2. Excessive routes available for water to enter MIC storage tanks.
3. Large scale, long-term storage of hazardous process material under improper conditions.
4. Poor zoning policy.
5. Inadequate preliminary evaluation of the process leading to the production of hazardous intermediates.
6. Safety systems were inadequate and not functioning.
7. Inadequate modification and evaluation process.
8. Poor maintenance of pipework, valves and instrumentation.
9. Failure to manage change and select inherently safer process routes.
10. Lack of safety training and technical experience.
11. Absence of emergency procedures.

3117 08 October 1984

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

A runaway chemical reaction built up enough pressure to force the emulsion out of the process into a tank.
[runaway reaction, processing, high pressure]

Lessons

[None Reported]

3071 08 August 1984

Source : ICHEME
Location : Lavera, FRANCE

Injured : 3 **Dead :** 0

Abstract

A fire occurred on a refinery hydrocracker plant. Source of ignition was autoignition.
[fire - consequence, refining, cracking]

Lessons

[None Reported]

3064 August 1984

Source : SEDGWICK LOSS CONTROL NEWSLETTER
Location : Carville; Louisiana, USA

Injured : 0 **Dead :** 0

Abstract

High pressure differential caused ethylbenzene dehydrogenation reactor internals to fail with subsequent loss of catalyst to process. Petrochemical plant. Styrene unit.
[reactors and reaction equipment, processing, low level of catalyst]

Lessons

[None Reported]

1006517 July 1984

Source : ICHEME
Location : Pernis, BELGIUM

Injured : 1 **Dead :** 0

Abstract

An explosion occurred on board a barge whilst loading it's cargo into unwashed tanks which had previously carried industrial gas oil.
The barge carried 10 tanks of similar size and a closed ullage system was fitted to each tank in accordance with regulations. At the time of the incident, the loading rate was 600m3 per hour with 1,2,3 and 4 (port and starboard) tanks being loaded concurrently. All tanks were approximately full.
Tank levels were monitored by the skipper and his mate. This is usually done using the fixed ulllage system but the skipper was checking the level on the fixed internal ullage board due to a suspected malfunction on the gauge of No. 2 starboard tank. The sighting port and flamescreen were consequently opened.
After the ullage reading and coincidental with the flamescreen closing, and explosion/flash fire occurred in the area of the tank hatch. The skipper suffered burns to the hands and face and required hospital treatment.
The barge suffered structural damage in the No. 2 starboard tank, with small fractures in the forward and aft transverse bulkheads and distortion of the outboard bulkhead.
[marine transport, river transport, fire - consequence, damage to equipment, cleaning inadequate]

Lessons

The following possible ignition sources to be considered:
- pyrophoric ignition
- electrostatic discharge
- electrical (fixed ullage system)
- sources external to the tank and barge
- impact ignition

None of these can be considered a likely cause but in the absence of any positive evidence, the closing of the flamescreen was thought to be most probable.
The flamescreen seat was rusty steel and it is possible that rust particles or some of the iron slag used for shot blasting during the refit of the barge prior to the incident may have become embedded in the seat contributing to the production of an incendive spark on impact.
The following recommendations were made:
1. Regulations prohibiting barges handling low flash cargoes from opening tanks to atmosphere should be strictly enforced at all times.
2. When handling known static accumulator oils, the recommendations given in ISGOTT regarding initial loading rates should be observed.
3. Custom officials should be reminded that manual dipping of barge tanks is not a desireable practice and should be encouraged to read remote gauge readings. Fixing sounding pipes should be used if manual dipping is insisted upon. If a sounding pipe is not fitted, then during loading and for at least 30 minutes after completion of loading, no dipping, ullaging or sampling equipment should be lowered into the tank. This is to remove any possibility of an incendive discharge. After 30 minutes, great care must be taken to ensure the equipment lowered into the tank is electrically bonded to the barge structure.
4. Gas supplied to open flame cookers and heaters should be isolated at the bottle and the lockers in which the bottles are stowed to be either locked or sealed until operations have been completed.
5. Present checklists, as comnpleted by ship and shore, should be supplemented by both regular and spot checking of equipment and procedures by Jetty supervisors who are fully conversant with all safety regulations.

2884 10 January 1984

Source : INSTITUTE OF INSURERS
Location : , UK

Injured : 0   **Dead :** 0

Abstract

Spontaneous ignition of waste gases within empty bitumen tank following failure of thermostat. Subsequent overheating by heating elements.
[autoignition, mechanical equipment failure]

Lessons

[None Reported]

1054616 October 1983

Source : ICHEME
Location : , BELGIUM

Injured : 0 **Dead :** 0

Abstract

When preparing a polyethylene plant for start-up after a 2 week shutdown, a gas leak developed at the spindle of the shut-off valve in the high pressure product receiver tailpipe. The release of hot gas was automatically detected and the water sprinkler system activated. Excessive force of the motor of the tailpipe shut-off valve bent the spindle, and consequently created a gas leak. This was also considered to have been exacerbated by an autopolymerisation / decomposition reaction of ethylene in the tailpipe, which could have blown out the valve spindle packing.
[unwanted chemical reaction, seal failure, gas / vapour release, auto decomposition, separation equipment]

Lessons

The following was extracted from a comprehensive investigation report:
1. Review all procedures with regard to seal blowing - reduce pressures in the plant if there is not a polymer seal in the tailpipe.
2. Train Shift Operators.
3. Reduce the pressure to the valve actuators.
4. Review the tailpipe valve safety interlocks.

13052October 1983

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

An 8000-litre batch reactor had been charged with a raw material and solvent when a fault on the refrigeration plant caused an interruption of the process for several days. The allegedly non-reactive chemicals remained in the reactor without supervision and with the agitator running. This had been the practice several times in the case of delays.
After 6 days, smoke was seen coming from the reactor. The temperature had risen from
60 degrees C to 160 degrees C and was still rising. Although full cooling was now applied, tar-like material was thrown out of the manhole and after a very short time the reactor exploded, although the 450mm manhole was fully open.
[storage, batch reaction, stirrer, explosion, spill, auto decomposition, safety procedures inadequate, overheating, thermal degradation, batch reactor, agitator]

Lessons

The investigation showed that the contents of the reactor had been at the solvent boiling point of 116 degrees C for 3 to 4 days. Causes for the first step of the temperature rise were probably the energy input from the stirrer with insufficient jacket cooling and a leaking steam valve on the jacket.
The second part of the temperature rise to 160 degrees C was caused by the autocatalytic decomposition of the mixture.

13143October 1983

Source : ICHEME
Location : ,
Injured : 0 **Dead :** 0

Abstract

An 8000-litre batch reactor had been charged with a raw material and solvent: then a fault on the refrigeration plant caused an interruption of the process for several days. The allegedly non-reactive chemicals remained in the reactor without supervision and with the agitator running. This had been the practice several times in the case of delays.
After 6 days, smoke was seen coming from the reactor. The temperature had risen from 60 degrees C to 160 degrees C and was still rising. Although full cooling was now applied, tar-like material was thrown out of the manhole and after a very short time the reactor exploded, although the 450mm manhole was fully open.
[storage, batch reaction, stirrer, explosion, spill, auto decomposition, safety procedures inadequate, overheating, thermal degradation]

Lessons

The investigation showed that the contents of the reactor had been at the solvent boiling point of 116 degrees C for 3 to 4 days. Causes for the first step of the temperature rise were probably the energy input from the stirrer with insufficient jacket cooling and a leaking steam valve on the jacket.
The second part of the temperature rise to 160 degrees C was caused by the autocatalytic decomposition of the mixture.

2667 22 July 1983

Source : HAZARDOUS MATERIALS INTELLIGENCE REPORT, 1983, 29 JUL.

Location : Baton Rouge, USA

Injured : 0 **Dead :** 0

Abstract

A road transportation incident. A road tanker of styrene overpressured and lifted the relief valve to release styrene vapour. Polymerisation occurred.
[overpressurisation]

Lessons

[None Reported]

1047827 April 1983

Source : ICHEME
Location : , USA

Injured : 5 **Dead :** 2

Abstract

A spontaneous decomposition reaction of cumene hydroperoxide (CHP) took place in a 70 gallon head tank (which fed shot tanks, in turn feeding reactors). The decomposition caused an explosion killing 2 people and burning a further 5. CHP is an intermediate in the manufacture of phenol from benzene.
The plant had been re-started some 6 weeks previously after a shutdown period of about 3 years. The head tank had not been drained, cleaned or totally isolated from the CHP supply system during the shutdown. Prior to start-up, some black sludge had been found in the head tank: this had been flushed out. However, the bottom outlet line from the tank was a stand-pipe extending several inches up into the tank, thus creating a stagnant pool which would not drain. CHP is evidently a highly reactive material, and it its thought that the presence of sludge catalysed the rapid decomposition. However, there was no proof that this could occur at room temperature.
There had also been some problems with the CHP feed system to the head tank, and it is possible that the feed pump had become hot, and thus fed hot CHP to the head tank.
[processing, charging reactor, reactors and reaction equipment, fatality, contamination, cleaning inadequate, overheating]

Lessons

No firm conclusions were reached about the precise mechanism which triggered the decomposition. However it may well have been a combination of catalysis by impurities (sludge) and a hot feed stream due to pumping problems.

1021105 January 1983

Source : ICHEME
Location : , USA

Injured : 0 **Dead :** 1

Abstract

Following a massive over - injection of a chemical additive severe foaming occurred in a cooling tower. The dense foam covered a large area, obscuring the pit and surrounding area. An employee entered the foam to cut off the chemical tank valve and fell through an open aluminium grating which had been moved by the foam. Rescue attempts were severely hampered by the dense foam.
[organic phosphonate, polycarboxylic, acid salt, caustic soda, mixing, cooling tower, fall, chemicals added incorrectly, fatality]

Lessons

Fasten down all gratings, including recessed gratings, that are located in potentially hazardous areas.

8729 1983

Source : COMMUNITY DOCUMENTATION CENTRE ON INDUSTRIAL RISK, MAJOR ACCIDENT REPORTING SYSTEM LESSONS LEARNT FROM ACCIDENTS NOTIFIED, INSTITUTE FOR SYSTEMS ENGINEERING AND INFORMATICS, COMMISSION OF THE EUROPEAN COMMUNITIES JOIN RESEARCH CENTRE, 1991, ISBN 9282622894.

Location : ,

Injured : 1 **Dead :** 0

Abstract

A failure of the cooling system of a epichlorohydrin reactor. The polymerisation heat caused a pressure increase and an explosion inside the vessel and afterwards a fire. The fire threatened the safety of storage tanks containing ethylene oxide and trimethylamine, as well as the nearby plants. The population was alerted. The plant was destroyed. Windows broke outside the establishment. Inspection of the plant by a team of experts was decided following this accident.

[damage to equipment, fire - consequence, reactors and reaction equipment, cooling equipment, high pressure, processing]

Lessons

[None Reported]

2387 21 August 1982

Source : EXPLOSION OF CHEMICAL PLANT DUE TO RUNAWAY REACTION. HSE TRANSLATION 10780

Location : Sakai City, JAPAN

Injured : 198   **Dead :** 6

Abstract

After the first explosion on the 20th August, record 2386, the power supply was switched on the next day and the agitators started turning. A runaway reaction occurred in a mixing vessel. Fatality.

Lessons

[None Reported]

2369 09 June 1982

Source : ICHEME
Location : , USA

Injured : 0 **Dead :** 0

Abstract

Fire at a refinery Fluid Catalytic Cracker Unit (FCCU) plant involving a pipe and fuel oil. Source of ignition was autoignition
[fire - consequence, refining, instrumentation failure, fluid cracker]

Lessons

[None Reported]

1132226 May 1982

Source : ICHEME
Location : , BRAZIL

Injured : 0 **Dead :** 0

Abstract

An explosion in an effluent gas treatment plant caused considerable plant damage, including destruction of the effluent gas blower but fortunately, no injuries to personnel. Air and vent gas (flammable ex acrylonitrile plant) were mixed and ignited by heat from an incinerator. As a result of electrical power failure, the incinerator was shut down and, while operators were removing catalyst from the associated reactor, three explosions occurred. Flammable gas, remaining in the plant absorber was purged to the vent stack and leaked into the incinerator which was still at about 500 degrees C.
[damage to equipment, accidental mixing, processing,

Lessons

The following measures were installed:
1. Ensure complete purging of flammable reaction gas.
2. Prevention of air inflow into the system.
3. Isolate the incinerator from the vent gas system by mean of a remote operated valve.

2363 12 May 1982

Source : LLOYDS LIST, 1982, 15 MAY.
Location : Shuaiba, KUWAIT

Injured : 0   **Dead :** 0

Abstract

Leak of fuel oil in cooling system ignited in refinery hydrocracker plant. Source of ignition was autoignition. Flange leak.
[fire - consequence, refining, cracking]

Lessons

[None Reported]

2343 19 February 1982

Source : ICHEME
Location : , ISRAEL

Injured : 0 **Dead :** 0

Abstract

Fire at a fertiliser plant involving an exchanger and fuel oil. Source of ignition was autoignition.
[fire - consequence, heat exchangers]

Lessons

[None Reported]

122831982

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

An explosion occurred during the manufacture of a batch of liquid resin at a plant causing severe damage to the reactor system and its related structure. Fortunately personnel sustained only minor injuries.
The explosion occurred due to a runaway reaction from failure of operations to commission water to the overhead condenser. The pressure build-up leading to equipment rupture resilted from exothermic hydrolysis of epichlorohydrin, which led to an explosive decomposition reaction.
The reaction was initiated by the addition of hot condensate to the reactor at the end of the vacuum distillation step. At that stage the reactor normally contains almost no epichlorohydrin. In this instance, however, the bulk of the epichlorohydrin was still present.
The lack of cooling water on the overhead condenser and the restricted capacity of the atmospheric vent line caused the reactor pressure to increase and hampered the required removal of epichlorohydrin.
[reactors and reaction equipment, damage to equipment, operation inadequate, processing]

Lessons

[None Reported]

2294 18 December 1981

Source : ICHEME
Location : , TAIWAN

Injured : 0 **Dead :** 0

Abstract

A runaway reaction occurred at a petrochemical cumene hydroperoxide plant causing an explosion and fire involving a column.
[fire - consequence]

Lessons

[None Reported]

9413 12 September 1981

Source : ICHEME
Location : , UK

Injured : 0   **Dead :** 0

Abstract

During start-up an attempt was made to commission a propylene hydrogenation reactor.
The C3 stream was routed through the bed as 90% H2 was admitted, the temperature inside the top of the bed increased rapidly and the hydrogen supply valve tripped. However, temperatures further inside the be continued to rise and only reduced and steadied out after isolating and depressurising to fuel gas.
The initial cause of this incident was overhydrogenation, which in turn generated sufficiently high temperatures to begin polymerisation of propylene.
No injury to personnel occurred as a result of this incident and there was no damage to the reactor shell.
[reactors and reaction equipment, commissioning]

Lessons

[None Reported]

1048312 September 1981

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

During the start-up of a propylene hydrogenation reactor, very high temperatures were generated in the catalyst bed. At the time, propylene and hydrogen were being fed to the reactor which contained a granular catalyst. The temperature rose rapidly, and the hydrogen supply valve tripped at 176 degrees C. Despite the removal of the reactant supply, the temperature continued to rise to more than 600 degrees C, only stabilising after the reactor had been isolated and depressurised.
It was concluded that the start of the incident was caused by wrongly setting the propylene/ hydrogen ratio as a result of faulty calibration of the flow instruments. This allowed the temperature to rise to the point where spontaneous exothermic polymerisation of propylene occurred.
Investigation of the incident was hampered by the loss of the relevant instrument record charts.
[processing, reaction, polymerisation, exothermic reaction, control failure, incorrect flow rate, reactors and reaction equipment, design or procedure error, competency lacking, fire - consequence, damage to equipment]

Lessons

The following recommendations were made:
1. Stops should be fitted to key controllers/valves to limit flows in the event of a malfunction.
2. Situations where hydrogenation reactors are isolated or have only low flows through them during commissioning, maintenance or other operations should be identified and avoided.
3. The integrity of the trip system should be improved.
4. Good maintenance procedures are required to avoid the possibility of incorrectly calibrated transmitters being returned to process.
5. All records should be retained for a period, and should and incident occur, all relevant records should be impounded immediately.

2227 19 July 1981

Source : 100 LARGEST LOSSES, MARSH & MCLENNAN, 9TH EDITION.
Location : Greens Bayou; Texas, USA

Injured : 0 **Dead :** 0

Abstract

A runaway hydrolysis reaction involving water and terephthaloyl chloride in a herbicide manufacturing process unit ended with the violent rupture of the reactor. The batch reactor had just been loaded with its normal charge when a rapid rise in pressure and temperature were noted. The reactor head was blown off before remedial action could be taken. The vessel was blown down from the third to the second floor.
[loading, reactors and reaction equipment, high pressure , high temperature, auto decomposition]

Lessons

[None Reported]

1018420 March 1981

Source : ICHEME
Location : ,
Injured : 0 **Dead :** 0

Abstract

A member of staff began to prepare a solution of sodium dichromate in 85% formic acid, acting upon instructions from the graduate chemist. Approximately 100g of dichromate had been weighed into a flask and after adding 500ml of formic acid, the technician observed that the mixture had started to effervesce. He quickly placed the flask in the adjacent sink and withdrew. Foaming continued for a few minutes and there was some splashing onto the drainer and back wall. The incident arose through an attempt to mix chemicals which were incompatible. The consideration of the question of chemical compatability would appear to be a weak point amongst the division's staff. There is a surprising lack of knowledge of fairly elementary chemistry. The problem may partially stem from a failure to recognise that some fairly common academic laboratory/titrimetric reagents are potentially explosive if prepared in higher concentrations or larger quantities. A number of operations ancillary to the main experiment possibly receive too little attention in the assessment of chemical and operational hazards. [sodium dichromate, formic acid, mixing, flask/container, spill, chemicals added incorrectly, faulty instructions]

Lessons

It was recommended that:

1. The incident and report should be publicised
2. The work safety sheet for methanol oxidation and immediately related operations should be updated
3. Divisional graduates should review current work safety sheets to ensure that any questions of possible incompatibility are covered
4. Bretherick's handbook on reactive chemical hazards should be publicised (maybe made available to each individual laboratory)
5. Information on incompatibility should be included in any future divisional safety induction course for new graduates
6. A divisional note on common instances of incompatibility should be issued
7. Consideration should be given to a divisional presentation on incompatibility for graduates and other staff.

2167 01 March 1981

Source : ICHEME
Location : , KUWAIT

Injured : 0 **Dead :** 0

Abstract

Fire at refinery storage involving a cone roof tank and naphtha. Source of ignition was pyrophoric.
[fire - consequence, refining, storage tanks, spontaneous combustion]

Lessons

[None Reported]

2147 03 February 1981

Source : ICHEME
Location : , SAUDI ARABIA

Injured : 0 **Dead :** 0

Abstract

Fire at a refinery crude distillation plant involving an exchanger and crude bottoms caused by a valve leak. Source of ignition was autoignition.
[fire - consequence, refining, heat exchangers]

Lessons

[None Reported]

2142 28 January 1981

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

Fire at a manufacturing plant involving bitumen. Source of ignition was autoignition.
[fire - consequence, instrumentation failure]

Lessons

[None Reported]

7732 21 January 1981

Source : CONTROL OF CHEMICAL EXOTHERMIC REACTIONS, ICHEME, SAFETY TRAINING PACKAGE, 023, 3.11.
Location : ,

Injured : 0 **Dead :** 0

Abstract

An explosion occurred at a plant making liquid epikote. Only relatively minor injuries to personnel were sustained, but one of the reactor systems and its related structure was severely damaged. There was no fire.
Resinous material from the reactor was deposited as a spray up to 2 km from the plant, causing a large number of complaints from the local community. All complaints were relatively minor, and quickly resolved.
The sequence of conditions leading to the explosion arose from a failure of cooling water to the ECH/H2O condenser. This led to only partial removal of the reaction excess epichlorohydrin in the post-reaction steps. A runaway hydrolysis of the epichlorohydrin took place, leading to an overpressure rupture of the vent chiller.
[overpressurisation, runaway reaction, damage to equipment, reactors and reaction equipment]

Lessons

The following recommendations were made:
1. Install a pressure relief able to cope with a runaway reaction.
2. Carry out a Hazop study on the liquid epikote production process, paying particular attention to the critical nature of the ECH/water flow to the condensers.
3. Review the operator/computer/instrument interface in plant control.
4. Conduct formal and thorough training for all operating personnel involved in the control of base epikote resin reactions.
5. Amend, and add to, as appropriate, the operating manuals and instructions for the operation and control of the base epikote resin reactions.

10481January 1981

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

A chemical process employed a vertical shell and tube reactor, with molten salt in the shell and reactants in the tubes. The reactor was being modified, when it was noticed that the shell was bulging. Further investigation showed that two tubes in the reactor had burst. These were tubes which had been found to be leaking in a previous overhaul and had been plugged top and bottom.
The calculated burst pressure of the tubes was 3800 psig (roughly 260 bar gauge). It was surmised that the bursting of the tubes produced a shock wave which was transmitted through the salt and caused the shell to bulge.
When the tubes were plugged, a hole had been drilled through the tube wall near the top plug in order to relieve any build-up of pressure. However, it was found that there were substantial plugs of catalyst and carbonate in the tubes between the burst and the relief hole.
It was concluded that water had been trapped in the tubes behind the catalyst/carbonate plugs, rendering the pressure relief hole ineffective. On re-commissioning the reactor, the water vaporised, and at the high temperatures within the reactor sufficient pressure was generated to rupture the tubes.
[maintenance, repair, modification, heat exchanger, shell and tube heat exchanger, reactor tube, near miss, explosion, overpressure, overpressurisation, solids deposition, cleaning inadequate, reactors and reaction equipment]

Lessons

When leaking tubes in heat exchangers or reactors are plugged at either one or both ends, it is essential to thoroughly clean the tubes by water jetting or drilling before plugs are inserted and vent holes drilled.

2111 24 December 1980

Source : ICHEME
Location : , USA

Injured : 0 **Dead :** 0

Abstract

A fire was discovered in the seal area of a floating roof tank, of sour coker naphtha, at a refinery.
An investigation following the fire revealed that the most likely cause was pyrophoric iron spontaneous combustion. Pyrophoric iron deposits are often found in tanks in sour service and the theory was put forward that ignition was due to exposure of pyrophoric iron following a sudden partial failure of the seal at its attachment to the roof. Either the fabric failed due to prolonged exposure to ultraviolet light, or failure of the stitch welds providing for attachment of the bars to the roof, thus allowing displacement of the seal. In either case, when exposed pyrophoric iron began to glow it ignited the flammable mixture in the area where the seal failed.
[fire - consequence, refining, seal failure]

Lessons

Frequent, thorough seal inspections are important for fire prevention as well as compliance with air quality regulations.

2108 20 December 1980

Source : ICHEME
Location : , CANADA

Injured : 0   **Dead :** 0

Abstract

Fire at a refinery hydrotreater plant involving a compressor and hydrogen. Source of ignition was autoignition.
[fire - consequence, refining]

Lessons

[None Reported]

2065 09 October 1980

Source : ICHEME
Location : , KUWAIT

Injured : 0 **Dead :** 0

Abstract

Refinery hydrocracker plant. Source of ignition was autoignition.
[fire - consequence, refining]

Lessons

[None Reported]

2051 02 September 1980

Source : ICHEME
Location : , NORWAY

Injured : 0 **Dead :** 0

Abstract

Fire in a refinery coker plant involving a pump. Source of ignition was autoignition.
[fire - consequence, refining]

Lessons

[None Reported]

10156September 1980

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

A chemical fire ignited on a town rubbish tip resulting in a gas cloud to drift over a residential area. It made people sick and produced burning throats and streaming eyes. It was believed that the cause was a dumped drum of ferric chloride which split and reacted with chemicals deposited by a nearby firm. It is believed that the gas was ammonia.
[fire - consequence, gas / vapour release, drums, accidental mixing]

Lessons

Independent experts were called into investigate and the results were given to the environmental health committee 18 months later. It recommended:
1. Alternative methods of disposal of hazardous chemical waste eg. strip disposal, converting rubbish into oil.
2. Development of sampling procedure to speed identification if there is a future emergency.
3. Mixed waste should not be accepted unless supported by proof that chemicals should not react hazardously
4. A review of staffing at a tip to determine its adequacy in coping with extra inspections, testing and the control of hazardous waste disposal
5. More tipping sites to be provided

9735 10 June 1980

Source : ICHEME
Location : , UK

Injured : 42 **Dead :** 0

Abstract

A road transportation incident. An articulated lorry carrying drums of dangerous substances overturned while negotiating the slip road of a motorway, an estimated 25-30 drums were strewn over the roadway and down the adjacent embankment, some of which were leaking their contents.
The drums labels identified their contents as 113 kilograms of sodium hydrosulphite.
Spontaneous combustion occurred due to chemical contact with air. The lorry began to burn vigorously, releasing sulphur dioxide fumes.
[spill, gas / vapour release, toxic fumes]

Lessons

Sodium hydrosulphite also known as sodium dithionite, is a white or yellowish, often odourless powder which is soluble in water. This chemical reagent is liable to spontaneous combustion on contact with moist air and would then give off toxic fumes. It is also reactive with water, forming sulphur dioxide gas. Heating containers of sodium dithionite causes a pressure rise with an accompanying risk of bursting.

7232 June 1980

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

A melt of 1,2-Bis-(chloromethyl)-benzene was held in a stainless steel (18/8 material) batch reactor at 78 degrees C. After 4 hours there was a spontaneous temperature rise and highly lachrymatory smoke issued from the gland. Heating was stopped and the building evacuated. In spite of an open vent line the safety valve lifted, allowing 400-500 kg of the melt to be ejected.
[batch reaction, gas / vapour release, overpressure, contamination, incorrect material of construction, unwanted chemical reaction, batch reactor]

Lessons

Investigations showed that the incident cannot be explained by self-heating of the solution in xylene under adiabatic conditions, starting from 78 degrees C. However, the addition of 0.1% of rust caused a highly exothermic polymerisation (by acting as Friedel-Crafts catalyst). It was concluded that contact with the stainless steel vessel and/or rust triggered the reaction.

10380February 1980

Source : LOSS PREVENTION BULLETIN, 139, 5-6.

Location : , UK

Injured : 0 **Dead :** 0

Abstract

Without warning, a small explosion occurred in the drier outlet screw conveyor. The only fault found was that the base of the conveyor trough, fabricated from aluminium, had been dented by being hit by the operators (to check if empty on shut-down). The flights of the screw conveyor were scraping on the base of the trough and shaving off aluminium metal. It was concluded that a dust explosion had been initiated by hot metal shavings, thermite reaction, or a decomposition.

Lessons

The screw conveyor was re-built using a stainless steel trough and soft tips to the flights of the screw. The trough was sufficiently robust to withstand abuse. Improved explosion suppression was fitted to the screw conveyor. Improvements were made to improve the security of the packing-off operator.

1927 15 November 1979

Source : 100 LARGEST LOSSES, MARSH & MCLENNAN; CHEMICAL MARKETING REPORTER, 1979, 26 NOV.
Location : Ponce, PUERTO RICO

Injured : 0 **Dead :** 0

Abstract

An explosion and fire at a refinery reformer plant. Source of ignition was autoignition. Failure of fractionation tower bottoms pump (probably the seal) in a refinery platforming unit spilled hydrocarbons (pentane) which ignited.
[fire - consequence, refining, seal failure]

Lessons

[None Reported]

9396 08 November 1979

Source : ICHEME
Location : , UK

Injured : 1 **Dead :** 0

Abstract

A bursting disc and reactor seal failed on a PFTE-lined autoclave in an autoclave room. The autoclave was being used to investigate the dimerisation of vinyl acetate. A cloud of sooty material escaped, filling the room. The works fire brigade were called but no fire fighting equipment was required. Only one person was present at the time of the incident.
The autoclave seal and bursting disc failed probably because of the dynamic shock of a rapid pressure and temperature rise resulting from a runaway reaction.
[seal failure, reactors and reaction equipment, spill, bursting disc failure]

Lessons

[None Reported]

1920 27 October 1979

Source : ICHEME
Location : , LIBYA

Injured : 0   **Dead :** 0

Abstract

Weld failure caused a fire involving a hydrogen pipe at a fertiliser ammonia plant. Source of ignition was autoignition.
[fire - consequence]

Lessons

[None Reported]

7296 1979

Source : LOSS PREVENTION BULLETIN, 055, 9.
Location : ,

Injured : 2 **Dead :** 0

Abstract

Work at a paper mill involved the use of a box for sealing a steam leak in a 200 mm elbow at 10 bar. The pipe material as given to the technicians was cast steel. During the work the elbow separated from the adjacent flange and both technicians suffered first and second degree burns over 15-20% of their bodies. After the accident, the elbow was found to be of cast iron and metallurgical examination showed that it was defective when installed, having a casting flaw.
[maintenance, incorrect material of construction]

Lessons

[None Reported]

1800 1979

Source : LOSS PREVENTION BULLETIN, 117, 18.
Location : ,

Injured : 1 **Dead :** 0

Abstract

A runaway reaction occurred in a batch reactor. Although the over pressure was safely vented through a bursting disc, a bellows in the vent line burst.
The process was normally operated at 100 degrees C and atmospheric pressure with phosphorus trichloride as one of the reactants. For the batch in question, the ratio of phosphorus trichloride to the other reactants became incorrect and resulted in the formation of "lower oxides of phosphorus" (LOOP).
The LOOP was inadvertently heated to 110 degrees C and resulted in a runaway reaction. The temperature in the reactor increased to 200 degrees C and beyond, phosphine gas was formed, the pressure rose, and the bursting disc ruptured. The bursting disc pipework discharged into the atmosphere to a high level via a liquid catchtank. However, very soon after the disc rupture the vent pipe bellows burst, resulting in a spray of material and a pillar of fume and flame. An operator making an escape was burned by corrosive chemicals but not seriously injured.
[batch reaction, emergency vent, burns, injury]

Lessons

An intensive investigation looked into the causes of the accident, but at the same time studied a number of associated factors including the bellows failure. The bellows were found to have completely disintegrated. Pieces of PTFE recovered were examined, and it was considered that the failure was due to over pressure rather than thermal degradation. Because the reactor emergency vent was not specifically designed for the events that actually occurred, it was considered likely that a pressure of several bars had been reached upstream of the disc.
Although not a cause of the accident, the bellows failure exacerbated its results. It highlights the importance of correct specifications and positioning of bellows to prevent them from being a weak link in a piping system.

1018324 November 1978

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

In order to carry out repairs to the steam coil in the caustic soda storage tank, 26m3 of caustic soda needed to be transferred. As it was difficult to obtain a tank, it was decided to salvage the old toluene resins tank and to rent 4 small tanks (3 polyester, 1 PVC). The PVC tank was emptied the day before. Since the temporary tank was dirty (paint peeling), it was decided to transfer the soda in the PVC tank before returning it to the storage tank.
Two thirds of the way through the filling operation, the PVC tank exploded showering the TRU operator who was wearing a protective suit. The second operator received some drops of soda on one foot since the protective trousers were inside the boots. He was given a shower and sent to hospital.
The lender of the tanks had given purchasing guarantees by telephone regarding the good condition of the material and had guaranteed that it was in good enough condition for the specific use stated. However, on examination of the tank, the accident appears to be due to a lightly-structured tank, made of breakable material which had already been repaired.
[caustic soda, storage, tank, explosion, inspection inadequate, incorrect material of construction]

Lessons

It was recommended that before using any tank for storing dangerous liquids, check:
1. The material selected is suitable for storing the liquid
2. The container is in good condition
3. The mechanical resistance of the container is able to cope with the stresses expected during use
4. The ground is properly prepared.

The use of PVC, which becomes breakable very quickly by ageing, should be prohibited for dangerous and toxic products. A choice of protective clothing will be provided for personnel working in effluents and anyone working in or passing through an area where people are handling caustic soda or acids must wear protective clothing, particularly a face mask.

1774 06 November 1978

Source : ICHEME
Location : , ITALY

Injured : 0 **Dead :** 0

Abstract

An explosion and fire occurred involving an exchanger at a petrochemical maleic anhydride plant which was caused by a runaway reaction. Source of ignition was autoignition.

Lessons

[None Reported]

6806 22 May 1978

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

The rinse recycle valve on the outlet of a demineralisation unit was left open during the regeneration cycle and allowed caustic soda to pass into the filtered water tank. This caused salts to precipitate and foul the cation beds of the units on line and slippage of caustic soda into the treated water. A complete charge of cation resin had to be dug out and replaced.
[sodium hydroxide, contamination, solids deposition, separation]

Lessons

The following recommendations were made;
1. Thorough training of operators in the recognition of fault conditions.
2.The use of fractionation area process condensate for supplementing demineralised water in the event of an emergency is recommended. Rerouting this water into the demineralised water storage tank in an emergency should be written into the operating procedures. Tests should be carried out by plant personnel and confirmatory samples should be sent to the laboratory to ensure that the condensate quality is satisfactory before rerouting. The condensate should be rerouted to the tank only with the permission of the plant superintendent or group shift superintendent.
3.The caustic injection stage to the mixed bed and the rinse cycle valves should be electrically interlocked so that the valves cannot be opened during caustic injection. This can be achieved by a signal from the timer microswitch operating a relay and a solenoid on the pneumatic systems of the rinse recycle valves. A microswitch on the recycle valve body linked to a light in the control room should be used to indicate that the rinse recycle valve opens after the caustic closing stage and as a warning to operators that the valve is open. Operating instructions should be amended to describe the purpose of the interlock and the warning light when installed.

1645 22 May 1978

Source : ICHEME
Location : , KUWAIT

Injured : 0 **Dead :** 0

Abstract

Explosion and fire occurred at a petrochemical crude oil stabilisation plant involving a cone roof tank. Source of ignition was pyrophoric.
[fire - consequence, spontaneous combustion, storage tanks]

Lessons

[None Reported]

1635 06 May 1978

Source : ICHEME
Location : , ITALY

Injured : 0 **Dead :** 0

Abstract

A fire occurred involving a column and fuel oil on a refinery visbreaker plant which was caused by a flange leak. Source of ignition was autoignition.
[fire - consequence, refining]

Lessons

[None Reported]

1626 25 April 1978

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

A road transportation incidnet. A full 85 kg ethylene oxide cylinder loaded on the back of a vehicle exploded and seriously damaged the vehicle and scattered other cylinders over a distance of 40 ft. Explosion was heard 3 miles away. The cylinder failed as a result of ethylene oxide polymerisation reaction catalysed by the presence of rust, chloride and low pH. Cylinder failed in the hydraulically full condition. Suck-back at customer's site suspected.
[rusting]

Lessons

[None Reported]

1607 23 March 1978

Source : ICHEME
Location : , CANADA

Injured : 0 **Dead :** 0

Abstract

A fire occurred involving a pump and fuel oil at a refinery vacuum plant. Source of ignition was autoignition.
[fire - consequence, refining]

Lessons

[None Reported]

10487 03 February 1978

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

A fire occurred in a carbon steel condenser on a phthalic anhydride plant. The condenser contained phthalic anhydride deposits. It was offline at the time, and had been for 10 weeks. It was cold and had been isolated from the plant by means of a butterfly valve, which was known to pass slightly. The condenser was purged with nitrogen, but the purging was ineffective (for reasons not documented). Consequently acid gases from the plant leaked into the cold vessel and condensation occurred. This led to the formation of corrosion products in the condenser. These were pyrophoric and ignited the phthalic anhydride. The fire was extinguished by blanketing the condenser with nitrogen.
[condensation, shutdown, fire - consequence, condenser, phthalic anhydride, spontaneous combustion, corrosion, valve failure]

Lessons

This is a repeat of an incident which had occurred 5 years previously. The dangers of leaving condensers off-line and cold, with the consequent formation of pyrophoric corrosion products were known.
Previous recommendations had been made that condensers should not be left in this condition for more than three days. However, plant personnel had changed since the first incident, and there were no enduring written instructions on the subject. As a result of the poor communications, the plant management at the time of the second incident had failed to fully appreciate the dangers.
A new safety procedure was written and entered into plant standing orders.

107481978

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

An explosion occurred in a chemical reactor during the production of salicylaldoxime. The investigation of the incident showed that the product contained free alkali, which suggested that too much alkali had been added to the mix and that the product had been heated to a higher temperature (120 degree C) than normal. Small scale simulation experiments showed that these two factors could have caused the explosion since, under these conditions, salicylaldoxime undergoes a vigorous exothermic reaction.
[reactors and reaction equipment, processing, incorrect chemical concentration, incorrect temperature]

Lessons

[None Reported]

9881 1978

Source : ICHEME

Location : , UK

Injured : 0 **Dead :** 0

Abstract

A high head, low flow gear pump had produced increasing levels of vibration due to wear. Its construction and materials were not best suited to the fluid being pumped. In the end a small bore nipples connected to the discharge failed as it was not adequately supported against vibration. The pump was in the tank farm so the spill was contained and there was no fire.

[hydrocarbon, pump, rupture, product loss, incorrect material of construction, joint failure, excessive vibration, design inadequate, inspection inadequate]

Lessons

A gear pump of mild steel construction is not very suitable for a corrosive low lubricity hydrocarbon distillate.

1. Increasing vibration levels should never be ignored by operators or supervision.
2. For these conditions the pump inspection and maintenance procedures were inadequate.
3. High speed, high head, low volume centrifugal pumps are available when gear pumps are unsuitable.
4. Supports for small bore piping adjacent to rotating machinery should be carefully designed.

1488 02 November 1977

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

A fire occurred involving an exchanger and naphtha at a refinery reformer plant which was caused by a flange failure. Source of ignition was autoignition.
[fire - consequence, refining]

Lessons

[None Reported]

1483 19 October 1977

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

Petrochemical acrylonitrile plant. Source of ignition was autoignition.
[operator error]

Lessons

[None Reported]

9374 16 October 1977

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

On 16 October 1977, a joint blew on the 15 cm recycle return line to the reactor, which released hydrocarbons to atmosphere. The joint failed because of the overpressure of this section of pipework brought about by a reaction runaway initiated within the pipework which could not vent adequately to the body of the reactor where the safety devices are situated. The runaway is believed to have been caused by the disturbance of a pocket of catalyst lying in the line.
[reactors and reaction equipment, catalyst, runaway reaction, joint failure, pipework]

Lessons

Recommendations resulting from the incident investigation included:
1. The standby recycle pump and associated pipework to be removed and the remaining pipework simplified to reduce the number of dead spaces in the system.
2. The non-return valve to be removed from the recycle pump to allow a reverse flow in the event of a high pressure being generated in the discharge line.
3. The recycle pump impellor diameter to be reduced to allow the pump to operate with the valves on the return line fully open.
4. Further consideration to be given to increasing the size of the connecting pipework to allow the maximum pressure to be transmitted to the atmospheric relief valves.

1462 05 September 1977

Source : CHEMICAL WEEK, 1977, 14 SEP.; ICHEME
Location : , USA

Injured : 2 **Dead :** 0

Abstract

A non-solvent unit autoclave overpressured and exploded during a routine start-up of a vinyl chloride polymerisation reaction. The resultant fire ball was approximately 300 feet in diameter and debris was hurled over a large area. One two-ton piece of the autoclave shell was blown 600 feet, indicating the force of the explosion.
The started-up phase of this type of polymerisation normally consists of batch charging chilled monomer to the reactor with agitators running and metering in the desired amount of catalyst through an orifice run. At this time steam is introduced to the reactants through a bottom nozzle to raise the temperature and pressure to the desired operating levels.
This incident was caused by an overcharge of Isopropyl Peroxy Dicarbonate (IPP) catalyst. Approximately 30 to 40 times the normal charge of catalyst was introduced, we believe inadvertently, through a tubing by-pass triggering a runaway reaction.
The runaway reaction was of such extreme intensity that it could not be contained in the standard design and operating practices, which are equivalent to or exceed industry standards. Once it was initiated, it could not be detected early enough by normal operating actions to be brought under control by emergency procedures.
No mechanical defects were found in the design or condition of the equipment and eyewitness confirmed all safety devices functioned as designed.
Metallurgical examination of recovered pieces of the autoclave indicates the initial vessel failure was in the head and was caused by simple overpressure.
Subsequently the vessel failed catastrophically in a brittle fracture mode, with failure originating in at least twelve sites in the lower shell of the autoclave.
There appeared to have been at least two deviations from the standard operating procedure:
i. The water blowback feed to the catalyst feed line was not set up properly using a double valve and vent system to isolate it from the catalyst header.
ii. The agitators were not turned on.
The first deviation allowed the huge excess of catalyst to be fed, initiating the runaway reaction. The second deviation escalated the event from a limited overpressure failure and fire to an overpressure with subsequent highly destructive detonation caused by homogeneous nucleation.
[overpressurisation, chemicals added incorrectly, explosion, fire - consequence]

Lessons

The following recommendations were made;
1. Catalyst should be batched charged for start-up of autoclaves.
2. Cross-ties to the catalyst system should be eliminated.
3. Agitators and steam (the heat source) should be interlocked to prevent heating up without agitation.

1442 09 August 1977

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

Fire at a refinery crude distillation plant. Source of ignition was autoignition. Equipment involved: pump. Substance: involved crude bottoms. Cause: flange leak.
[fire - consequence]

Lessons

[None Reported]

1414 02 July 1977

Source : ICHEME
Location : ,

Injured : 0   **Dead :** 0

Abstract

Fire at a refinery lube oil plant. Source of ignition was autoignition.
[fire - consequence, refining]

Lessons

[None Reported]

1384 26 May 1977

Source : ICHEME
Location : ,
Injured : 0 **Dead :** 0

Abstract

Fire at a refinery reformer plant. Source of ignition was autoignition. Equipment involved: heat exchanger.
[fire - consequence, refining]

Lessons

[None Reported]

1048918 April 1977

Source : ICHEME
Location : , UK

Injured : 28 **Dead :** 0

Abstract

Large quantities of maleic anhydride vapour were discharged from a low level vent on a heat soak tank. Oil was being charged to the tank through a manifold. The manifold had another connection to a reactor, which at the time contained maleic anhydride at elevated temperature and pressure. A manual valve isolating the reactor from the manifold had inadvertently been left open. This allowed hot maleic anhydride to enter the tank along with the oil.
Twenty-eight people received treatment for fume inhalation, though none was seriously hurt.
The investigation showed that the manifold arrangement constituted an accident "waiting to happen" as a single wrong operation of the manual valve (leaving it open in this case) would cause mis-routing of potentially hazardous process material. The problem was compounded by poor design or siting of the valve, making it hard to establish whether it was open or closed.
A further complication was that the emergency procedure in use at the site was tailored to address fires and explosions arising from releases of flammable material, and did not deal with toxic emissions. Consequently the evacuation alarm was not sounded.
[maleic anhydride, gas / vapour release, poisoning, manually operated valve, manifold, design fault, operation omitted, accidental mixing, chemicals added incorrectly]

Lessons

All operators were formally briefed about he incident.
It was recommended that the pipework should be modified to eliminate manifolded connections to the heat soak tank (and thus prevent mixing of incompatible materials), and a study made of similar situations on the works. The reactor isolation valve should be fitted with an indicator arm and scale to make its open/closed status obvious.
The vent on the heat soak tank should be improved.
The works emergency procedure should be reviewed and modified to deal additionally with toxic releases.

5904 1977

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

A runaway reaction occurred in a batch polymerisation reactor.
The bursting disc failed to burst and the polymer escaped through some of the reactor flanged joints, covering the reactor in brown sticky polymer.
The bursting disc failed to burst because it had been fitted on the wrong side of the vacuum support, thus raising the effective bursting pressure of the disc from 150 psig to 400 psig.
Calculation showed that for the class 150 flanges fitted to the reactor branches, their bolts would stretch and the flanges leak before the reactor or associated pipes burst. However this gratuitous pressure relief cannot obviously be relied on for flanges with a higher pressure rating.
[polymerisation, reactors and reaction equipment, bursting disc, flange, runaway reaction, installation inadequate, spill]

Lessons

Consequently new designs for bursting disc assemblies have been developed which will be harder to install incorrectly and easier to check after assembly.
This entails permanently attaching the disc to the vacuum support during manufacture, identification tags and arrows, and where possible so designed that inversion is not physically feasible.

117011977

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

Twenty four hours after a recycle gas compressor trip, a fire occurred on the reactor effluent exchangers of this catalytic reformer. Hydrocarbons and hydrogen leaking from the exchangers spontaneously ignited, and flames engulfed the exchangers and were carried upwards towards the adjacent fin-fan coolers. Steam snuffing to the exchanger flanges via the installed steam rings, removal of unit feed and purging with nitrogen successfully controlled and extinguished the fire. A foam blanket was laid under the exchangers and a water curtain established to protect adjacent equipment.
Damage was limited to replacement of certain exchanger and nozzle flange joints, and tightening up of other joints, at a cost of some £12,000 (1977), but there was some 16 days lost production.
Whilst the above type of incidents, caused in the main by thermal shocks, have not been uncommon in a number of refineries over the years one feature of the above incident attracted particular attention. This was that the exchanger flanges had been covered with lagging boxes during the 1976 overhaul as an energy conservation procedure.
On reflection it is now appreciated that for these light hydrocarbon/hydrogen duties this meant that any leakage was difficult to detect, accumulating beneath the lagging boxes, eventually igniting, and due to the insulating properties of the boxes causing expansion of the exchanger bolts with subsequent increased leakage rate.
Before the installation of the lagging boxes, although there had been several small flange fires these had been successfully extinguished using steam without needing to shutdown the plant.
[refining, catalytic reformer, heat exchanger, spontaneous combustion, leak, design inadequate, fire - consequence]

Lessons

Refineries are advised against such insulation of tube sheet and channel flanges on heat exchangers on hydrogen service, and advised only to provide partial protection for bolts against rainfall whilst still allowing sufficient gap for leakage to dissipate.
Bolt tensioning techniques should also be reviewed.

110481977

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

A leak of hot heavy residual oil occurred on the suction line flange inside a fractionator support skirt. The leak got progressively worse and autoignition followed.
The cramped conditions inside the skirt could have contributed to the fact that the joint was badly made up in the first place.
It certainly made it impossible to tighten up the flange studs once the leak has started.
[heavy hydrocarbon, start-up, distillation, blowout, fire - consequence, joint failure, design or procedure error, maintenance inadequate]

Lessons

The report stated:
1. The installation of flanges inside fractionator skirts is no longer permitted.
2. Breaking of existing flanged joints in such locations should be minimised.

122561977

Source : ICHEME
Location : ,

Injured : 2 **Dead :** 0

Abstract

During operation of a 25 tonne batch alkoxylation reactor used in the production of a polyether from glycerine and ethylene oxide, a run-away reaction occurred resulting in the rupture of the reactor and causing metal parts and valves to be propelled over a distance of approximately 700 metres.
It is thought that the ethylene oxide reached a temperature of 560 degrees C and so decomposed explosively.
The incident occurred due to the incorrect operation by the operator.
Two people were injured in the incident.
[normal operations, runaway reaction, reactors and reaction equipment, explosion / pressure release, injury]

Lessons

[None Reported]

1288 13 December 1976

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

Fire and explosion at a refinery hydrocracker plant. Source of ignition was autoignition. Equipment involved, pipe. Substance: involved hydrogen. Cause: erosion.
[fire - consequence, cracking]

Lessons

[None Reported]

1022202 December 1976

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

Two explosions occurred at a road loading facility (the second explosion occurring within about two hours of the first) during switch loading. Switch loading can produce a flammable atmosphere, but an ignition source has be to present, for example, an electrostatic discharge.
It is believed that cause could have been static electricity, as a possible ignition source. Methods to eliminate explosions is focused upon. This is particularly important to ascertain the causes as loss of life or injury could be caused.
Suggestions are made to possible solutions, including the use of an Anti-Static Additive, charge generation mechanisms, inerting the tank atmosphere. In conclusion, the incident could have been due to static electricity ignition sources. But other ignition sources are possible. Reducing flow rates will minimise the electrostatic ignition risk, but not eliminate it. In order to eliminate the risk:
1. Use of an anti-static additive.
2. Inerting the tank atmosphere.
Both methods would increase costs. The anti-static additive would be simpler.
[road tanker, autoignition]

Lessons

The adoption of anti-static additive was recommended to eliminate electrostatic ignition risk.

1159328 November 1976

Source : ICHEME
Location : , USA

Injured : 0 **Dead :** 0

Abstract

This explosion in a slops tank, eventually involved six tanks in the same area, the fire being fuelled from a 24 inch rupture in the slops tank base. A control room wall, 400 ft. away was cracked by the heat.
Ambient temperature at the time was 34 degrees F, but earlier temperatures had been below 10 degrees F and product demands had caused many tank levels to be much lower than normal. All the process units were operating normally but some pipelines (especially waxy distillates) were having blockage problems. In an attempt to clear one line a light furnace oil at about 150-160 degrees F was put into the line. The contents of the line were fed to the slop tank. About 1 hours later the explosion occurred.
The subsequent investigation arrived at the following conclusions.
About 30 barrels of furnace oil had been fed to the line which was just sufficient to displace the contents of the line into the slop tank. The steam tracing had heated these line contents to about 160-180 degrees F during the static condition. The tank level was raised by about 1-2 inches. Also, an unknown stream was added to the tank raising the level a further 12 inches. This brought the steam coils (which were at 250 degrees F) into contact with the tank contents.
Heat transfer to the tank water layer eventually raised the temperature to above 212 degrees F. Frothing and steam formation then caused a rupture in the tank roof and release of a vapour cloud. Ignition was probably obtained from this metallic rupture; the 10,000 bbl tank was over 20 years old and not in perfect condition.
Refinery actions included replacing the slop tank further away from the process area and equipping it with remote level indication.
Operators were instructed to keep comprehensive records of disposal of materials to tankage.
[shutdown, modification, repair, commissioning, modification procedures inadequate, accidental mixing, unwanted chemical reaction, explosion, fire - consequence, hydrofluoric acid, potassium hydroxide]

Lessons

There should be provision for adequate temperature, level indication and alarms on any heated slop, or other heavy oil tank which might be contaminated with free water or light product. Wherever possible, heating of slop tanks should be avoided and the heating coils blanked off.
Frequent drainage and bottoms level checks and care with the use of any installed mixers must be included in operational procedures.
In the past years, refineries have been warned in a variety of ways of the potential hazards of slops tanks, where these are fitted with heating coils. The introduction/accumulation of water or light oils in slops tanks containing heavy oils can well have serious results with heat transfer from the coils preferentially to one layer, causing rapid vapourisation and overpressure of the tank, leading to rupture

9346 28 November 1976

Source : ICHEME
Location : , USA

Injured : 0 **Dead :** 0

Abstract

At a major shutdown, repairs and modifications were carried out on this HF Alkylation Unit. The modifications included replacing the liquid caustic neutraliser with a tower containing solid potassium hydroxide. Not all the associated controls and alarms for this modification were installed at the time.
The plant was subsequently recommissioned, and on the 28th November 1976 there was a plant upset which resulted in the carryover of a slug of hydrofluoric acid into the potassium hydroxide tower. It would appear that just before the incident the HF stripper tower was not operating satisfactorily. Although they were aware of this, their operating manuals had not been updated, the operators were therefore unaware of the implications and of the corrective actions to be taken.
The exothermic reaction between the HF and KOH caused an explosion and fire. The force of the blast carried away the side of a cooling tower sited some 300 feet away from the source of explosion. (However if this was a wooden construction it might not be a significant parameter of the force of the blast).
The fire fighting facilities were sufficient to contain the fire in the area of the tower, although it is considered that additional fixed monitors would have eased the task of the firemen. There were no problems with HF, although small quantities undoubtedly were released from the stripper tower these did not affect the fire fighting operations.
[shutdown, modification, repair, commissioning, modification procedures inadequate, accidental mixing, unwanted chemical reaction, explosion, fire - consequence, hydrofluoric acid, potassium hydroxide]

Lessons

The incident again illustrates the dangers of uncontrolled mixing of acids and alkalies which are capable of producing sufficient heat of reaction to rupture equipment. This is obviously not specific to Alkylation Plants but could occur with other processes, and therefore refineries are reminded of this hazard.
The release of HF under fire conditions with diffusion in the rising combustion products did not produce problems in this particular incident, and the same situation has been observed in other HF unit fires. Escape of HF without an associated fire could obviously present toxicity problems, depending on the leak size, atmospheric conditions etc.

1265914 November 1976

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

A serious fire occurred in a grinding plant resulting in damage and material loss estimated at £2,500 (1976).
An investigation into the incident established two possible causes, spontaneous combustion of fines or ignition by extraneous metal.
[fire - consequence, solids processing equipment, damage to equipment, product loss]

Lessons

[None Reported]

1250 23 September 1976

Source : THE FIRE ON HMS GLASGOW, HSE REPORT, HMSO
Location : Newcastle Upon Tyne, UK

Injured : 0   **Dead :** 8

Abstract

Fire broke out on the lowest deck of HMS Glasgow which was fitting out at the shipyard. The fire was fierce. A leak of oxygen caused enrichment and hence the fierce fire. Fatality.
[welding, oxygen enrichment, fire - consequence]

Lessons

[None Reported]

1245 09 September 1976

Source : CHEMICAL MARKETING REPORTER, 1976, 13 SEP.
Location : Perth Amboy; New Jersey, USA

Injured : 24 **Dead :** 0

Abstract

Explosion of a reactor in unit used in the manufacture of surfactants, possibly caused by runaway reaction.
[reactors and reaction equipment]

Lessons

[None Reported]

1169207 September 1976

Source : ICHEME
Location : , GERMANY

Injured : 0 **Dead :** 0

Abstract

On the 7th September 1976, at 06.00 hrs an explosion occurred in the incinerator system of the No.1 Sulphur Recovery Plant due to a carryover of LPG from the 3 / 4 - H 2 S Absorber Column on the Catcracker Unit via the Amine regeneration Column. There were no injuries to personnel but damage amounted to some £30,000 (1976), confined mainly to the unit stack and the incinerator air blower. The internal packing of the 3 / 4 absorber column required cleaning, and the column was therefore being taken out of service for water flushing. The flow of LPG to the H2S absorber column 1 was stopped, and diverted into the fuel gas system, and the column depressured to approximately 5 bars. The bottom level gauge on the absorber was unreliable due to blockage with deposits, and therefore an indirect system of measuring the drainage rate from the absorber was used.
Draining from the absorber column 1 commenced via the bypass valve of its bottom level control valve into the amine regeneration column 2 of the sulphur recovery plant. At the same time amine was drained from column 2 into the amine tank at such a rate as to keep the level in column 2 constant. By gauging the increase in level in the amine tank the operators were able to indirectly measure the loss in level of the absorber column 1, although the diameter of the latter was much less than that of the former. Approximately 1 hour after draining started, a high level alarm indicated in the amine regeneration column, and draining of amine from the absorber was therefore reduced to a minimum. About 1 minute later, the high flow alarm of the H2S flow from the regeneration column sounded. Draining of amine was ceased immediately, but it was too late to stop a large LPG carry over to the sulphur recovery section of the plant, which was still in commission. Liquid seals on the sulphur recovery section were blown gaseous and LPG was released into the sulphur pit. From here it was drawn into one of the air blowers via a line which had recently been installed to remove foul odour gases from the sulphur pit for disposal in the incinerator. The air blower 6,as well as removing foul gases from the sulphur pit provided combustion air for the incinerator and cooling air for the incinerator flue duct. LPG vapours were therefore carried forward from the sulphur pit into the incinerator and also into the flue duct. At the same time, LPG vapours travels through the reaction system into the incinerator, but these remained mainly in an unburnt state due to insufficient oxygen being available in the reaction system. Two eye-witnesses described two distinct explosions. The first explosion was in the blower 6, whilst the second some 3 seconds later occurred in the stack within the flue gas inlet area, causing a collapse of stack internal brickwork.
The investigating team considered that the first explosion was probably initiated by a flash back from the incinerator burner travelling back through the air line to the air blower. The second explosion was considered to have occurred due to a delayed autoignition of the induced LPG in the stack.
[heating, draining, incinerator, absorption, instrument/controller, autoignition, process causes]

Lessons

Recommendation made by the refinery include the proposal that the vent line from the sulphur pit should be fitted with a flame arrestor, and various improvements are also being considered to improve the drainage control from absorbers.

1170209 August 1976

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

A major failure of a tank which contained crude oil occurred. This resulted in a spillage which filled the bunded area to within 2 ft 6 inches of the top of the bund wall. The tank had been standing with no significant level movements since the 31st July 1976.
The experience of handling this large crude oil spillage is interesting but only really relevant when the oil involved has a very high pour point. It was found that this waxy crude formed a wax crystallised film on the surface of the sand floor and walls of the bund limiting oil penetration to a depth of 1 inches to 2 inches. During the warmer parts of the subsequent days the oil "melted" sufficiently in the bunded area to allow it to be pumped away and recovered.
Tests for gas during the incident, on the downwind side immediately above the bundwalls, gave readings up to 5% of the lower explosive limit. Breathing apparatus and lifelines were used by employees when working in the area, but vapour loss was not a substantial problem.
In this incident it was fortunate that from both the pollution and vapour loss aspects the spillage was a high pour point crude. With most crude oils the problems would have been considerable greater and with a higher fire risk.
The tank in question was some seven years overdue on the recommended inspection period. Other tanks are similarly overdue for inspection by a number of years and this may have been partially attributable to problems in cleaning large quantities of sludge from some of the crude oil tanks producing a general slowing down in the overall programme of tank cleaning.
[storage, tank, inspection inadequate, cleaning inadequate, tank failure, spill, crude oil]

Lessons

[None Reported]

1219 24 July 1976

Source : ICHEME
Location : ,

Injured : 0   **Dead :** 0

Abstract

Explosion at a petrochemical lube oil additives plant. Source of ignition was autoignition. Equipment involved reaction vessel. The cause was operator error. [processing]

Lessons

[None Reported]

1203 27 June 1976

Source : THE EXPLOSION AT THE CHEMICAL FACTORY, KING'S LYNN, 27 JUNE 1976, HSE REPORT, HMSO,1977, ISBN 0118830031. LOSS PREVENTION BULLETIN, 030, 163.

Location : Kings Lynn; Norfolk, UK

Injured : 0 **Dead :** 1

Abstract

An explosion with a force of 200 to 300 lb of TNT occurred. A poultry feed additive (3,5-dinitro-o-toluamide) was dried in a batch vacuum drier with steam supplied to the heating jacket at 150 degrees C. Drying was completed after 24 hours at which time the steam was turned off and the vacuum broken. This was Saturday afternoon. The batch was left in the drier to await the Monday morning shift. On Sunday afternoon the drier exploded killing one man.
A report of the incident noted that neither previous experience, nor available thermal data had suggested that the compound was thermally unstable at the drying temperature of 120 degrees C, to 130 degrees C. Examination of the compound by differential thermal analysis has shown it to be thermally unstable at higher temperatures, but it was not known that the compound could self-heat to destruction if held under adiabatic conditions of 120 degrees C, to 130 degrees C, for 24 hours. This was subsequently shown by thermal stability tests using similar to those prevailing in the drier. Fatality.
[unwanted chemical reaction, explosion, processing, heating, design inadequate, zoalene]

Lessons

The incident review suggested that the zoalene had undergone a self-accelerating decomposition. It exploded with an energy equivalent to 100 150 kg of trinitrotoluene (TNT). A member of the works fire-fighting team was killed as he was proceeding to the assembly point on hearing the fire alarm. He was passing the Clopidol drier when it exploded. Missiles formed from fragments of the drier were scattered widely. One fragment weighing 12 kg was found 700 m from the site of the explosion. This was well outside the perimeter fence. The total damage was estimated to be approximately £1.25 million (1976).
Root causes included:

1. Poor quality of imported zoalene.
2. Inadequate technical understanding by staff of the process.
3. Inadequate engineering provision - old plant was reused for a new process.
4. Improper storage and handling of process material.
5. Drier was not designed for Zoalene.
6. Absence of automatic deluge system for Zoalene.
7. Inadequate management of change.
8. Risk of nitro-aromatics was not appreciated.
9. Extent of explosive nature of Zoalene was unknown at the site.
10. Inadequate emergency plans - staff were directed towards the hazard.
11. Weekend staff were unaware of the status of the plant.

1179 16 May 1976

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

Fire at a refinery desulphuriser plant. Source of ignition was autoignition. Equipment involved, heat exchanger. Substance involved: kerosene. Cause: flange leak.
[fire - consequence, refining]

Lessons

[None Reported]

1183 May 1976

Source : 100 LARGEST LOSSES 9TH EDITION, MARSH & MCLENNAN PROTECTION CONSULTANTS, 1986; CHEMICAL MARKETING REPORTER, 1976, 3 MAY.

Location : Geismar; Louisiana, USA

Injured : 0 **Dead :** 0

Abstract

Explosion involving a large polyglycol reactor with the release of unreacted ethylene oxide, propylene oxide, glycol and glycerine. Cause of the failure is believed to be due to loss of agitation and/or failure of temperature transmitter and/or the introduction of insufficient catalyst to the reactor. The explosion threw the reactor head 1400 ft, fragments ruptured a polyglycol tank and broke the sprinkler riser. Fire extinguished in 1.5 hours.
[agitation failure, low level of catalyst, instrumentation failure, reactors and reaction equipment]

Lessons

[None Reported]

1166 May 1976

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

An exothermic runaway reaction occurred in a batch reactor for unsaturated polyesters. Various joints leaked due to overpressuring and when the pressure relief system failed to work a release occurred. The reactor bursting disc assembly was ineffective because the vacuum support was wrongly positioned. Improvements to design and instrumentation are recommended and more frequent process readings. It was found that even when the vacuum support ring was correctly positioned it reduced the flow area of the bursting disc by half.
[overpressurisation, safety equipment failure, gas / vapour release]

Lessons

[None Reported]

1165 28 April 1976

Source : FIRE PREVENTION REVIEW, 1977, FEB.
Location : Wyke; Yorkshire, UK

Injured : 2 **Dead :** 0

Abstract

Dichlorophenol, butanol, caustic soda and gamma butyrolactone where being added to a reactor when there was a runaway reaction causing the release of material and an explosion.
[reactors and reaction equipment]

Lessons

[None Reported]

1011014 February 1976

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

Chlorine gas was released from the absorption section of a chlorine manufacturing plant. The release was quickly stopped by the addition of caustic soda.
Two men were treated for slight exposure to chlorine.
The section of the plant involved was designed to absorb (in caustic soda) any excess chlorine from the manufacturing process. In this incident, there seems to have been a substantial leak of gas from the high pressure chlorine line through a pressure control valve. Over a period of some hours, this resulted in depletion of the caustic soda in the system to the point where breakthrough occurred.
Plant operators failed to diagnose the source of the problem, and disregarded readings from a chlorine flow recorder which they believed to be faulty. In addition, there were serious discrepancies in the recording of caustic soda concentrations.
The investigation concluded that proper response from the operators would have prevented the chlorine release.
[venting, scrubber, gas / vapour release, incorrect chemical concentration, relief valve, leak, testing inadequate, operator error]

Lessons

It was recommended that:
1. monitoring of caustic soda concentrations needed to be improved
2. operators needed better information on the reliability status of instruments
3. operators needed additional training to emphasise the importance of maintaining correct operating conditions

1108 03 January 1976

Source : LOSS PREVENTION BULLETIN, 065,26; NORTHERN ECHO, 1976, 5 JAN.
Location : Seal Sands; Middlesbrough, UK

Injured : 4 **Dead :** 0

Abstract

A road tanker containing acrylic acid was left overnight with steam heating to the contents. Polymerisation occurred and ruptured the tanker causing damage to the surrounding plant. The tanker explosion is believed to have been caused by the thawing of a layer of crystallised acrylic acid by warm water which was being used to maintain the tank temperature above its freezing point of 14 degrees C. The crystallisation of the acrylic acid occurred during the operation and would take place without its attendent inhibitor. On thawing in the tanker, a liquid layer formed without the polymerisation inhibitor. Polymerisation started in this layer and consumed the inhibitor in the bulk leading to the subsequent rupture of the tank.
[road transportation]

Lessons

The following precautionary measures were suggested:
1. Temperature measurement is the easiest and most effective method of monitoring the condition of a monomer. This should preferably be taken of the bulk of the monomer. It is also a considerable advantage to know what influences are being made on the monomer by heating media etc., and so their temperature measurement is important.
2. If crystallisation of an inhibited monomer can occur, thawing should not be carried out-with out some means of agitation and a positive control on the heating fluid. Such agitation could be mechanical or gas sparge and though preferably continuous, it can be intermittent, the frequency of agitation being dependant on the rate of heat input.
3. The heating fluid should be controlled to a maximum safe temperature which will be specific for each monomer. The objective must be to prevent layering and layer heating of low inhabited material.
4. When gas sparging acrylic monomers, air should be used to maintain the activity of the inhibitor. Nitrogen will deactivate inhibitors of this nature.

1109 03 January 1976

Source : LOSS PREVENTION, VOL 11, AICHE, 1977; CHEMICAL MARKETING REPORTER, 1976, 12 JAN.
Location : Deepwater; New Jersey, USA

Injured : 6   **Dead :** 0

Abstract

Fire and explosion in chloramines plant. A destructive runaway reaction occurred during the operation of a large batch hydrogenation reactor used in the production of 3,4-dichloroaniline. The manway cover was blown off and the autoclave was dislodged from its support and driven into the floor. below. After investigation the following conclusions were reached:
1. The primary cause was a sudden pressure increase at the auto decomposition temperature of the reaction mass. This occurred somewhere above 260 degrees C.
2. The autoclave reached autodecomposition due to the buildup and rapid exothermic disproportionation of an intermediate - 3,4-dichlorophenylhydroxylamine (DCPHA). The most likely trigger for the reaction was a 10 degrees C increase in the reactor tempertaure set point.
[reaction]

Lessons

[None Reported]

7234 03 January 1976

Source : LOSS PREVENTION BULLETIN, 065, 26.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A road transportation incident. A road tanker containing 30,000 lb (13.6 tonnes) of glacial acrylic acid burst open with explosive violence. Upon rupturing, the gelatinous polymer, which was above its auto-ignition temperature, was thrown blazing over a 150 m (500 ft) diameter semi-circle. The tanker explosion was believed to have been initiated by the thawing of a layer of crystallised acrylic acid by warm water which was being used to maintain the tank temperature above its freezing point of 14 degrees C. The crystallisation of the acrylic acid occurred during the loading operation and would take place without its attendant inhibitor. On thawing in the tanker, a liquid layer formed without the polymerisation inhibitor. Polymerisation started in this layer and consumed the inhibitor in the bulk leading to the subsequent rupture of the tank.
[chemical missing]

Lessons

[None Reported]

7586 1976

Source : LOSS PREVENTION BULLETIN, 125, 27.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A 'hard' resin, solid at room temperature, and the finishing process was to run it out into large steel trays, allow it to cool, then dig the resin out of the trays and crush it into sacks.
A large volume of vapour was emitted when the resin was run into the trays, and this subsequently became the target of air pollution inspectors. However, the feature relevant here was a long-standing theory, or belief, or suspicion, something in the 'everybody knows' category, that the vapour emitted by the hot product was highly flammable but was quite safe because the reactor exit temperature was specified to be below the unknown-but-somewhere-about-there ignition temperature.
One the night of the incident the proof that the vapour was flammable was obtained. The batch was pushed out of the reactor a few degrees hotter than standard, perhaps twenty, the vapour contacted the oxygen in the atmosphere, and, being above the autoignition temperature, ignited. The roof over the trays was severely damaged and had to be demolished and replaced.
[fire - consequence]

Lessons

This incident occured well into afternoon shift, when there was reduced supervision, and because the batch temperature was higher than specified.

116881976

Source : ICHEME
Location : ,

Injured : 1 **Dead :** 0

Abstract

When a contractor's welder was removing a mechanical plug from the inside of a 10 inch gasoline pipeline, a small flash fire occurred slightly burning the man's chest.
The metallic part of the plug was constructed of aluminium alloy and the inner surface of the carbon steel gasoline line was rusty. A thermite reaction due to frictional movement between the aluminium alloy portion of the plug against the pipewall is suspected as having produced an incendive spark. The pipe had been water washed, but not fully freed of hydrocarbon so that a flammable vapour could have been present.
A section of the 10" line had been removed and a flange welded to each cut end with a final distance between the two flange faces of about 500 mm. In this somewhat restricted space the welder would have had some difficulty in removing the plug from the line, and it is considered that sufficient twisting of the plug occurred for the aluminium to contact the pipewall and promote the thermite reaction mentioned above.
As a result of the incident, the refinery has discontinued the use of aluminium alloy plugs. The other possible ignition sources considered by the refinery and ruled out were:
1. The welding machine was not running at the time of the incident and the welding leads were disconnected
2. One flange weld was completed some one and a half hours before the incident and the other half an hour before. The lines were cold to the touch. Weld heat was therefore not the source of ignition
3. Scale taken from the line was tested and found to contain no iron sulphide nor was any evidence of any pyrophoric action found
4. There were no adjacent, external sources of ignition
An investigation found that the metallic portion of mechanical plugs may be made of a number of metals, such as cast steel, galvanised iron plate, or aluminium alloy. There will be a tendency for the larger size plugs to be manufactured from light alloys to reduce their weight.
[welding, pipeline, thermite reaction, fire - consequence, burns,
gasoline]

Lessons

Although this incident is not sufficient cause to ban aluminium alloy plugs, care should be taken as to their method of use. It should possible to wet the inside of the pipewall ends with water before removing an aluminium alloy plug.

116981976

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

A light oil fixed roof slops tank was found to have sustained roof damage. There were no witness to the damage and only tentative conclusions can be drawn as to the cause. Investigation showed the roof to be badly scaled and corroded to the extent that air was undoubtedly entering through corrosion formed holes in the roof as well as through the normal fixed roof breathing and venting points. A hydrocarbon air mixture containing some 15% oxygen frequently existed above the oil phase in the tank and the liquid contents were typically composed of 30% SRB, 20% Naphtha, 30% Kero, and 20% LGO, with a flash point of about ambient temperature.
Pyrophoric scale is suspected as the source of ignition due to its oxidation in the relatively high oxygen content vapour space.
The refinery have considered installing a sweet gas blanketing system for the repaired tank or alternatively storing light slops in a nearby floating roof tank, the latter being the most favoured solution.
[storage, tank, solids deposition, damage to equipment, corrosion, unwanted chemical reaction]

Lessons

The storage of sour light slops in fixed roof tanks is condusive to the formation of pyrophoric scale, and the refinery's intention to store light material in a floating roof tank is favoured. Only during grounding and refilling of a floating roof tank can there be a possible explosive mixture, and at these rare times suitable precautions can be taken, such as limiting filling rate to 1m/sec until roof floats and water spraying beneath the roof if pyrophoric is suspected.

9873 1976

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

An alert operator noted a loose tube sheet flange stud on a high temperature, high pressure heat exchanger in an hydrodealkylation unit.
The stud was found to be cracked through an on testing it proved to be standard steel rather than the alloy type specified. Some of the other studs had started to crack.
The studs had been replaced on the previous shutdown when the heat exchanger was opened up to clean the tube bundle.
[heating, shell and tube heat exchanger, near miss, incorrect material of construction, crack, maintenance inadequate, hydrogen]

Lessons

Quality control of replacement parts used in maintenance is as important as for new equipment.

116771976

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 1

Abstract

During isolation of equipment, an explosion followed by a very short duration fire occurred within the extract and raffinate vacuum flash towers of this furfural plant and flame propagated through an open flange near to where the a man was working. The man's clothing was set on fire but he managed to leave the immediate platform and collapsed some distance away where assistance was given to him before being taken to hospital. He died later.
The particular sections of the plant involved in the incident were being spade isolated before going on to the steaming out stage. Both the towers had been washed with vacuum gas oil as part of the normal shut down procedure aimed at recovery of maximum residual furfural. The fire which followed the explosion was seen to be in the area between the two towers. The flames lasted for a few seconds and subsided quickly leaving a slight fire at the inlet flanges of the feed lines of both towers. There was no evidence of an external pressure wave or blast damage outside the towers, but there was superficial scorching of the cladding of both towers. Subsequently it was found that all the trays had collapsed inside both towers, indicating an internal explosion, probably originating in the raffinate vacuum flash tower.
The investigating team concluded that the source of ignition could not be attributed to fired heaters, smoking, mechanical work, electrical equipment or static electricity, but that a chemical reaction such as the oxidation of deposits was responsible for ignition. It is conjectured that some vapour was evolved within the tower from the chemical heating of the residual gas oil which covered the internal surfaces of the towers and lines. Some of this oil would have impregnated the solid deposits which are commonly found inside equipment on furfural units.
At this refinery there had never been any evidence in 20 years of furfural unit operation to indicate that pyrophoric material was present in such plants. Nor did any of the plant designer's literature give any indications of this possibility. It had been normal practice to open up heat exchangers while still hot so as to remove build-up of deposits, and no evidence of any self heating of these had been noted.
The Inquiry team approached 4 refineries where furfural units are operated asking whether there was any experience of heat generation within their plants. Of the 4 refineries concerned, 2 had no such experience and 2 quoted isolated instances where vessels had been opened up and where some smouldering and smoke had been noted, but without flame or explosion. On this evidence therefore the Inquiry team concluded that by an unforeseen coincidence of untypical events there had been heating up of residual material in the raffinate vacuum flash tower to the point where it had generated vapour from the light oil around it and finally reached a temperature where ignition occurred. (Self or auto-ignition of the vacuum gas oil occurs at about 400 degrees C whilst its flash point is around 134 degrees C).
[isolation, separation, separation equipment, blind/spade/slip plate, unwanted chemical reaction, autoignition, fire - consequence, explosion, fatality]

Lessons

[None Reported]

1017117 September 1975

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

A marine transportation incident. An explosion and fire was reported in the cargo tank on a chemical tanker. The ship loaded with acrylic acid and ethylidene norbornene in the USA and was proceeding to Antwerp. Temperature in the acrylic acid tank started rising during the passage and caused the ship's plates to be moved 6 inches and ruptured the tank resulting in mixing with the ethylidene norbornene. The problem involved a chemical reaction in the dead space between two leaking tanks of different and reactive materials. There was no fire or explosion and the temperature was due to exothermic polymerisation of the acrylic acid. The vessel was out of service for 3 months being cleaned of polymer and repair.
[fire - consequence, acrylic acid, ethylidene norbornene, marine tanker, tank, unwanted chemical reaction, leak, polymerisation, high temperature]

Lessons

[None Reported]

1266912 July 1975

Source : ICHEME
Location : ,

Injured : 2 **Dead :** 0

Abstract

A fire occurred during cleaning of a light gas oil pump strainer when a gate valves ahead of the strainer released hot light gas oil which most probably autoignited on the hot equipment in the immediate vicinity of the hydrocarbon release. On employee suffered severe burns and another was slightly injured.
An investigation into the incident found that coke in the suction line of the light gas oil pump prevented the gate valve from being totally closed and this provided inadequate isolation of the suction strainer. Subsequent to the fire the valve was inspected and found to be in good condition. Traces of coke were found around and under the gate.
The source of the fire was leaking hot light gas oil vapours from the suction valve to the light gas oil pump which most probably autoignited on hot surfaces in the pump row.
Adequate emergency shutdown procedures were employed.
[fire - consequence, mechanical equipment failure, autoignition, burns, injury]

Lessons

[None Reported]

1257306 June 1975

Source : ICHEME
Location : Kurashiki City, JAPAN

Injured : 0 **Dead :** 0

Abstract

A small explosion occurred at the upper part of a reactor on an acrylonitrile plant. The incident occurred when one of two reactors was stopped due to short supply of starting propylene.
The reactor was purged with nitrogen. The feed lines were also purged to expel residual gases (propylene, ammonia, etc) in them from them into the reactor when the explosion occurred.
The cause of the incident is due to the residual gases that were purged into the reactor with a considerable amount of remaining heat, so that an un-controlled local reaction took place, leading to the explosion.
No one was injured in the incident.
[reactors and reaction equipment, purging, uncontrolled reaction, gas - flammable]

Lessons

[None Reported]

997 02 February 1975

Source : LAYTON D W, ET AL, ACCIDENTAL RELEASES OF SOUR GAS FROM WELLS AND COLLECTION PIPELINES IN THE OVERTHRUST BELT, LAWRENCE LIVERMORE NATIONAL LABORATORY, USA 1983.

Location : Denver City; Texas, USA

Injured : 0 **Dead :** 9

Abstract

Nine people were fatally injured when they were exposed to gas containing hydrogen sulphide escaping from a well injecting gas into an oil reservoir as part of an enhanced oil recovery project. The gas composed of 93% by volume carbon disulphide and 5% hydrogen sulphide. At about 05:00 hrs a pipe connection in the top of the wellhead failed, releasing gas into the atmosphere. A person living 183 metres from the well noticed the odour and warned people in a house 61 m from the well of the possible danger. Eight people in this house died.
[connector, incorrect material of construction, connector failure, fatality, gas / vapour release]

Lessons

[None Reported]

7233 1975

Source : LOSS PREVENTION BULLETIN, 065, 26.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A marine transportation incident. A marine tanker was carrying acrylic acid in a tank when it was found that the temperature was rising. Despite efforts at the receiving port to off load the material, this was not possible. In the end the tank had to be cut out of the ship. Polymerisation had been initiated by a leak from an adjacent cargo.
[contamination, high temperature]

Lessons

[None Reported]

8058 1975

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

In polyester tests, fibre samples are boiled over an electric hotplate in a glass beaker containing 25-30 cc of 64 per cent hydrazine. The procedure calls for use of glass rods for handling the sample. In this case, the laboratory technician used a pair of metal tweezers which were old and somewhat rusty.
When the tweezers were put into the hot hydrazine solution to remove the samples, the hydrazine ignited. The fire remained within the beaker and there was no damage or personal injury.
The cause of this incident was spontaneous ignition of hydrazine in the presence of iron oxide introduced on the tongs.
The ignition temperature is 75 degrees F in the presence of iron oxide and 518 degrees F in a glass container.
In the presence of iron oxide, the spontaneous ignition temperature of 75 degrees F is below the normal flashpoint of 100 degrees F. The technician involved in this incident was not aware of this unusual characteristic in hydrazine.
[laboratory work, testing, unwanted chemical reaction, rusting, spontaneous combustion]

Lessons

Emphasise the need for using glass utensils with hydrazine.
Select lab equipment with minimal iron content (such as a ceramic-top hotplate) for working with hydrazine.
The reduction in spontaneous ignition temperature due to the presence of iron oxide is interesting and certainly indicates what could happen if a hydrazine soaked rag was discarded into a rusty rubbish drum.

1076304 July 1974

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

A phenol manufacturing plant was being started-up after maintenance shutdown. The oxidation section operated sparging compressed air into the base of the of cumene liquid in each of 3 oxidation vessels. Liquid overflowed from one to the next and then to a settler drum and excess air was routed to atmosphere via a cooler and knockout drum.
Due to low pressure in the oxidiser vessels the superficial air velocity was much higher than normal, causing frothing and liquid carry over to the knockout drum, which filled over a 45 minutes period. After this 45 gallons/minute excess liquid was released from the vent to atmosphere. About 400 gallons were released.
The settler drum was fitted with a high level alarm, however, the valve from the 3rd oxidiser was left closed in error after the shutdown so no liquid entered the drum. The knockout drum was fitted with a level indicator but no alarm.
The operating team was lacking in expertise and experience to sickness and holidays in the normal team and failed to open the valve to the settler drum, or detect the low oxidiser pressure, or the high knock-out drum level. The source of ignition was probably a 500 psig steam pipe. Although this operated below the autoignition temperature of the reaction mixture the autoignition temperature was depressed to below steam temperature:
1. Preferential carryover of lighter components in the froth, hence material released was lighter than that in the reactors.
2. The high surface area provided by lagging on the steam pipework.
The fire lasted for 15-20 minutes and was extinguished by isolation of the fuel source. Plant fire water hoses were used by fire-fighters.
[start-up, processing, cumene hydroperoxide, gas / vapour release, fire - consequence, hot surface, reactors and reaction equipment]

Lessons

1. A high level should be fitted to the knockout drum.
2. Routine checks of plant equipment should be made to ensure their true state is known.
3. Plant condition/status readings to be undertaken during plant shutdown, and start-up, alert at reduced frequencies.
4. A review to be undertaken of potential to form explosive/flammable mixtures in the plant under start-up conditions.

905 22 June 1974

Source : AMMONIA PLANT SAFETY VOL.18, 1976
Location : Manali; Madras, INDIA

Injured : 1 **Dead :** 9

Abstract

A 16 inch carbon steel elbow in the carbon dioxide removal system of an ammonia plant ruptured due to erosion by impingement of a high velocity stream of hot liquid from a faulty control valve upstream of the elbow. Hot potassium carbonate solution splashed into the control room. A stainless steel elbow was fitted.
[incorrect material of construction, processing]

Lessons

[None Reported]

1078417 June 1974

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

A road transportation incident. A batch of water-based phenol-formaldehyde resol resin was being carried in a road tanker. It reacted violently and ruptured the rear end of the two compartment tanker shell. In order to reduce further risk, part of the contents of the front compartment were discharged to a road drain, this caused pollution of agricultural land.
This resin, and similar formulations, had been made in large tonnage quantities for many years without incident. Drum stock of the same make and age was perfectly normal in its behaviour. It was concluded that the incident was due to the loaded tanker having been left in exceptionally hot sunshine for 48 hours before despatch. It was well known that the resin should be stored and despatched at temperatures no higher than 30-350C.
A few weeks later another batch of the same resin exothermed in a storage tank.
[phenolic resin, road transportation, spill, overpressure, uncontrolled reaction, hot weather, high temperature]

Lessons

Further investigation suggested that current batches of the resin were exceptionally reactive. Manufacturing changes were proposed.

1256809 March 1974

Source : ICHEME
Location : Mizushima, JAPAN

Injured : 0 **Dead :** 0

Abstract

An explosion occurred on an oxygen plant during preparation for turnaround maintenance. The explosion occurred at the blow-down tank into which liquid oxygen was being introduced from the distillation section.
The cause of the explosion was due to liquid oxygen being introduced into the blow-down tank containing water causing sharp boiling. No one was injured in the explosion.
[preparation for maintenance, accidental mixing]

Lessons

[None Reported]

111811974

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

An air receiver explosion occurred minutes before employees were due to enter the factory and no-one was injured. The violence of the explosion completely wrecked the compressor house and projected debris into adjoining properties.
Subsequent investigations established that the compressor air outlet temperature had been excessively high and the discharge pipe to the air receiver contained carbon deposits. Indications were that lubricating oil had passed through the compressor into the discharge pipe where it had carbonised. Under such conditions it is possible for the carbon deposit to reach the ignition temperature of the oil. Normal overpressure safeguards are of no avail because the pressure built-up by the igniting air/vapour mixture can be many times the normal working pressure of the receiver and the speed of build-up too quick to relieve by the operation of a safety valve.
[processing, compressor, solids deposition, unwanted chemical reaction, high temperature]

Lessons

The following recommendations were made:
1. Where the outlet temperature of an air-cooled compressor is high, a water cooled compressor may be more suitable.
2. The temperature of air discharge from the compressor should be well below the ignition temperature of the lubricating oil used. A fusible plug should be fitted in the outlet pipe close to the compressor.
3. The compressor intake should be in a cool place, preferably outdoors away from dust, fumes, exhaust gases, drips or splashes of oil and the air should be screened.
4. The air-receiver should be located in a cool, well ventilated place.
5. The air-receiver should be drained regularly.
6. Regular internal inspection of the air-receiver should be carried out.
7. The correct grade of lubricating oil should be used and consumption should be kept to a minimum.
8. Regular maintenance checks of the compressor are necessary.
9. Compressor discharge valves in poor condition can cause an increase in temperature. In particular they should be kept free of carbon deposits.
10. The interconnecting piping between the compressor and after-cooler or air receiver should be removed frequently and inspected for the presence of carbon. Fusible plugs fitted in this piping should also be regular inspected as deposits of carbon can create an insulating effect on the probe plug, rendering it inoperable. The fusible disc should be renewed every two years.

1116925 October 1973

Source : ICHEME
Location : , FRANCE

Injured : 0 **Dead :** 0

Abstract

A fire occurred near the upper part of a residue exchanger on the distillation unit and quickly spread to the ground covering a wide area. No injuries to personnel were reported and only minor equipment was damaged, the fire was extinguished using portable powder appliances.
As a result of poor housekeeping on the plant, fire extended beyond the immediate spillage area into:
1. A drain duct which was contaminated with benzine from a leaking vale on the pump-out circuit of the benzine coolers.
2. A desalter cable trench that had previously been impregnated with inhibitor from a leaking joint on the corrosion inhibitor tank; the paving below this leaking joint sloped preferentially towards the cable trench rather than the drain
Subsequent investigations indicated that ignition had occurred spontaneously from one of two causes, the more probable being the spraying of hot residue exchangers with a corrosion inhibitor.
Two days previously it is known that water hoses had been used to transfer the corrosion inhibitor and the hoses had not been emptied or rinsed. It is thought that one of these contaminated hoses was laid out to wash down the area beneath the bank of residue exchangers and in washing down, a hot exchanger was sprayed with the inhibitor which ignited spontaneously. Nearly the whole length of the hose was burnt.
The other possible source of spontaneous ignition was contaminated insulation on one of the hot residue exchangers.
[fire - consequence, hose, spontaneous combustion, cleaning inadequate, contamination]

Lessons

The following recommendations were made:
1. Keeping unit clean, i.e. good housekeeping.
2. Immediate tightening up of any leaking joint.
3. Protection of insulation so that no leaking product is absorbed.
4. Use of water washing hoses on product duty, or vice versa, to be avoided.

11167July 1973

Source : ICHEME

Location : , SWEDEN

Injured : 0 **Dead :** 0

Abstract

A road transport incident. A road tanker was damaged by a low order explosion in one compartment whilst being loaded with heating oil at a terminal. The oil was being bottom loaded through a hose at a linear velocity of some 5 metres/second when the explosion occurred. Fortunately the tank did not rupture and the shock of the explosion closed the lid of the compartment smothering the fire and the incident developed no further. The previous day the tanker had been used to carry motor spirit and although the driver had drained the compartment and hose it is almost certain that some petrol remained. Samples of the oil in the vehicle proved to have a flash point of 56 degrees C where as samples from the tank from which the vehicle was being filled had a flash point of 63 degrees C. There was no possibility of a product mix because each product is delivered via a separate pipe.

In the absence of any other source of ignition, it is concluded that the mixture of heating oil and petrol caused a flammable vapour in the compartment which, it is assumed, was ignited by an electrostatic spark. It is significant to note that after the incident the hose was checked for electrical continuity and found to be defective.

[loading, accidental mixing, cleaning inadequate, gasoline]

Lessons

This incident emphasises the need for frequent checking of conductive hoses where they form the only earth connection with the vehicle.

1008806 May 1973

Source : ICHEME
Location : , USA
Injured : 4 **Dead :** 0

Abstract

Following a catalyst regeneration a fire occurred on a hydrocracking unit during unit pressure testing prior to start-up. The fire resulted from ignition of high - pressure hydrogen-rich gas that was escaping from two shell-to-shell nozzle flanges on the hydrocracker reactor charge - effluent exchangers. Four pipefitters who were in the process of tightening the leaking flanges when the gas ignited, received first and second degree burns. The unit was depressurised to the relief system and the fire was extinguished after burning for approximately 45 minutes. Unit damage was confirmed to the insulation.
The hydrocracking unit was shutdown for a scheduled regeneration of the preheater and hydrocracker reactors and minor maintenance. Following this preparations were made to bring the unit on stream. The unit was nitrogen purged and evacuated several times and nitrogen was then fed into the pretreating an hydrocracking sections checked for leaks at 100 PSIG. The nitrogen was then vented to the relief system and the system evacuated Hydrogen-rich gas was introduced and again the preheater and hydrocracker were checked for leaks up to 450 PSIG. The make-up hydrogen compressor was placed in service and the pretreater system was checked for leaks at 1250 PSIG. A moderate leak was successfully stopped. The hydrocracker section was being raised to a final test pressure of 1600 PSIG when two shell-to-shell nozzle flange leaks developed in the inner connections of the hydrocracker reactor charge-effluent exchangers. These severe leaks developed from flanges that had not been disturbed during shutdown regeneration and start-up.
The make-up hydrogen compressor was shut down at about the same time due to vibration. The loss of this and the leaks caused the system pressure to fail. Four pipe-fitters were instructed to tighten the exchanger flanges using a steel maul and a steel hammer wrench. By the time the pipefitters had assumed position pressure had dropped to 1050 PSIG. At the instant the hammer wrench was struck for the second time ignition occurred. The gas in the area of both leaks flashed and continuous burning followed at both flanges. The fire extinguished itself after 45 minutes.
Probable causes of ignition were.
1. Spark caused by striking the hammer wrench
2. Static build-up from the escaping hydrogen
3. Autoignition of hydrogen due to expansion heating
4. Autoignition of iron sulphide scale.
[fire - consequence, flange leak, spark, hydrocracker, damage to equipment]

Lessons

Flange leaks are not unusual where hydrogen is circulated during start-up. It is common practice to fit known leak prone flanges with stream rings to prevent flash-fires and to heat flanges that are leaking as quickly as possible to normal process temperatures. Leaking flanges not equipped with permanent steam rings to protected with steam lances until the leak stops.
Unit operating and current maintenance practices include corrective measures:-
1. Continued use of nitrogen for evacuating and testing equipment prior to start-up; nitrogen to be used through the full range of test pressures.
2. Should major leaks occur during or after start-up with hydrogen in the system, the system pressure will be reduced to minimise leak. If a leak should continue at low pressure nitrogen will be readmitted before work is initiated.
3. Employees will wear protective clothing and equipment as required while stopping leaks occuring during and after start-up.
4. Exchanger flanges that have been opened and have leaked in the past will be tightened using hydraulic torque wrench equipment prior to pressure testing. This equipment will also be used in stopping process leaks that are found during unit start-up.

9722 28 March 1973

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

An uncontrolled runaway reaction occurred in the polybutene plant reactor. Despite operation of the two relief valves, the vessel was overpressurised resulting in the displacement of the gasket and a number of flanged joints, with subsequent discharge of flammable material to the surrounding area.
The fire service were requested to stand by, but in the event were not required to take action.
The discharge lasted for 20 to 30 minutes.
[overpressurisation, spill, near miss]

Lessons

1. The capacity of the relief system should be re-appraised.
2. Flange joints which are subject to repeated cycling by pressure and temperature should be checked for condition and tighten at scheduled intervals.

9347 28 March 1973

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

Release of flammable material occurred causing a runaway reaction in which relief valves and reactor kill system appeared to be inadequate.
[leak, reactors and reaction equipment]

Lessons

[None Reported]

1123110 January 1973

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

A failure occurred on a shield tube in the bottom row of the convection bank of the catalytic cracker feed preheater furnace. A severe fire followed lasting approximately two hours but there were no injuries to personnel. Some forty tubes suffered fire damage, distortion and sagging, and had to be replaced. Subsequent metallurgical examination indicated that tube failure occurred as a result of 'creep' which developed from overheating. No signs of this creep were found in adjacent shield tubes or selected radiant tubes and it was concluded that the overheating of the failed tube arose from the incomplete removal of coke from its middle section at the previous overhaul, in September 1970. This is believed to have accelerated localised coking creating high skin temperatures which resulted in the formation of creep voids and ultimate tube failure. The centre section of the shield tubes in the bottom row of the convection bank are susceptible to high heat flux rates as they receive both radiant and convective heat. These tubes were previously replaced in 1964 because of oxidation along the underside of the middle twelve feet.
[refining, heating equipment, catalytic cracker, creep, overheating, tube failure, cleaning inadequate, fire - consequence]

Lessons

Recommendations arising from the incident:
1. Replacement of the carbon steel shield row tubes with 5% Cr and 1/2% Mo, the maximum allowable temperature of the latter being 1,150 degrees F compared with 950 degrees F for carbon steel.
2. Installation of thermocouples to help assess the heat load in the centre region of the bottom row of shield tubes and the effect of burning deodoriser stink gases in the preheater through the floor mounted ports.

700 02 November 1972

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

Unreacted cumene hydroperoxide accumulated in the cleavage reactor due to a slow down of the decomposition by a shortage of mineral acid. Lower acid levels were being used and the ingress of other salts including some sodium carbonate was considered.
[reactors and reaction equipment, low level of catalyst, reaction]

Lessons

[None Reported]

1023225 March 1972

Source : EXPLOSION DISASTERS IN THE DISSOLVED ACETYLENE INDUSTRY, YUKIO HASHIGUCHI, OCTOBER 1976.
Location : Amagasaki City, JAPAN

Injured : 2 **Dead :** 0

Abstract

An explosion occurred in a bucket conveyor of the acetylene gas generating plant and completely destroyed the cover of the conveyor. Immediately after the explosion, a fire broke out in the acetylene filling plant and 47 cylinders filled with acetylene burst one by one and some of the fragments flew out to a house outside the plant.
The estimated cause to the incident: The explosion in the bucket conveyor appears to have been caused by a mixture of acetylene and air inside the conveyor. The iron cover of the conveyor was completely destroyed over the whole length of 15 metres and the fragments were blown off in all directions. The building housing the bucket conveyor, the hoppers and the generator is a three-storey steel frame structure with slate walls and roof. The slates were all blown off and window glasses reinforced with wire mesh were broken to pieces except some on the second story.
[fire - consequence, damage to equipment, accidental mixing, material transfer]

Lessons

In recent years, it has become a general practice to cover conveyors to prevent scattering of calcium carbide powders from the viewpoint of environmental control. It is essential in design works to exercise sufficient care to prevent back flow and stagnation of acetylene. In the low-pressure section, explosions are also known to occur frequently in the recovery operation of the solid purifying medium in the purifier when the apparatus in question is opened to the atmosphere. In this case, it is necessary to prevent explosions by purifying thoroughly with nitrogen.

5600 19 August 1971

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

A small fire broke out at a flange on a motor spirit line on the 19th August 1971. The 8 inch motor spirit header at the adjoining pumphouse was to be dismantled for modification and had been water flushed 10 days earlier but when the flanges were being broken a mixture of water and spirit emerged. A hose was turned on to flush away this material while the remaining bolts in the flange were undone. The last of these bolts was rusty in places and considerable force was required to move the nut, space was restricted and a cut-away ring spanner was used with a 4 ft. piece of piping to give extra leverage. This bar slipped as force was being applied and immediately a small quantity of motor spirit on the ground caught fire. Dry powder fire extinguishers were fetched from the nearby pumphouse and quickly put out the fire. No-body was injured and there was no damage.
In this case, it is most likely that the iron extension bar struck an aluminium painted pipe as it fell and initiated a thermite reaction. Much less energy is required to produce an incendive spark by this means than by iron-to-iron contact.
[fire - consequence, maintenance]

Lessons

Where `strong force' has to be applied in a situation where flammable material is present, then it is advisable to wet the flanges and bolts first.

1099202 August 1971

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

Contractors noticed a fire had started in a friction dust plant. The plant supervisor raised the alarm and on investigation found that the fire was taking place in a mixer rework hopper. The fire was rapidly put out using water and carbon dioxide. The friction dust in the hopper was removed and made safe. There were no injuries to personnel and there was minimal damage to the hopper. The contents of the hopper, 300 - 400kg of friction dust, were dumped. The hopper had not been used in production for the last month and had been normal when inspected a few days earlier. Although welding had been taking place on the roof of an adjacent building no way was identified of sparks entering the hopper. Examination of the material in the hopper after the fire showed that only the surface material had ignited. Prior to the fire the weather had been hot and dry for 4 days. Although the exact cause of the fire was not established, autoignition was though to have occurred, and likely to have been initiated by the presence of oxidisable or high volatile content material in the hopper.
[fire - consequence]

Lessons

1. The hopper is to be emptied and the area vacuumed in the event of shutdowns of any significant time.
2. Potentially oxidisable fines should be damped down, drummed and dumped.
3. Temperature indicators were to be fitted to the fines and rework hoppers and their readings were to be monitored.
4. The testing programme for auto-ignition was to be extended to cover the materials thought to be in the hopper.

6881 June 1971

Source : ICHEME
Location : ,

Injured : 1 **Dead :** 0

Abstract

A production plant had always received benzyl chloride which the supplier had stabilised with aqueous caustic soda. A new batch of benzyl chloride was to be separated from the caustic soda in a 1,000 litre glass-lined vessel. The operator had sucked the benzyl chloride into the batch reactor and opened the ventilation line. Immediately the benzyl chloride started to polymerise with the formation of smoke and hydrochloric acid. The valve in the ventilation line soon plugged and the safety valve lifted. The temperature in the kettle rose to 55 degrees C and escaping acidic gases forced an evacuation of the building.
[iron oxide, batch reaction, gas / vapour release, overpressure, lack of stabiliser/inhibitor, contamination, batch reactor]

Lessons

Investigation showed that the benzyl chloride had not been stabilised by the supplier, but instead had been supplied in drums with a polypropylene liner. An operator had noticed that one drum fumed when opened.

1072502 April 1971

Source : NATIONAL TRANSPORTATION SAFETY BOARD, 20591, NTSB-HAR-71-7.
Location : , USA

Injured : 6 **Dead :** 0

Abstract

A road transportation incident. A hose used for transferring a bulk liquid chemical cargo from a semi-trailer to a storage tank was incorrectly attached to a fill line leading to an indoor open-top tank. When the transfer began, the cargo mixed with the incompatible chemical stored in the indoor tank resulting in a chemical reaction which generated toxic hydrogen sulfide gas. Six workers died from the inhalation of the toxic gas.
The cause of the accident was the failure of the carrier's drivers and the tannery foreman to establish an error-free exchange of information required to accomplish the safe transfer of the cargo from the vehicle into a plant storage tank. The likelihood of this happening was increased by the absence of instructions or training in information validation procedures during such exchanges and by the absence of markings, devices or other measures on the vehicle or tannery property which would have permitted such validation to be made unilaterally by either party.
[storage tanks, material transfer, gas / vapour release, training inadequate, accidental mixing]

Lessons

The National Transportation Safety Board recommended that:
1. A comprehensive investigation should be conducted into the risks associated with the delivery of bulk liquid cargoes from motor carrier vehicles, and initiate the implementation of risk-reduction measures.
2. Trucking associations and councils to call their member's attention to the risks associated with communications failures during bulk liquid deliveries and to the need for development of training and enforcement of procedures which incorporate information validation techniques to be used during such deliveries.
3. To consider the establishment of rules, regulations or standards which require the display of the name of the material to be delivered into each fill line connection at these connections inall facilities where bulk liquid materials are delivered from a motor carrier vehicle
4. To develop and implement requirements which would reduce the risks to employees and carrier personnel in the event of accidental mixing of incompatible bulk liquid materials at all locations where such materials are delivered by motor carrier vehicles.
5. To initiate rulemaking action to require all carriers to report accidents occurring in connection with the delivery of bulk liquid materials from motor carrier vehicles, whether or not the carrier's employees, vehicle, or cargo suffered damages in the accident.

66 30 March 1971

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

On the 30th March 1971, oil sprayed from a leak at the connecting flange between the top and bottom reactor feed effluent heat exchangers of a catalytic reformer unit. The oil spray fell on to an adjacent heat exchanger and caught fire causing the shut-down of the plant for 43 days.
There was no evidence to suggest that any unusual plant operational conditions initiated the leakage, and the primary cause was attributed to the use of a solid, flat, stainless steel gasket.
[operation inadequate, fire - consequence, damage to equipment, plant shutdown, processing, incorrect material of construction]

Lessons

Use spiral wound gaskets not solid, flat, stainless steel gasket.

822 12 March 1971

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

On the 12th March, 1971 following the loss of the catalytic reformer unit recycle gas compressor, the reactor feed effluent heat exchangers were subjected to extensive thermal shock.
Liquid hydrocarbon leaked from the heat exchanger channel head joints and, after a short period, ignited spontaneously, resulting in a serious fire. Damage was limited to cladding and insulation of the heat exchangers, but the plant was offstream for several days.
[fire - consequence, spontaneous combustion, thermal degradation, damage to equipment]

Lessons

Resulting from this incident, the following recommendations were put forward by the local investigating committee:
1. The reactor feed and reactor furnace fuel systems to be linked into the recycle gas trip-out instrumentation to ensure immediate shut-down of the systems on a compressor failure (the existing shut-down device, located in the control room, is not desirable in such instances as it is designed to shut down other sections as well as the reformer).
2. Installation of a manually controlled vent valve to flare from the suction side of the recycle gas compressor, so that the unit could be depressured in 30 minutes.
3. Fitting of snuffing steam rings as a permanent fixture around all exchanger shell/channel head joints.

69 22 February 1971

Source : ICHEME

Location : ,

Injured : 0 **Dead :** 0

Abstract

At 19.15 hours on the 22nd February, 1971 a severe flange fire occurred on the outlet of the reactor charge/effluent heat exchanger. Leaking oil ignited spontaneously causing a serious fire in which a great deal of material damage was caused. The unit was out of commission for 11 days.

The unit was operating normally prior to the fire, and no mechanical failures or defects in equipment were found after the fire to cause the leak.

[fire - consequence, damage to equipment, spontaneous combustion, heat transfer]

Lessons

[None Reported]

9330 11 December 1970

Source : ICHEME
Location : , UK

Injured : 0   **Dead :** 0

Abstract

A fire occurred on a polyethylene plant. This was due to defective gland packaging. A second fire occurred due to a runaway reaction following catalyst contamination.
[fire - consequence]

Lessons

[None Reported]

1294010 February 1970

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

A fire occurred in the operators side of a cell in an area used for running off batches of product of tertiary butyl peroxides into containers for storage and despatch.
A number of filled solvent and organic peroxide containers were situated within a few feet of the fire. Fortunately the fire was confined to the cell area.
It is thought that the cause of the fire was due to spontaneous combustion.
[fire - consequence, loading]

Lessons

[None Reported]

436   03 October 1969

Source : ICHEME

Location : ,

Injured : 0   **Dead :** 3

Abstract

Butadiene plant. Source of ignition: auto decomposition. Fatality.
[processing]

Lessons

[None Reported]

1000608 August 1969

Source : LOSS PREVENTION A.I CHEME, VOL 5.
Location : Illinois, USA

Injured : 4 **Dead :** 0

Abstract

An autoclave, being used for the manufacturing of nitroaniline (NA) ruptured, causing extensive damage to the plant and buildings. Four people were injured. NA is produced by reacting nitrochlorobenzene (NCB) with aqueous ammonia in an autoclave under high pressure. The autoclave was ruptured, parts of it being projected as far as 200 feet.
Investigation showed that the incident was caused by the reaction proceeding at too high a rate, caused by the high reaction temperature. This, in turn, was due to heat removal being slower that heat generation, in other words a "runaway reaction".
[damage to equipment, processing, material of construction failure, high pressure, injury]

Lessons

The batch charge was abnormal i.e. overcharged of NCB, and undercharge of ammonia. A number of factors, or actions, might have prevented the incident, had they been present, or taken. These were:
1. Stronger aqueous ammonia and correct amount of ammonia. This would have had the effect of giving higher pressures, and suppressing temperature excursion.
2. No overcharge of NCB, the reaction would have proceeded normally.
3. Opening of the manual release line in good time. This was not done.
4. Functioning (rupture) of the bursting disc/relief valve system at design pressure. This did not happen.
5. Full cooling flow onto the cooling jacket at all times.
6. Adequate instrumentation to indicate correct temperatures.
Other potential causes were considered but it was concluded that none of these could account for the circumstances.

431   17 July 1969

Source : PUBLIC INQUIRY INTO A FIRE AT DUNGEONS WHARF, CMND. 4470, HMSO, 1970.; DECOMMISSIONING HAZARDS, HAZARDOUS CARGO BULLETIN, 1983, APR, 29 & 32.

Location : Dungeons Wharf, UK

Injured : 0   **Dead :** 0

Abstract

A tank farm, which had been used for the storage of different oils, was being cleared. Work was being carried out on a welded tank that had been used to store myrcene, a hydrocarbon oil. Oxy-propane cutting equipment was being used on the tank roof, when flames emerged through the incision and shortly afterwards through the roof manhole which was open. The flames died out but the tank was inspected by a fire officer and water was sprayed through the cut. To make sure no particles were smouldering under the roof of the tank an attempt was made to open a manhole at ground level. The manhole bolts could not be opened manually and an oxy-propane cutter was being used to release the first bolt when there was an explosion and the tank roof was blown off.
The fire was undoubtedly caused by the ignition of the deposits of polymerised myrcene which had not been removed by steaming or otherwise from the underside of the roof, the roof supports and upper surfaces of the inside of the tank. Although the tank had been steamed for a considerable period, it had not been known that this treatment would have no effect on the myrcene. The cause of the explosion was disputed, but a majority of the experts who gave evidence were of the opinion that following the fire, a mixing of the contents of the tank, including the vapours given off by the polymerised myrcene which when united with oxygen and a source of ignition were explosive. This mixing was due to various factors including the entrainment of air and the introduction of the water spray.
[cleaning inadequate, fire - consequence, storage tanks]

Lessons

[None Reported]

8305 31 March 1969

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

Cyanuric chloride was being reacted with methanol in the presence of sodium bicarbonate. By mistake, two 100kg drums of cyanuric chloride were added instead of two 50 kg drums. Although the reactor was cooled with brine, the temperature rose to 60 degrees C within 30 minutes. There was a violent eruption of solvent, and gaskets on the vessel were blown out and the vent line was broken. Luckily the vapours did not ignite.
[batch reactor, batch reaction, chemicals added incorrectly, uncontrolled reaction, overpressure, gas / vapour release]

Lessons

The reaction of cyanuric acid with methanol is catalysed by acid: therefore the additions of cyanuric acid and sodium bicarbonate must be balanced. Due to the overdose of cyanuric chloride, the hydrochloric acid formed in the reaction could not be neutralised by the available sodium bicarbonate and the reaction accelerated.

419 24 February 1969

Source : ICHEME
Location : Texas, USA

Injured : 0 **Dead :** 0

Abstract

The first acetaldehyde column (stripping section) of the ethylene oxide plant had an explosion without warning. The explosion destroyed the entire upper section of the column between the reboiler vapour return and the top head. The vessel shell broke into very small fragments but one piece of 500 lb hit the ground at a low angle, bounced, cut a high voltage cable and came to rest 500ft away. Only 50% of the column was found and samples showed brittle fracture. The top head was separated from the column at the weld seam and was essentially intact suspended in air at the end of the overhead pipe connection. The Glitsch valve trays were blown out of the column and none were in the bottom section of the column. Only 7 were recovered, these were segmented and intact. The downcomers were coated with a goeey black polymer. The bottom section of the column (about 3 feet deep) had not burst apart. Adjoining sections of plate had unwrapped at a fairly high velocity but not before the section had bulged a few inches. The plate near the tear had thinned down to about 1/8 inch from 1/4 inch and the break showed a shear failure. The shards and pieces of the upper column substantiated a detonation in the top part of the column. Plant instrument charts and log sheets gave no indication of trouble. The pressure of 68 psig and temperature 60-65 degrees C on the 10th tray were constant up to the point of detonation. Investigation concluded:
1. Trouble began within the acetaldehyde column stripping section without a preceding fire or gas escape.
2. There had been a true detonation not a deflagration reaction.
3. The source was auto-polymerisation of ethylene oxide which raised the temperature of a zone to about 571 degrees C. polymer diverted the flowing liquid and insulated the hot spot so that the hot spot could build up in temperature.
4. The polymerisation was catalysed by iron oxide which was found in the black polymer taken from the tray downcomers (10% iron).
5. The detonation was a vapour detonation of ethylene oxide.
[distillation, liquid liquid separation, normal operations]

Lessons

The revision of the plant included:
1. The elimination completely of the aldehyde column.
2. The refining column previously containing 30 bubble caps was re-equipped with 1 1/2 inch aluminium flexi-rings(similar to Pall rings). This reduced the acetaldehyde content of the product to 50-60 ppm.
3. A new column was added.
4. All magnesia insulation was replaced by aluminium cladded insulation.
5. Minimum flow bypasses on all pumps.

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

Ethylene oxide filter left full of ethylene oxide and blocked in leading to polymerisation and explosion.
[flow restriction, processing]

Lessons

[None Reported]

409 1969

Source : LOSS PREVENTION, 1976, 10, 76-79

Location : Basle, SWITZERLAND

Injured : 31 **Dead :** 3

Abstract

A batch exploded with detonation when a more concentrated nitrosyl sulphuric acid of 40% was used instead of the normal lower strength material. The product was also more concentrated and was later tested to be detonatable when heated. Fatality.
[processing, incorrect chemical concentration, reactors and reaction equipment]

Lessons

[None Reported]

398   31 May 1968

Source : ICHEME
Location : ,

Injured : 5   **Dead :** 0

Abstract

A storage tank was being recalibrated and an amine was pumped into the tank. There was a violent reaction with large gas evolution and rupture of the tank. A mixture of the amine, a diketene, occurred forming achrylamide in a runaway reaction. Temperature rise caused polymerisation of the diketene and decomposition of diketene to acetone and carbon dioxide.
[storage tanks]

Lessons

[None Reported]

397 23 April 1968

Source : MARSHALL VC, MAJOR CHEMICAL HAZARDS, ELLIS HORWOOD, 1987. ENVIRONMENTAL PROTECTION BULLETIN, 035, 15.
Location : Bolsover; Derbyshire, UK

Injured : 79 **Dead :** 1

Abstract

The oil temperature control of a heater on a reactor containing 2,4,5-trichlorophenol failed causing a runaway reaction. The reactor exploded releasing dioxins.

[reactors and reaction equipment, temperature meter/control, explosion, fatality]

Lessons

[None Reported]

Source : FATAL CHEMICAL PLANT EXPLOSION, FIRE JOURNAL, 1967, SEPT; LEWIS D.J, CASE HISTORIES OF PAST ACCIDENTS THE CAUSES AND CONSEQUENCES, MAJOR HAZARD INSTALLATIONS PLANNING AND ASSESSMENT SEMINAR; VERVALIN C.H (ED.), FIRE PROTECTION MANUAL, 2ND ED. GULF, 1973.

Location : La Salle, CANADA

Injured : 1 **Dead :** 11

Abstract

A fatal explosion occurred on a chemical plant, completely demolishing a polystyrene building.
A runaway reaction occurred on styrene polymerisation reactor causing styrene monomer vapours to escape from a flange on a jacketed reaction vessel and after mixing with air, ignited explosively, breaking the sprinkler system and other pipelines in the area. Although the force of the explosion upset a tank car of acetone and six cars of styrene, the cars did not rupture because firemen protected them with hose streams.
Investigation:
Critical equipment items and auxiliaries were carefully examined, first when they were found in the wreckage of the polystyrene building and again after removal. All polymer kettles were found completely intact, their manhole covers and other closures in place. The safety disc on the runaway kettle had ruptured. However, neither this nor the partial dumping and venting of the kettle to the yard and roof could account for the massive amounts of styrene fog and vapour that had filled the building just before the explosion.
The runaway kettle was equipped with an inspection port that wyed off the rupture disc vent line just above the disc. The purpose of this port was to permit examination of the rupture disc surface for telltale bulges indicating polymer build-up on the kettle side of the disc. The inspection port was capped with a heat and pressure resistant sight glass, which was missing when the kettle was examined after the disaster. The sight glass was broken by a combination of extraordinary thermal and hydraulic shocks caused by kettle syrup entering the vent line at high velocity when the rupture disc relieved. Rupture of the sight glass would have permitted large quantities of boiling material to escape into the building while some also flowed up the vent line to the roof. The inspection port is considered to be the most likely source of the vapour that filled the polystyrene building, inasmuch as the investigation did not turn up any other source.
No obvious source of ignition was to be found. The possible place of ignition was not limited to the building interior, ignition was not limited to the building interior, ignition could have occurred outdoors as well. Employees saw a fireball in the yards south of the polystyrene building where there was a concentration of styrene fog and vapour resulting from dumping the kettle. It is not known, however, whether the outdoor fireball appeared before the explosive ignition of the styrene air mixture in the interior of the building. Static electricity has also been considered as a possible source of ignition.
Damage is estimated at $4 million (1966).
[reactors and reaction equipment, fatality]

Lessons

[None Reported]

334 1966

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

An explosion occurred on a chemical plant caused by a runaway reaction.
[processing]

Lessons

[None Reported]

311 April 1965

Source : ICHEME
Location : ,

Injured : 1 **Dead :** 1

Abstract

One man entered a vessel which had contained recovered butadiene to remove some sticky white-ish rubbery residue from the vessel bottom prior to inspection of the vessel. While removing some of the residue with a beryllium-copper shovel there was a flash and both the man inside the vessel and the one standing by outside were burnt. Investigations showed that the most likely cause of the explosion was the presence of a small but concentrated amount of butadiene peroxide held in a pocket of the residue on the floor of the tank. When disturbed by the shovel it spontaneously ignited, either by contact with the air, or because of the shock received from the shovel hitting it. This caused a mild explosion and the flash ignited the two men's latex contaminated clothing.
Fatality.
[cleaning, entry into a confined space, cleaning inadequate, hand tools, burns]

Lessons

As a result of the investigation into this accident, and the analytical report, the following recommendations have been made to prevent a similar formation of butadiene peroxide occurring.
1. The inhibitor concentration (tert. butyl catechol) in recovered butadiene should be maintained at not less than 200 ppm. The maximum permissible concentration of oxygen in the recovery system to be set at 2000 ppm. and this must not be exceeded.
2. All vessels and other containment places in the recovery system in which butadiene peroxide may form should be boiled out with water, the temperature being raised at a rate not greater than 0.5c/min. and held at boiling point for at least 12 hours once every 12 months. If experience shows that butadiene peroxide may have formed at an increased rate more frequent boiling out of these vessels should be done.
3. Before any person enters any vessel which has contained butadiene the vessel should be boiled out as recommended.
4. If, after this treatment any residue is found, a sample should be taken (preferably by a grab method) and tested by the hot plate test to observe how the residue decomposes. Where this test indicates rapid decomposition the vessel should be further treated by boiling out with a suitable alkaline solution.
5. That trials to be carried out with known fire resistant clothing and with available methods of laundering contaminated clothing.

9992 1965

Source : ICHEME
Location : , USA

Injured : 0 **Dead :** 0

Abstract

A fire occurred due to leakage in the furnace return header of a high pressure thermal cracking heater. The cracking furnace was processing a high sulphur gas oil under normal operating conditions. An operator heard a dull thump and saw hydrocarbon vapour coming from behind a header box hatch cover near the midpoint tube in the heater side of the furnace. The vapours immediately flashed, either from autoignition or from the fired heater. The temperature of the gas oil was about 840 degrees F at this point.
A fixed monitor was immediately put into operation covering the fire area. The unit was shut down without further incident. However, the fire continued to burn during the depressuring and purging sequence. The heavy flow of water being directed at the fire area from the fixed monitor held heat damage to a minimum. Damage consisted primarily of shattered transite heater sheeting and loss of local thermocouples and lighting circuits.
Subsequent examination at the point of release indicated that a corrosion failure of a header box plug seat liner was the cause. These liners were specified to be 9% chrome. The liner that failed had been inspected twelve months previous to the failure and at that time over half an inch of the seat liner remained. The liner had therefore corroded at a rate in excess of half an inch per year. The normal rate of corrosion of 9% chrome liners was approximately one fifth of this. Chemical analysis of the failed liner proved it to be carbon steel.
[fire fighting equipment, lining failure, incorrect material of construction, damage to equipment, gas / vapour release]

Lessons

The following conclusions were made:
The plant was booby trapped into failure by a component which did not meet the specification as ordered. Procedures called for checking one liner in each order received for proper alloy. Installation was made without additional metallurgical checks. After the failure, ten additional carbon steel liners were found in service and seven unused carbon steel liners were found in the warehouse. The key lesson learned from the incident was to emphasize the importance of a carefully developed quality control programme for purchased materials.
The following recommendations:
· Purchase orders for materials must include minimum specifications where applicable.
· Purchase only from reputable suppliers.
· Subject all critical material as delivered to random statistical checks to determine that the material is acceptable.
· Permit no substitutes in material purchase or local usage without prior approval of designated engineering personnel.
· Check all alloy pipe, tubing, fittings and valves for alloy composition at time of use.
· Check all pressure-containing equipment as received to ensure that wall thickness is no less than specified.
· No salvage material to be reused with specific checks that material is suitable.
· Refinery warehouse is responsible for identification and safe storage of all material until released for use.
· Foremen to be alerted to the probability that quality control exercised by suppliers is declining.

275 20 April 1964

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

Prior to start-up of a catalytic cracking unit the oil side is purged of air with nitrogen. Due to an error by the supplier, it was purged with oxygen and an explosion occurred damaging towers, instruments and exchangers The normal purge procedure was followed, but two hours after the first oil had been introduced into the system, two loud almost simultaneous explosions were heard. The main fractionator and overhead accumulator were seen to vibrate severely and two quick surges of gas and dust were emitted from the relief system protecting the overhead accumulator.
[damage to equipment, human causes, catalytic cracker, chemicals added incorrectly]

Lessons

As a result of this incident all tube trailer gases are tested for composition. In addition a portable oxygen meter to improve purge procedures and provide a positive control of certain purging operations in the field was purchased. The use of the purge gas test procedure on the day of this incident would certainly have prevented the explosion.

9857 1964

Source : ICHEME
Location : , WEST INDIES

Injured : 0 **Dead :** 0

Abstract

In a unit for hydrogenating benzene to cyclohexane the temperature rise in the reactor was limited by recycling a large volume of cyclohexane product. This was essential because if the temperature rose more that 25 degrees C, runaway demethylation would start.
The protection against a runaway was a set of 16 thermocouples in the reactor connected to a multipoint recorder with a shutdown trip.
However, when the recycle pump failed the slow response of the thermocouples and the 2 second per point speed of the recorder permitted a runaway before the shutdown was actuated. One reactor bed temperature went off scale at 500 degrees C and only rapid depressuring of the reactor prevented a rupture.
[hydrogen, exothermic reaction, reaction vessel, catalyst, near miss, reactors and reaction equipment, pump failure, runaway reaction, design inadequate]

Lessons

1. When designing safety shutdown s the rate of response of the detection system must be allowed for.
2. The best shutdown systems measure the primary cause of the fault rather than its consequences.
3. The unit was fitted with an additional shutdown which measured the ratio of the recycle cyclohexane flow to the benzene charge flow. It was triggered when the ratio fell below a safe level.

247 October 1962

Source : DARTNELL RC, VENTRONE TA, LOSS PREVENTION VOL 5, AICHE, 1971, 53
Location : Bound Brook; New Jersey, USA

Injured : 0 **Dead :** 0

Abstract

An explosion followed by a flash fire occurred in a 3,000 gallon storage tank containing 1,500 gallons of p-nitro-m-cresol. It was determined that the p-nitro-m-cresol was unstable above its melting point and gradually undergoes a free radical polymerisation which evolved much heat.
[fire - consequence, storage tanks]

Lessons

[None Reported]

240 27 April 1962

Source : 100 LARGEST LOSSES 9TH EDITION, MARSH & MCLENNAN PROTECTION CONSULTANTS, 1986; VERVALIN C.H (ED.), FIRE PROTECTION MANUAL, VOL 1, 2ND ED., GULF, 1973, 81.

Location : Marietta; Ohio, USA

Injured : 3 **Dead :** 1

Abstract

A benzene recycle pump in a phenol production unit became plugged with residue. While employees were attempting to clear the plug with steam, pressure built up in a stripper column causing a 6 inch relief valve to operate, discharging benzene vapours which became ignited. Flying debris from the resultant explosion ruptured piping, releasing 40000 gallons of various flammable liquids which in turn ignited. Damage is estimated at M$2.8 (1962).
[processing, vapour cloud explosion, safety relief valve, fatality, fire - consequence]

Lessons

[None Reported]

233 31 March 1962

Source : LOSS PREVENTION BULLETIN, 101, 3-7.
Location : , UK

Injured : 0 **Dead :** 0

Abstract

Longitudinal splitting of a HCN (hydrogen cyanide) tank led to an explosion and fire. The explosion displaced another tank such that it collided with a pipe bridge which caused the rupture of a number of lines. It was concluded that there had been a rapid polymerisation in the tank causing a rise in temperature and pressure which led to the rupture of the tank.
[fire - consequence, high temperature]

Lessons

The following recommendations were made:-
1. All HCN manufactured should be stabilised as it is made. No unstabilised material should be put into storage tanks.
2. No HCN weaker than 95% should be put into tanks. Weak material should be recycled or neutralised.
3. Storage quantities should be kept to a minimum.
4. The storage temperature should be constantly monitored by a recorder with alarm.
5. HCN in stock should be kept at a low temperature.
6. Facilities should be provided so that stabiliser can be added to the tanks in an emergency.
7. The vent system should be increased.
8. Each stock tank should be pumped down to a minimum level every two days.
9. Each tank should be emptied, opened, cleaned and acid pickled at regular intervals.

217 October 1961

Source : VERVALIN C.H, FIRE PROTECTION MANUAL, 2ND ED., VOL 1, GULF, 1973.
Location : Chicago, USA

Injured : 250 **Dead :** 1

Abstract

A runaway reaction took place in a vessel containing vinyl acetate, ethyl acetate and benzoyl peroxide. When this exothermic reaction went out of control, the safety relief valve discharged a large volume of flammable liquids vapours into the interior atmosphere of the building. These vapours were ignited, and a violent explosion resulted. Fatality.
[reaction vessel, processing]

Lessons

[None Reported]

212 11 April 1961

Source : VERVALIN C.H (ED.), FIRE PROTECTION MANUAL, 2ND ED.,GULF, 1973;
Location : Wood River, USA

Injured : 0 **Dead :** 0

Abstract

This explosion fragmented the inlet section of a small mixing chamber in naphtha processing equipment. Solvent naphtha was being treated with an aqueous caustic hypochlorite solution. A routine injection of chlorine was made to enhance the hypochlorite solution when there was a violent explosion followed by a fire. Immediately prior to the incident, an operator had shut the caustic pump down, weighed 15 lbs. of chlorine into the caustic line and then started the caustic pump. A moment later there was an explosion at the mixer in which the special naphtha and caustic were mixed. Naphtha released as a result of the explosion was ignited and produced a substantial fire.
[fire - consequence, runaway reaction, sodium hypochlorite]

Lessons

[None Reported]

207 1961

Source : DE OLIVEIRA D.B, THIS PARAFFIN CHLORINATION UNIT, HYDROCARBON PROCESSING , 1973, 52, MAR, 112-126.
Location : , BRAZIL

Injured : 1 **Dead :** 1

Abstract

A violent explosion occurred in the paraffin wax chlorinating system in the lube oil section of a plant. The explosion occurred in a chlorine feed line trap. The investigation indicated that the cause was chlorinated paraffins which had backflushed and had been subjected to a violent uncontrolled free radical chlorination reaction. Fatality.
[uncontrolled reaction, processing]

Lessons

[None Reported]

107101960

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

Over 12 months, four explosions and fires occurred in pitch storage tanks at refineries, shortly after turning vacuum pipe still pitch production into unfluxed pitch tankage.
In a typical sequence of events, vacuum pipe-still pitch was cut to the utility plant at 11.40 am and the fluxing oil in the rundown line was flushed with pitch to a fuel oil tank at the utility plant. At 11.55 am, the pitch (at a temperature of 505 degrees F) leaving the vacuum unit was cut into the tank. At 12.05 pm a fire was noticed in the tank. Investigation revealed that insufficient time had been allowed for displacement of the line fill to the fuel oil tank. Thus flux oil was delivered to the tank.
On another occasion vacuum unit pitch production was diverted from the asphalt plant to a tank. A few hours later an explosion occurred in the tank. Inspection of the tank contents showed a contamination of 16% light cycle oil, the flushing oil involved in the operation. The origin of the flux oil could have been valve leakage.
Conclusion:
Three sources of ignition were suggested: static electricity, iron sulphide and auto-ignition of vaporized fluxing oil components. Static build-up should not be a problem, as impurities in the pitch make it reasonably conductive. Laboratory analysis of scrapings from the tank showed no iron sulphide. It was concluded that the explosions occurred as a result of auto-ignition of gas oil contaminants which vaporized in the presence of 500 degrees F+ pitch giving rise to explosive mixtures in the vapour space above the liquid.
[material transfer, autoignition, fire - consequence, contamination]

Lessons

The following recommendations were made:
1. Fluxing oil should be kept out of pitch tankage, and unfluxed pitch out of bunker fuel oil tankage. Line washing involves either contaminating pitch storage with gas oil or running hot unfluxed pitch into fuel oil storage. Thus lines used for delivery of pitch from vacuum pipe stills to storage should be steam traced and insulated to alleviate the necessity of line washing.
2. Pitch can be satisfactorily used as fuel at a temperature of 350-400 degrees F. To prevent accidents in the event of low auto-ignition components reaching pitch storage due to unforeseen circumstances, the temperature of pitch to tankage should not exceed 400 degrees F.
3. Tankage should always be gauged before and after oil movement to detect contamination that might occur while the tank is standing.
4. Measures should be taken to prevent the leakage of lighter oils into pitch tankage - for example, by installing blanks in series with the valves through which fluxing oil leakage may be expected.

9861 1960

Source : ICHEME
Location : , WEST INDIES

Injured : 0 **Dead :** 0

Abstract

On a naphtha catalytic reformer with redial flow reactors, distorted scallop screens and/or careless loading of catalyst resulted in a patch of the space inside the annular screens being filled with catalyst.
This resulted in a much lower flow and space velocity in the adjacent section of the catalyst bed. The result was a runaway demethylation reaction which overheated one area of the reactor shell which then ruptured. As the runaway was local it was not detected by a rise in reaction outlet temperature until too late.
[hydrogen, methane, reactors and reaction equipment, rupture, fire - consequence, product loss, runaway reaction, vessel failure, installation inadequate, inspection inadequate, design inadequate, start-up]

Lessons

Mesh scallop screens were replaced by slotted scallop screens which were welded to prevent leakage.
The scallops were all dipped after loading catalyst to ensure that none had got behind the screens.
The methane to hydrogen ratio in the recycle gas was measured to check for demethylation during start-up.

9899 1960

Source : ICHEME
Location : , UK

Injured : 0 **Dead :** 0

Abstract

On a vacuum unit processing the residue from a naphthenic crude, heavy corrosion-erosion nearly perforated the heater discharge header where the flow from the pass outlets impinged on the wall. This pipe was lined with stainless steel.
[hydrocarbon, shutdown, pipe, near miss, incorrect material of construction]

Lessons

[None Reported]

178 December 1958

Source : BOND J, SOURCES OF IGNITION
Location : , ARABIAN SEA

Injured : 0 **Dead :** 22

Abstract

A marine transportation incident. While water-washing tanks on a marine tanker, magnesium anodes, part of cathodic protection system, were dislodged and fell inside tank, possibly causing explosion which removed midships housing from hull. Tank size was 1250 cubic metres. Fatality.
[cleaning, thermite reaction]

Lessons

[None Reported]

174 11 June 1958

Source : ICHEME

Location : ,

Injured : 3 **Dead :** 1

Abstract

An explosion occurred in the cleavage reactor of a phenol plant. The reactor vessel, constructed of stainless steel, was situated in the open, in the midst of the other plant and supported on reinforced concrete pillars. It was provided with a stainless steel stirrer. A pipe was connected to the upper part of the side of the reactor. The pipe contained a right angled elbow on the side of which was a bursting disc. On the morning of the incident, whilst the process was in operation, a decomposition occurred in the reactor but it was relieved by the bursting disc. After inspection a new bursting disc was inserted. The reactor was started up again in the evening when another more violent decomposition occurred destroying the reactor.
The most probable cause of the incident was a deflagration in the reactor caused by an uncontrolled reaction in that vessel. Fatality.
[reactors and reaction equipment, processing]

Lessons

In order to avoid a similar occurrence, the following recommendations were made:
1. The reactor should be segregated from the other plant, if this is possible.
2. The reactor should be housed in a cell provided with three walls. The walls should be constructed of brick and not less than 13½ inches thick. The fourth side, which should be open, should be provided with a blast wall of brick not less than 13½ inches thick in order to prevent the projection of debris.

170 22 January 1958

Source : HAZARDOUS CARGO BULLETIN, 1983, SEPT, 36-37; FIRE AND EXPLOSION RISK CONTROL IN THE PETROCHEMICALS INDUSTRY, TECHNICAL REPORT NO. 2 COMMERCIAL UNION RISK MANAGEMENT LTD, 1976.

Location : Niagara Falls, NEW YORK

Injured : 200 **Dead :** 0

Abstract

A rail transportation incident. Rail tanker car containing nitromethane suffered an autodecomposition and detonated. A crater 26 m by 11 m by 5 m deep was created.

[explosion]

Lessons

[None Reported]

9843 1955

Source : ICHEME
Location : , WEST INDIES

Injured : 0 **Dead :** 0

Abstract

On the first shutdown of a catalytic reformer unit, hydrogen blistering was found in the top manway nozzle of one of the four reactors.
On checking the pipe, the nozzle was found to be made from mild steel.
The other seven nozzles were all chrome-moly alloy as specified and as shown in the material certificates.
[reactors and reaction equipment, near miss, incorrect material of construction]

Lessons

1. Even with reputable manufacturers some independent checking of quality control is required.
2. Inspection of a new process unit as its first shutdown should be very through.

122 1954

Source : VERVALIN C.H, HPI LOSS INCIDENT CASE HISTORIES, HYDROCARBON PROCESSING, 1978, 57, FEB, 183-190; DAVENPORT J.A, A SURVEY OF VAPOUR CLOUD INCIDENTS, CHEMICAL ENGINEERING PROGRESS, 1977, 73, SEPT, 54-63.

Location : West Virginia, USA

Injured : 44 **Dead :** 0

Abstract

A rail transportation incident. 6000 US gal (23m3) of acrolein explosively dispersed into a vapour cloud when rail tanker car ruptured. Acrolein was contaminated causing a runaway polymerization which overtaxed car relief vent.
[gas / vapour release, explosion / pressure release]

Lessons

[None Reported]

Source : CHEMISCHE INDUSTRIE, JUNE 1954 VOL 6 SAFETY SUPPLEMENT P3; ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

Liquid ethylene oxide was being transferred under nitrogen pressure from a transport container to a stirred reaction vessel. The container was half empty when it suddenly shattered and released gaseous ethylene oxide which then exploded on mixing with air in the room causing extreme damage. It was thought that backflow of the alkaline product from the reaction vessel had occurred at some time initiating exothermic polymerisation reaction of ethylene oxide.
[material transfer]

Lessons

[None Reported]

1008929 November 1952

Source : ICHEME
Location : , USA

Injured : 0 **Dead :** 8

Abstract

An explosion occurred in a hot oil feed charge accumulator supplying a mixture of gas oil reduced crude and recycle stock to the TCC feed preheater furnace. The blast was so violent that the 25 tonne accumulator was torn loose from its piping and foundations and hurled to a height of around 200 feet. The main portion landed some 290 foot away while an 8 by 29 foot section landed 600 feet away. The area was sprayed by hot oil and debris and the resulting fire was fed by the incoming flow of hot reduced crude and the depressurising effect of the TCC reactor trough the ruptured lines.
The feed accumulator was a former distillation tower which had been converted to its new duty when the TCC unit was revamped from an aviation gasoline treating unit to a gas oil cracking unit.
The charge to the accumulator was a mixture of hot reduced crude from outside the area, gas oil from storage and TCC recycle stock. Normal operating temperature in the accumulator averaged about 580 degrees fahrenheit. Regular inspection periods this vessel and always been reported adequately safe for the source in which it was used.
The TCC unit had been in normal operation until 3 days before the explosion. At that time the unit was shut down to repair a loose deflector cone in the vertical vaporising furnace. It was not a complete shut down as certain equipment was closed-in, in anticipation of resuming operation within a short space of time. During shut down the cracked oil fractioning tower was water washed and steamed to alleviate indications of tray fouling. The unit was down approximately 2 days during which the accumulator and contents had cooled to 95 degrees F. Operation of the TCC was resumed about 29 hours before the explosion oil from the accumulator was circulated through the furnace and temperature brought up gradually in compliance with normal "drying out" procedure. Fresh gas oil was brought in from storage as needed to maintain levels. After the unit was considered dry, temperatures were brought up more rapidly and hot reduced crude was started into the accumulator . Two hours before the explosion the unit was reportedly on stream and in fine condition.
From this point on everything is conjecture as the control room, together with instruments and records, as well as all personnel were destroyed. An examination of accumulator fragments showed that the relief valve was still in good working order and that it was the bottom of the accumulator that was blown out by the force of the explosion. This indicated that the explosion had occurred there rather than in the vapour space above the liquid. Following a re-enactment over two barrels of liquid water had to be present at the bottom of the accumulator probably present at the Start-up or introduced during the initial warm-up operation. It is possible it came from the make-up gas oil from storage although this tank only showed a slight trace of water. It is also possible it happened when the cracked oil tower was water washed and steamed by backing up through or condensing in the vent system. Start-up procedure calls for testing the water draw on all hot oil and all charge accumulator although there is no assurance that this was done. The blind on the water draw connection was found to be in place after the explosion and inspection on the bolts indicated that it had not been removed for start-up. Other operators testified that the water-draw test on this particular accumulator was sometimes omitted during start-up because
1. only a trace of water had ever been found there
2. Drainage facilities were such that the black oil had to run over a concrete slab to reach a surface drain 3) There was a fear of drawing hot oil.
Records show that the presence of moisture in the charge accumulator was probably indicated on the day before the explosion as the charge pump was lost twice early in the start-up and an unexplained pressure surge took place on the accumulator causing the oil level to move.
Following this incident the company investigated the following change:
1. All potential water traps in hot oil should be eliminated.
2. Suction lines were moved to the low point of vessel.
3. Suction risers within the vessel were cut off flush with the surface and drilled to prevent water accumulation.
4. Piping was rearranged where necessary to eliminate low spots.
5. Temporary piping and connections were removed.
6. The TCC unit was rebuilt without a feed charge accumulator and has operated satisfactorily despite predictions to the contrary.
7. All venting equipment was checked for adequacy.
8. Vapour lines from certain distillation towers were insulated to prevent steam condensation there.
9. Start-up and shut-down procedures were given special attention to stress the importance of testing all water draw connections.
10. Water draw connections were designed where necessary to overcome some operator fear of using them.
11. Training sessions for all employees on "Hazards of water in the process system"
[fire - consequence, design or procedure error, refining, cleaning inadequate, fatality, additional chemical present, oil - hot]

Lessons

Subsequent laboratory testing set up to duplicate conditions in the accumulator showed that it was entirely possible to circulate 580 degrees F oil for extended periods over a 2 and a half foot layer of stagmant oil without raising the bottom temperature to the boiling point of water.
Calculations show that slightly over two barrels of water vaporising within a short space of time could fill the vapour space in the accumulator with sufficient steam to exceed the 275 psi bursting pressure before the relief and vent system could prevent it. Also calculations show that the heat reservoir in the oil was sufficient to vaporise this amount of water with only a 40 degrees F decrease in temperature.

101 06 May 1951

Source : ALEXANDER D.S, EXPLOSIONS IN BUTADIENE SYSTEMS, INDUSTRIAL ENGINEERING CHEMISTRY, 1959, 51, (6), 733-738.
Location : Sarnia; Ontario, CANADA

Injured : 0 **Dead :** 0

Abstract

This article describes an explosion in a butadiene extraction plant and discusses three theories for the accident. In conclusion it was found that oxygen had got into a tank vapour space forming peroxide and violent polymerisation causing the rupture of the tank. Tertiary butyl catechol is now added to tank.
[contamination,tank failure, separation equipment]

Lessons

[None Reported]

76 1948

Source : BOOTH, G, PROCESS CHANGES CAN CAUSE ACCIDENTS, LOSS PREVENTION, 1976, 10, 76-79.
Location : ,

Injured : 0 **Dead :** 0

Abstract

Sulphonation with oleum of 4-chloronitrobenzene resulted in a runaway reaction at 115 degrees C. There had been a change in the process when the 20% oleum was changed to 65% oleum.
[reactors and reaction equipment, sulphur trioxide, sulphuric acid]

Lessons

[None Reported]

17 13 June 1917

Source : KLETZ T.A, ASHTON MUNITIONS EXPLOSION 1917
Location : Ashton-Under-Lyne, CHESHIRE UK

Injured : 120 **Dead :** 46

Abstract

This incident took place in a trinitrotoluene (TNT) factory located in a built up area. During the final stage of production, the addition of nitric acid to convert dinitrotoluene to TNT, the nitrator pan started to give off nitric fumes. Acid flow was stopped but the contents still boiled over. Hot acid fell onto the wooden staging around the pan, starting a fire. Soon afterwards the stocks of TNT in surrounding equipment and in drums exploded. At the time of the explosion the wooden stagings were being replaced by iron but the work was going slowly as the materils needed were rationed. The pan overflowed because of a process change, in which the amount of sulphuric acid added during the final stage of the process was reduced. This made the reaction less stable. In addition, as less acid was added the pan was not as full as usual and the top stirring blades were above the surface of the liquid. The temperature rose and a runaway reaction occurred. Fatality.
[processing]

Lessons

[None Reported]

1429 Date Unknown

Source : ICHEME

Location : ,

Injured : 0 **Dead :** 0

Abstract

A batch reactor used for nitrating benzonitrile was fed from two charge tanks, tank 1 and tank 2.
Tank 1 was used to feed benzonitrile to the reactor via a measuring vessel M and a feed line 1.
Tank 2 was used to feed nitration acid and sulphuric acid directly into the reactor via a second feed line 2. This system worked satisfactorily for many batches.
In order to carry out a different reaction, the feed system was changed so that both tank 1 and tank 2 fed via the measuring vessel.
The system was again used to nitrate benzonitrile without separating the two feed lines - thus both nitration acid and benzonitrile were fed to the reactor via the measuring vessel. During the manufacture of the second batch, an explosion occurred in the measuring vessel.
[batch reaction, chemicals added incorrectly, modification procedures inadequate, uncontrolled reaction, benzonitrile, explosion]

Lessons

Clearly an uncontrolled reaction had occurred between benzonitrile and the nitration acid in the measuring vessel M.
It was recommended that, wherever possible, each charge tank should have a separate feed line to the reactor. In the event of alterations to the equipment, the possibility of hazardous interactions between chemicals should be investigated by risk analysis.

4430 Date Unknown

Source : LOSS PREVENTION BULLETIN, 025, 19-20.
Location : ,

Injured : 0 **Dead :** 0

Abstract

During the reaction of cyanuric chloride with methanol in presence of sodium bicarbonate, an oversight occurred and two drums of 100 kg cyanuric chloride were charged instead of two drums of 50 kg. Although the kettle was cooled with brine, the temperature rose to 60 degrees C within 30 minutes. At this stage, solvent vapours started to emanate from the manhole cover laying loosely on the flange, and 30 seconds later there was a violent eruption of solvent. The main gasket of the kettle and other gaskets were blown out and the fiberglass vent line was broken. Fortunately, the solvent vapours did not ignite. The reaction of cyanuric chloride with methanol is catalyzed by acid. Therefore, the quantities of sodium bicarbonate and cyanuric chloride must be balanced. Due to the cyanuric chloride surplus, an excessive quantity of hydrochloric acid was generated that could no longer be neutralized by the bicarbonate present and thus the reaction accelerated. The cooling system could not dissipate the much higher heat of reaction being generated per unit time.
[gas / vapour release, chemicals added incorrectly, charging reactor]

Lessons

When using cyanuric chloride the following potential hazards should be taken into account:
1. The readiness of the compound to react with many chemicals like water, alcohols, amines etc.
2. The quantities of heat being liberated by such reactions, which can easily lead to the overheating of a reaction mixture.
3. The liberation of up to 3 moles of hydrochloric acid for each mole of cyanuric chloride taking part in the reaction.
4. Catalytic hydrolysis or alcoholysis of the cyanuric chloride: reacts with methanol in an acidic medium.
5. The formation of carbon dioxide gas when cyanuric chloride reacts in presence of sodium bicarbonate.
The technical and organizational measures to ensure safe processing of cyanuric chloride have to be determined by a systematic search for the hazards involved and a careful hazard analysis.

4576 Date Unknown

Source : LOSS PREVENTION BULLETIN, 023, 132-133.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A large polystyrene plant was protected on one part of the installation by a 8" monobloc graphite bursting disc. These discs can be significantly affected by torque values and for that reason the installation instructions, including torque charts, should be carefully read. The fitter concerned, however, had to fit the disc at an awkward point in the site and was unsupervised, so that for a variety of reasons he over-torqued the disc. This produced a crack in the annulus of the disc and when the vessel started up, the cracked section was forced out by working pressure and exited laterally from between the pipe flanges. As a result, the pressure cap on the medium in the vessel was lost and a runaway reaction occurred. An expanding mass of polymer was discharged on to the site, coating the surrounding plant with a hard deposit that proved expensive to remove.
[operational activities, gas / vapour release]

Lessons

The company concerned, in this instance, needed to considerably tighten up supervisory and checking procedures. But in order to avoid repetition of the accident under any circumstances, they replaced the graphite disc with a non-torque sensitive metal disc (from a material selection point-of view, less suitable than graphite) which has increased their spare disc costs. An alternative solution might have been to adopt, if they did not feel confident in their fitting routines, a non-torque sensitive graphite disc known as an armoured disc where the graphite carrier is encased in a steel ring.

4990 Date Unknown

Source : ICHEME
Location : ,

Injured : 5 **Dead :** 0

Abstract

An epoxy resin is manufactured by the addition reaction of a primary/primary diamine and epichlorhydrin. A thermally unstable chlorohydrin intermediate product results, which is dehydrochlorinated with caustic soda to the desired epoxy compound. The resin formed in this step is dissolved in methylethylketone, the residual NaCl filtered off, and the solvent distilled off under vacuum at 125 degrees C.
Immediately before the required temperature was reached during distillation, an explosion occurred in the raw resin. Although both rupture discs of the reactor were blown, the entire dome of the vessel was lifted off. A secondary fire broke out, and five men sustained injuries and burns.
[amine, still, fire - consequence, injury, damage to equipment, runaway reaction, chemical missing]

Lessons

Due to an oversight, insufficient NaOH was charged for dehydrochlorination. Thus a substantial quantity of the thermally unstable intermediate was left. This led to the explosion during distillation.

2192 Date Unknown

Source : ICHEME
Location : , FINLAND

Injured : 0 **Dead :** 1

Abstract

A road transportation incident. Phenol was being transferred from a road tanker to a storage tank via a wire-reinforced gum (rubber?) transfer hose and electrically driven pump. The hose was new, but was not suitable for phenol.
Shortly after the pump was started, the hose between the truck tank and the pump ruptured and sprayed the truck driver with phenol. He was immediately taken to a shower; his overalls were removed. He was later taken to hospital, but died about one hour after the accident. The post-mortem stated that death was caused by sores in the eyes, face and legs and by phenol absorbed through them leading to poisoning.
[material transfer, road transportation, fatality, overpressurisation, hose failure, safety procedures inadequate, incorrect material of construction, protective safety equipment]

Lessons

Investigations showed that:
1. The transfer pump was running in the wrong direction, and was thus pumping phenol from the storage tank to the truck tank. Since the valve on the truck tank was not fully open, a high pressure built up.
2. The driver was not wearing safety goggles: his protective overalls were acid resistant but not suitable for phenol.
3. Phenol had run into the driver's rubber boots, and partially dissolved his nylon socks which then stuck to his skin.

6478 Date Unknown

Source : LOSS PREVENTION BULLETIN, 023, 136-137.
Location : ,

Injured : 0 **Dead :** 0

Abstract

The hydraulic oil system of a machine had to be modified. The system can reach a pressure of 3600 p.s.i. The man carrying out the work asked what was the safe working pressure of three eighths of an inch copper pipe. He was told 10,000 p.s.i. and went to withdraw three eighths of an inch copper pipe from the stores.
The three eighths of an inch copper pipe of 10 swg wall thickness was obtained in a grade suitable for use at 10,000 p.s.i. However, the three eighths of and inch copper pipe stocked in the company concerned is 18 swg wall thickness and its safe working pressure was only 1555 p.s.i.
Fortunately the mistake was discovered before the system was put on-line.
[maintenance, incorrect material of construction, near miss]

Lessons

Always specify the grade, thickness, heat treatment and other relevant properties so that only the correct material is used.

7282 Date Unknown

Source : LOSS PREVENTION BULLETIN, 086, 23-25.
Location : ,

Injured : 0 **Dead :** 0

Abstract

Leaks occurred at two valve flanges after start-up of a new chlorine pipeline. It was found that titanium gaskets had been supplied by mistake.
[flange leak, spill, incorrect equipment installed, incorrect material of construction]

Lessons

Currently all the gaskets in the chlorine line have been removed. New gaskets are on order from another supplier. All gaskets to be used in future chlorine services at the works will be tested by the company for positive identification of their materials of construction. This is expected to evolve into a system to test all materials, i.e. valves, lines, etc. that will be used in chlorine service for positive identification of their materials of construction.

12462Date Unknown

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

To manufacture hydrazobenzene, zinc dust, caustic soda and water were charged into chlorobenzene and heated to 90 degrees C. Then melted azobenzene was charged over a period of 30-40 minutes. When the incident occurred, the entire quantity of azobenzene had been charged at about twice the normal rate. Shortly after the addition of the azobenzene, a 'reaction shock' occurred. The connection between the kettle and reflux cooler was ruptured and toxic reaction mass was released into the room.
[batch reaction, batch reactor, overpressure, runaway reaction, chemicals added incorrectly, high loading rate]

Lessons

Thermal investigations showed that initially the reduction reaction proceeds slowly, and only after a certain time the velocity becomes high. The 'reaction shock' which then occurs causes a sudden evaporation of chlorobenzene. With double the feed rate, the system could no longer handle the vapourisation rate and the pressure increased until rupture of the vapour line occurred.

8000 Date Unknown

Source : ICHEME
Location : , USA

Injured : 0 **Dead :** 0

Abstract

A refinery hydrodesulphurisation unit had been shut-down and was being purged with nitrogen from a tank truck. During this purging process, the temperature in the top part of the catalyst bed rose to nearly 8000 degrees C. When the nitrogen supply from the tank truck was checked, it was found to contain 20% oxygen. The temperature rise was due to reaction between a pyrophoric iron crust on the top of the catalyst bed with the oxygen contaminating the nitrogen supply.
Only minor damage to equipment occurred to the reactor internals.
It was established that the nitrogen supplier had bypassed safety regulations by changing the service of the truck without changing the truck filling connections. In addition, the vendor did not verify the purity of the shipment.
[shut-down/decommissioning, reactors and reaction equipment, contamination, incorrect chemical present, spontaneous combustion, safety procedures inadequate]

Lessons

1. Discussions were held with nitrogen suppliers to emphasise the hazards of contaminated nitrogen supplies, and to ensure proper verification procedures.
2. Procedures were set up to check purity of nitrogen supplies on receipt. This was extended to other bought-in materials.

9436 Date Unknown

Source : ICHEME
Location : , USA

Injured : 0 **Dead :** 0

Abstract

A refinery deethanizer column was shut-down due to leakage of hydrocarbons into the steam side of the reboiler. Before maintenance work started, steam condensate from the reboiler was drained to the sewer system. Since high concentrations of hydrogen sulphide were normally present in the process, the system was being back-flushed with propane to reduce the H_2S content (this purge stream being sent to flare).
About 90 minutes after completing this back-flushing operation there was a violent explosion in the sewer system: this blew up a substantial length of sewer pipe, despite this being buried 1.5m below ground, and covered by a 100mm concrete pad. Pipework and cabling 4m above ground level was damaged by the explosion, but there were no injuries and no fire resulted.
The atmosphere in the sewers was normally expected to be above the upper explosive limit. However, surface openings to the sewer had no traps, and it was suggested that steam traps discharging into the sewers could have blown air into the system, thus creating an explosive mixture. The presence of H_2S may have widened the explosive range.
The source of ignition was unclear, although the autoignition of pyrophoric iron sulphide was suspected.
[damage to equipment, air leaking into system, design error or omission, drains & sewers]

Lessons

Water filled traps were fitted to all open drains to prevent air from entering the sewer system.

11338Date Unknown

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

In the amination of chloro-4-nitrobenzene in aqueous ammonia to produce 4-nitroaniline, the raw materials are charged to a batch reactor at room temperature. The reaction is initiated by heating to 160-190 degrees C and the pressure is 30-40 bar. With this procedure, a number of explosions with severe human and material losses have occurred over the last 60 years.
In one particular case the reactor exploded although it was equipped with a bursting disc.
[4-chloronitrobenzene, batch reaction, explosion, fatality, damage to equipment, runaway reaction, auto decomposition]

Lessons

Thermal investigations show that at the upper range of reaction temperatures (about 190 degrees C) a highly exothermic, formally autocatalytic decomposition reaction takes place. If the heat of reaction is not fully dissipated, the temperature (and vapour pressure of the ammonia) continues to rise.
In the particular case noted above, an insufficient quantity of ammonia had been charged: as a result the reaction pressure was lower than normal. The relief pressure of the rupture disc was only reached at an advanced stage of the decomposition reaction: effective relief was by then impossible.

600 Date Unknown

Source : LOSS PREVENTION BULLETIN, 030, 162-163.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A violent explosion occurred in a plant, resulting from the spontaneous ignition of the flammable gases released from a solution of 13 kg of sodium borohydride dissolved in 70 kg of dimethyl formamide (saturated solution at 17 degrees C).
On reinvestigating the stability of such a solution using 3 g of sodium borohydride in 17 mole litres of dimethyl formamide (mole ratio 1:2:8), it was discovered that a runaway reaction would occur after a temperature dependent induction period. On this scale the induction period ranges from 45 minutes at 90 degrees C to 45 hours at 62 degrees C. Following the runaway reaction, a mercury thermometer in the solid residue suddenly reached 310 degrees C, well above the 190 degrees C autoignition temperature of the trimethylamine were also literated. Ignition was avoided in the laboratory by preventing air from mixing with the trimethylamine in contact with the hot residue.
At twice the dilution the reaction is similar but somewhat less violent.

Lessons

[None Reported]

1066 Date Unknown

Source : ICHEME
Location : ,
Injured : 2 **Dead :** 0

Abstract

A basic epoxy resin was being produced by addition reaction between epichlorhydrin and an amine, followed by dehydrochlorination and distillation. Pilot plant work was being carried out to try to speed up the dehydrochlorination step using a 15% excess of NaOH. To remove the excess caustic, the intermediate product was washed in a reaction kettle and the mother liquor decanted off. (In the full-scale process a centrifuge was used for this step).
The process normally used a thin-film evaporator for the concentration step, but difficulties were encountered because too much water was left.
In the absence of the plant manager, the chemist in charge decided to carry out the concentration step by distillation in a kettle. When a temperature of 130 degrees C was reached (under vacuum), the raw resin suddenly started to solidify: the temperature exceeded 200 degrees C within 2 minutes. The contents of the kettle polymerised spontaneously and pyrolised. The kettle was flooded with water.
[batch reactor, additional chemical present, runaway reaction, polymerisation, design or procedure error]

Lessons

Because the washing step was carried out in an agitated vessel (instead of a centrifuge), too much alkali was left in the raw resin. The decision to carry out the concentration step in a reaction kettle (without first determining the cause of high alkali content) led to the incident.

4416 Date Unknown

Source : LOSS PREVENTION BULLETIN, 023, 143.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A road tanker, used for internal transport looked as if it was made from stainless steel. It was therefore filled with 50% caustic soda solution. Twelve hours later the tanker was empty.
The tanker was made of aluminium which dissolves in caustic soda solution.
[incorrect material of construction]

Lessons

[None Reported]

7516 Date Unknown

Source : LOSS PREVENTION BULLETIN, 122, 19-21.
Location : ,

Injured : 0 **Dead :** 0

Abstract

While charging acrylonitrile (AN), a reactor operator noticed a yellowish colour in the AN. A sample from the AN storage tank was tested for inhibitor concentration and found to be low (16 ppm inhibitor instead of the specified 35 - 45 ppm). Plant personnel added inhibitor and recirculated the AN for 3 to 4 hours. Subsequent measurement the next day indicated a storage tank inhibitor level of 36 ppm.
Two days later a test of inhibitor level indicated a concentration of only 2.5 ppm. Plant personnel fed an additional 50 ppm inhibitor to the storage tank and recirculated. The plant personnel then started a series of eight production batches to use all the suspect AN. An additional 50 ppm inhibitor was added to the storage tank and after tests a low inhibitor level was confirmed. All the AN was consumed within the next two days. While it was being used, no problems were noted during production. Final products met all specifications.
Inhibitor is added to monomer by the suppliers to impart enough stability that onset of polymerisation does not take place during routine storage and handling. Contamination, heat, lack of oxygen, or age can all result in inhibitor depletion which may lead to unscheduled (runaway) polymerisation.
Near miss.
[charging reactor, lack of stabiliser/inhibitor]

Lessons

As result of the incident, the following actions were taken:
1. The tank was cleaned and inspected internally.
2. A programme of frequent analysis was instituted to ensure the stability of the AN (two samples per week plus every shipment) until consistent results are confirmed.
3. The AN unloading procedure was reviewed.
4. Emergency response procedures for monomer stability problems were documented.

7721 Date Unknown

Source : SAFE USE OF CHEMICAL ADDITIVES, ICHEME, SAFETY TRAINING PACKAGE, 018, 3.4.
Location : ,

Injured : 0 **Dead :** 3

Abstract

A runaway polymerisation occurred in a distillation column causing the death of one person and two others fighting the subsequent fire. The explosion damaged a storage tank, two distillation columns and moved a vessel 0.5 metres.
The cause of this accident is not known. Fatality.
[damage to equipment, fire - consequence, storage tanks]

Lessons

The rupture of a vessel is caused by overpressure resulting from the liberation of heat. Heat can arise from a number of causes such as:
1. Heat of combustion when a product catches fire and the gases cause a rise in pressure if they are contained in the vessel. If the fire is outside the vessel then the heat will raise the temperature and the pressure in the vessel. The vessel may be protected by a relief valve in which case the pressure reached may not be sufficient to rupture the vessel.
2. Heat of polymerisation when the product polymerises. This heat is sufficient to raise the temperature in the product hence increase the rate of polymerisation. The pressure also rises with the increased temperature. This pressure may cause the relief valve to lift and relieve the pressure but in some cases the relief valve may become blocked. Relief valves, when operated, have a twist action to overcome this problem but this may not always be sufficient. If a flame arrester is positioned in the vent, this is most likely to become blocked and hence is not recommended for products liable to polymerisation.

7725 Date Unknown

Source : SAFE USE OF CHEMICAL ADDITIVES, ICHEME, SAFETY TRAINING PACKAGE, 018, 3.10.
Location : ,

Injured : 0 **Dead :** 0

Abstract

Hydrogen cyanide tank explosion. There was a hissing noise followed by two explosions and flames 20 - 50 ft high. A building housing two 13 ton storage tanks containing hydrogen cyanide were demolished. No. 2. tank was split open with one dished end completely blown off. A 20 ton tank outside the building was moved and collided with a pipe bridge support causing the rupture of steam, cooling tower, river water, concentrated sulphuric acid and other services. Many windows were broken and debris was spread over a wide area.
The cause of the incident was due to a rapid polymerisation with temperature and pressure rise which occurred in No 2. tank. The vent was insufficient to cope with the conditions and the vessel ruptured under the pressure.
[storage tanks]

Lessons

The following recommendations were made:
1. Keep residence time short.
2. Avoid dilution with water.
3. Keep temperature low.
4. Avoid polymer in tank.
5. Stabilise product.
6. Avoid alkali.
7. Provide adequate vents.
8. Avoid promotors.

7823 Date Unknown

Source : BARTON J AND ROGERS R, CHEMICAL REACTION HAZARDS, 2ND EDITION, ICHEME, 1997, APPENDIX 1, 191.
Location : ,

Injured : 0 **Dead :** 0

Abstract

Ethylbezylaniline (EBA) had to be charged to a stainless steel measuring vessel before beginning the first batch of a product campaign. Immediately after the pumped transfer of EBA started, a violent reaction occurred in the measuring vessel. The pressure in the vessel rose, resulting in rupture of the glass vent line. The measuring vessel was normally used for holding nitrating acid. Apparently the vessel was not cleaned before use, so that it still contained residual mixed acid which reacted with the EBA.
[batch reaction, additional chemical present, cleaning inadequate, unwanted chemical reaction]

Lessons

[None Reported]

7804 Date Unknown

Source : BARTON J AND ROGERS R, CHEMICAL REACTION HAZARDS, 2ND EDITION, ICHEME, 1997, APPENDIX 1, 186.

Location : ,

Injured : 0 **Dead :** 0

Abstract

A cooling water supply to a condenser was blocked by pebbles and the operator did not turn on the emergency cooling system to the reactor jacket. However, when the runaway started the reactor contents were safely emptied to a dump tank. Near miss.
[runaway reaction, reactors and reaction equipment]

Lessons

[None Reported]

7764 Date Unknown

Source : BARTON J AND ROGERS R, CHEMICAL REACTION HAZARDS, 2ND EDITION, ICHEME, 1997, APPENDIX 1, 164.
Location : ,

Injured : 0   **Dead :** 0

Abstract

The equipment involved in an explosion was designed to produce p-nitrophenol and p-nitro-m-cresol, key intermediates used in the manufacture of organophosphate pesticides. The explosion resulted from spontaneous decomposition reactions, which had both been found in small scale laboratory trials. P-nitro-m-cresol is unstable when held at temperatures above its melting point. The melt gradually undergoes a free radical polymerisation evolving heat.
[reactors and reaction equipment]

Lessons

[None Reported]

4545 Date Unknown

Source : LOSS PREVENTION BULLETIN, 025, 21,; BARTON J AND ROGERS R, CHEMICAL REACTION HAZARDS, 2ND EDITION, ICHEME, 1997, APPENDIX 1, 181.

Location : ,

Injured : 0 **Dead :** 0

Abstract

The 11000 litre reaction kettle of an open air production plant held a finished batch of a chlorotrazine. The alkaline batch contained, besides the product, water, caustic soda and approximately 5500 L methyl ethyl ketone (flash point -14 degrees C).
Due to an error, 1500 kg cyanuric chloride, ready for the next batch, were dumped into this kettle before its contents had been transferred. This caused a rapid rise in temperature. The batch erupted through the charge opening. A large cloud of solvent vapour was quickly formed. The vapours penetrated into nearby buildings and ignited at several locations. The resulting unconfined vapour cloud explosion devastated buildings and structures and caused considerable damage throughout the works.
The cause of this incident was the exothermic reaction of cyanuric chloride with water.
[chemicals added incorrectly, damage to equipment]

Lessons

When using cyanuric chloride the following potential hazards should be taken into account:
1. The readiness of the compound to react with many chemicals like water, alcohols, amines etc.
2. The quantities of heat being liberated by such reactions, which can easily lead to the overheating of a reaction mixture.
3. The liberation of up to 3 moles of hydrochloric acid for each mole of cyanuric chloride taking part in the reaction.
4. Catalytic hydrolysis or alcoholysis of the cyanuric chloride: reacts with methanol in an acidic medium.
5. The formation of carbon dioxide gas when cyanuric chloride reacts in presence of sodium bicarbonate.
The technical and organizational measures to ensure safe processing of cyanuric chloride have to be determined by a systematic search for the hazards involved and a careful hazard analysis.

4008 Date Unknown

Source : ICHEME
Location : ,
Injured : 0 **Dead :** 0

Abstract

An explosion occurred after smoke was discovered coming from the ruptured shell/roof seam of a bitumen cone roof storage tank.
The tank's direct fired heater was shut down, transfer operations were stopped and steam was introduced via a 1 inch gauge pipe into the roof of the tank to prevent the possibility of re-ignition.
At the time of the incident, the 10,000 bbl tank measuring 12.8 m diameter x 12.6 m contained 60/70 penetration bitumen. A temperature at a thermowell showed 170 degrees C, a thermocouple showed 270 degrees C and a thermocouple attached to the heater coil indicated 480 degrees C.
A physical dip of the tank after the explosion revealed that the actual level in the tank was much lower than that indicated by the gauge reading, allowing the heater coil to be exposed.
The explosion was probably caused by the exposure of the overheated coil above the liquid level which ignited (autoignition) a flammable hydrocarbon vapour mixture above the liquid surface.
The exposure of the heater coil and low level in the tank would have contributed to the breakdown of the bitumen and formation of a flammable mixture.
[instrumentation failure, overheating, storage tanks]

Lessons

It was recommended that more frequent manual dips should be done to check the accuracy of the board gauge and re-affirmed the importance of shutting off the heater before the level was drawn below the coil.

2525 Date Unknown

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

An explosion occurred in a sulphur recovery unit at a refinery during regeneration.
The plant had been regenerating for roughly 24 hours, when a boiler leak was discovered in the tail gas thermal oxidiser waste heat boiler. The thermal oxidiser was shut down, and the waste heat boiler depressured, vented, and drained.
The thermal oxidiser blower was used to cool the firebox and waste heat boiler as the regeneration continued. Burns in each catalyst bed were well established and after operating for a further 8 hours pressure drop across the unit began increasing.
Increased back pressure caused combustion air to leak out of the main reaction furnace, so the main air blower speed was increased to force more air into the plant. In adjusting the main air blower speed, too much excess oxygen caused a high exotherm in the first catalyst bed. Operators increased natural gas to the main reaction furnace to consume some of this excess oxygen. Plant pressure drop continued to increase, and air flow continued to fall. The main reaction furnace flame became dark and smoky, and the decision was taken to shutdown the unit. Before shutdown was completed an explosion occurred.
Cause of the explosion was unburned natural gas from the front end mixed with purge air from the thermal oxidiser air blower. This mixture ignited at the stack gas heater.
The pressure drop was caused by plugging in the thermal oxidiser or waste heat boiler from either of two possible causes. Since the thermal oxidiser firebox was cold, it probably condensed the water produced from combustion, and the water from the quench steam in the main reaction furnace. A water balance calculation has shown that water condensation could fill the firebox with water in 12 hours, restricting flow from the front of the plant. The other possible cause of plugging was -sulphur deposition on the cold waste heat boiler tubesheet.
[catalyst regenerator, separation equipment, flow restriction, solids deposition, refining, incinerator, incorrect pressure, plant shutdown]

Lessons

Specific detailed procedures are required for any "Special Operation." The procedures must be completely thought-out to ensure that all potential hazards have been considered. Impromptu operations as seen from this incident can be extremely risky.

7737 Date Unknown

Source : CONTROL OF CHEMICAL EXOTHERMIC REACTIONS, ICHEME, SAFETY TRAINING PACKAGE, 023, 3.51.
Location : ,

Injured : 0 **Dead :** 0

Abstract

An explosion occurred during the manufacture of a phenolic resin by a phenol-formaldehyde reaction catalysed by caustic soda, in a 5.9 m3 reaction vessel. The explosion ruptured the vessel and caused considerable damage to the building.
The incident occurred due to an insufficient heat transfer rate on scaling up the process. The reaction process was scaled up from 2.3 m3 to 5.9 m3 without taking into account the increased rate of heat production. This resulted in an increased reaction temperature which caused a runaway exothermic reaction.
[runaway reaction]

Lessons

The following recommendations were made:
1. Each vessel should be fitted with an adequately sized bursting disc and vent.
2. The bursting disc should be as close as possible to the vessel. The vent should be as straight as possible and should be strong enough to withstand the pressures developed in a thermal explosion. It should direct any emitted material to a safe place.
3. Each vessel should be fitted with a high temperature alarm, stirrer failure alarm, coolant flow.
4. Monitor and thermometer probes should be long enough to give representative readings.
5. Management should ensure that personnel are familiar with the hazards of carrying out exothermic reactions through training.
6. When scaling up a reaction, calculations should be made to ensure that the cooling capacity is adequate.
7. The company should investigate the possibility of carrying out the reactions either continuously, or by gradual feed of one reagent to the other.
8. The company should also consider the provision of a suitably located control room for all the reactors, capable of withstanding such an explosion.
9. Temperature of the reactions should be registered on a chart recorder.

12913Date Unknown

Source : ICHEME
Location : ,

Injured : 19 **Dead :** 0

Abstract

A boilover of a slops floating roof tank incident.
The incident occurred when hot vacuum gas oil at 204 degrees C (400 degrees F) was accidentally transferred to a cold slops tank containing a mixture of water and hydrocarbon liquids.
The boil-over caused the sinking of the internal roof and overpressured the tank rupturing the seam between the fixed roof and shell. The subsequent release of hydrocarbon vapour affected nineteen workers. An estimated 10 tonnes of material vaporised to atmosphere or was released to the tank bund area.
The immediate cause of the boil-over was the transfer of very hot oil at 204 degrees C into a cold slops tank due to the misalignment of valves.
[accidental mixing, material transfer, gas / vapour release, injury]

Lessons

[None Reported]

11921Date Unknown

Source : ICHEME
Location : , UK

Injured : 1 **Dead :** 0

Abstract

An operator was trying to open a 4 inch manual valve located in an acid circulation line. The valve spindle and hand wheel parted from the valve and the operator was sprayed with concentrated acid which flowed under pressure through the gland opening. He was wearing goggles and a heavy serge jacket and trousers. An emergency shower was used to remove the acid. The operator received minor facial burns but extensive burns to the thighs and groin. This was caused by water from the shower washing diluted acid through his clothing onto his skin. Later investigation showed that the body, bonnet and gate on the valve were of the correct material for acid service (cast iron). but the valve trim and spindle were of an unsuitable material (high tensile brass).
[sulphuric acid, burns, incorrect material of construction]

Lessons

1. All valves in similar acid service were checked and two others were found to be made of incorrect materials. These were replaced.
2. It was emphasised to personnel that it was essential that materials for acid service were correctly specified.
3. A search was started for suitable clothing to be used in such operations.
4. Consider completely stripping when using emergency showers.

12789Date Unknown

Source : CHEMICAL HAZARDS IN INDUSTRY, JUNE 2000,; GILLARD, T. LOSS PREVENTION BULLETIN, OCT 1998, (143), 21-22.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A runaway reaction occurred during heating to a batch reactor for the production of phenol-formaldehyde resulting in the rupture of the bursting disc and the release of 75% of the reactor contents on to a nearby road.
An investigation into the cause of the incident revealed a blockage in the bell-end inlet to the condenser cooling unit.
[reactors and reaction equipment, spill]

Lessons

[None Reported]

12819Date Unknown

Source : QUARTERLY SAFETY SUMMARY, 1971, VOL.42, NO. 167.

Location : ,

Injured : 0 **Dead :** 0

Abstract

A violent explosion occurred whilst charging acetic anhydride to a glass measure vessel, which ruptured. The measure vessel had previously contained nitric acid as part of another process but had been cleaned out prior to the starting the new process.
The supply pipe to the measure vessel was examined after the incident and it is thought to have been full of nitric acid at the time of the incident.
The explosion in the measure vessel was due to mixing of acetic anhydride and nitric acid.
[contamination, accidental mixing]

Lessons

[None Reported]

12844Date Unknown

Source : QUARTERLY SAFETY SUMMARY, 1977, VOL.48, NO. 189.

Location : ,

Injured : 1 **Dead :** 0

Abstract

An exothermic reaction occurred when a chemist followed a process involving a solution of bromine in methanol.
The chemist used a measuring cylinder and after a short time after making the solution, an exothermic reaction occurred, ejecting the contents of the cylinder.
The chemist sustained bromide burns.
An investigation into the incident revealed that mixing 9ml bromine with 15ml methanol at room temperature, leads to a rapid evolution of heat, the mixture reaching boiling point in approximately two minutes. It appears that it was this evolution of heat rather than an explosive reaction that caused the mixture to eject from the cylinder.
[laboratory work, thermite reaction, injury]

Lessons

The following lessons were learned:
The incident underlines the necessity for extra caution when preparing a mixture of reactants for the first time.
It is vital is for workers in chemical laboratories to adopt adequate eye protection.

12845Date Unknown

Source : QUARTERLY SAFETY SUMMARY, 1973, VOL.44, NO. 174.
Location : ,

Injured : 0 **Dead :** 0

Abstract

An explosive polymerisation of acrolein occurred in a laboratory. The acrolein was an old sample that had been stored for two years in a screw-top bottle in a refrigerator.
The incident occurred at night when fortunately no one was in the laboratory. The damage indicated a large explosion had occurred.
It is thought that traces of dimethylamine also present in the refrigerator may have entered the arolein bottle and initiated polymerisation of the acrolein.
[laboratory work, explosion, contamination, damage to equipment]

Lessons

The following lessons were learned:
1. Acrolein reacts with sudden polymerisation and exotherm when in contact with even minor amounts of acids, including SO_2 (sulphur dioxide) and notrose gases, alkalis, volatile amines, salts, thiourea, oxidants (air), on exposure to light and heat.
2. Do not use CO_2 (carbon dioxide) as protective gas.
3. Stabiliser content (nomally 0.2% hydroquinone) must be checked during prolonged storage.

12861Date Unknown

Source : QUARTERLY SAFETY SUMMARY, 1976, VOL.47, NO's. 185, 186.
Location : ,

Injured : 4 **Dead :** 0

Abstract

A tanker of glacial acrylic acid polymerised with explosive violence whilst being held with warm water on the heating coils to prevent freezing.
An investigation into the incident revealed that some crystallisation had occurred, which was then reliquefied. This produced a reduction in the level of the inhibitor concentration of the reliquefied material.
Glacial acrylic acid with such a reduced inhibitor level is quite unstable and unpredictable in its activity.
The unmixed layer of acid on top of the heating coils is believed to have polymerised and initiated a runaway polymerisation in the bulk liquid.
Four plant operators were injured in the incident. Severe damage occurred to equipment.
[explosion, injury]

Lessons

[None Reported]

11917Date Unknown

Source : LOSS PREVENTION BULLETIN, 035, 7-9. CASE HISTORY.
Location : ,

Injured : 0 **Dead :** 0

Abstract

At a multi-purpose plant, preparations were being made for a change of batch, involving thorough cleaning of the three reaction vessels 1, 2, 3.
Reactor 3 was filled with toluene via a drum-hose-pump-manifold, the manifold valve closed and the toluene boiler under reflux. After a short cooling period, the toluene was forced with nitrogen, via bottom valves, half and half into vessels 1 and 2 and also boiled under reflux. The cooled toluene was filled into drums. The same cleaning process was then carried out with isopropanol. Through washing out of the three vessels with water completed the cleaning phase.
During a last check of the reactors, the foreman discovered a thin dust-like film on the inside wall of 1. His entry in the shift book was: 'Agitate 1 with 150 1 HNO_3 solution for 4 hours at 80 degrees C'.
He assumed that the usual method which had been used for some years, i.e. filling the vessel with ca. 3.5 m water and then pumping in 150 l 53% nitric acid, would be used.
The shift manage, however, interpreted the foreman's instructions differently. First the concentrated nitric acid was pumped into 1 with the same pump via the same manifold as before with toluene and isopropanol. After reactor 1 was filled with ca. 120 l concentrated nitric acid, the shift manager noticed a strong development of gas in the vessel. The pressure in the vessel increased rapidly and the safety valve responded. The shift manager ran to the emergency exit. As he reached the door of the emergency exit, the vessel exploded emitting a reddish-brown cloud of nitrous gas.
Due to his quick reaction, the shift manager received no injuries.
The cause of the incident was examined and it was found that after filling reactor 3 with isopropanol the pump's pressure-side pipe had not been completely emptied because the drain valve was too high.
It was basically impossible to drain the suction-side pipe and the pump. Ca.5 l isopropanol went into reactor 1 with the concentrated nitric acid. According to the temperature recorder, the temperatures in the vessel shortly before the explosion were 77 degrees C and in the heating jacket 72 degrees C.
[reactors and reaction equipment, explosion, cleaning inadequate]

Lessons

These constituted the conditions for forming unstable isopropyl nitrate from isopropanol and concentrated nitric acid. In addition, concentrated nitric acid, in a secondary reaction, cases the oxidation of alcohols (here isopropanol). The nitrous acid thus formed might have accelerated further oxidation of the alcohol explosively. In all probability, the explosive breakdown of the isopropyl nitrate formed from ca 5 l isopropanol, to acetone, NO_2, NO and water led to the reactor exploding.
The following measures were implemented:
1. Drawing up of operating instructions for cleaning production plants.
2. The use of nitric acid for cleaning plants is limited to special cases and is closely supervised.
3. Before pumping nitric acid into the plant to be cleaned, the appropriate dilution is carried out in a separate vessel.
4. Complete residual draining from all parts of the plant is guaranteed by measures concerning equipment.

13046Date Unknown

Source : ICHEME
Location : ,
Injured : - **Dead :** 3

Abstract

Nitrosyl sulphuric acid was charged to a 2,500 litre glass lined batch reactor and then, while the reactor was cooled with chilled water, 6-chloro-2,4-dinitro aniline was shovelled in. The temperature was to be kept at 30 to 40 degrees C and subsequently raised to 50 degrees C. Shortly after this temperature was reached, a violent explosion took place. Three people were killed and many injured. The reactor was blown to pieces - some bits travelled as far as 130m. Investigations after the incident showed that, at the concentrations chosen for the process, the viscosity of the reaction mass were so high that the solid amine shovelled in was probably not well mixed. A sudden reaction of the accumulated components caused first a temperature rise due to the heat of diazotation. Then, within seconds, decomposition of the diazo compound took place. The energy potential of this decomposition was sufficient to initiate the decomposition of the nitro compound. Detonation tests showed that the detonation wave could propagate through the reaction mass.
[dintroaniline chloride, batch reaction, charging reactor, fatality, rupture, runaway reaction, chemicals added incorrectly, safety procedures inadequate, batch reactor, injury]

Lessons

The reaction is now carried out with lower concentrations, and with temperature controlled dosage of the nitrosyl sulphuric acid. For emergencies, a process procedure is available for alarm and immediate drenching with large quantities of water.

13047Date Unknown

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

After continuous tetrazotation of a diamine slurry the tetrazo solution was held in a buffer vessel pending the azo coupling. A sudden violent explosion blew a blind flange of a spare nozzle of the buffer vessel, a manhole funnel was blown away and a 5m piece of ventilation pipe was totally destroyed.
The nitrite addition had been very uneven and, during an excess phase, a significant amount of nitrous gases was generated.
An investigation proved that deposits of tetrazonium dichloride in the dome of the vessel and in the ventilation duct had reacted with nitrous gases to a highly shock sensitive dinitrite. The extent of the damage led to the conclusion that several such deposits must have existed: the explosion of the first one initiated the other ones.
[tetrazo compound, nitrogen oxides, batch reaction, batch reactor, rupture, gas / vapour release, unwanted chemical reaction, contamination, cleaning inadequate]

Lessons

1. The formation of dried residues must be avoided by thoroughly washing the equipment after each campaign. Thorough inspection even of nozzles (which are difficult to check) is essential.
2. The formation of nitrous gases due to an excess of nitrite can be avoided by accurate metering of the reaction compounds.

13050Date Unknown

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

In the exhaust air system of a laboratory building with many animal rooms, massive deposits had formed in the duct work and especially on the rotor of the central exhaust blower. To facilitate a clean-out, the blower was switched off and an opening cut into its housing using a 'sabre saw'. This started a fire within the blower, which spread quickly through the plastic ductwork and developed into a major blaze. Damage caused by smoke was very high.
[animal products, maintenance, cleaning, fire - consequence, solids deposition, cleaning inadequate, nitrate, ozone, ducting, blower]

Lessons

The suction grills in the animal rooms were not fitted with dust filters, and organic material like animal hair, dried excrement etc was sucked up and formed deposits in the ventilation system. The system had not been cleaned during 12 years of operation. To prevent the emission of bad odours, ozone was dosed into the system, causing the formation of nitrates in the organic material.
When the 'sabre saw' was used, it produced hot cuttings, which ignited the readily combustible deposits. Melted, burning, polypropylene dropped through vertical ducting and spread the fire throughout the building.

13137Date Unknown

Source : ICHEME
Location : ,

Injured : - **Dead :** 3

Abstract

Nitrosyl sulphuric acid was charged to a 2,500 litre glass lined batch reactor and then, while the reactor was cooled with chilled water, 6-chloro-2,4-dinitro aniline was shovelled in. The temperature was to be kept at 30 to 40 degrees C and subsequently raised to 50 degrees C. Shortly after this temperature was reached, a violent explosion took place. Three people were killed and many injured. The reactor was blown to pieces - some bits travelled as far as 130m. Investigations after the incident showed that, at the concentrations chosen for the process, the viscosity of the reaction mass were so high that the solid amine shovelled in was probably not well mixed. A sudden reaction of the accumulated components caused first a temperature rise due to the heat of diazotation. Then, within seconds, decomposition of the diazo compound took place. The energy potential of this decomposition was sufficient to initiate the decomposition of the nitro compound. Detonation tests showed that the detonation wave could propagate through the reaction mass.
[dintroaniline chloride, batch reaction, charging reactor, fatality, rupture, aniline, dintroaniline chloride, nitrosyl, sulphuric acid, batch reactor, runaway reaction, chemicals added incorrectly, safety procedures inadequate, injury]

Lessons

The reaction is now carried out with lower concentrations, and with temperature controlled dosage of the nitrosyl sulphuric acid. For emergencies, a process procedure is available for alarm and immediate drenching with large quantities of water.

13138Date Unknown

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

After continuous tetrazotation of a diamine slurry, tetrazo solution was held in a buffer vessel pending the azo coupling.
A sudden violent explosion blew a blind flange of a spare nozzle of the buffer vessel, a manhole funnel was blown away and a 5m piece of ventilation pipe was totally destroyed.
The nitrite addition had been very uneven and, during an excess phase, a significant amount of nitrous gases was generated.
An investigation proved that deposits of tetrazonium dichloride in the dome of the vessel and in the ventilation duct had reacted with nitrous gases to a highly shock sensitive dinitrite. The extent of the damage led to the conclusion that several such deposits must have existed; the explosion of the first one initiated the other ones.
[tetrazo compound, nitrogen oxides, batch reaction, batch reactor, rupture, gas / vapour release, unwanted chemical reaction, contamination, cleaning inadequate]

Lessons

The following recommendations were made:
1. The formation of dried residues must be avoided by thoroughly washing the equipment after each campaign. Thorough inspection even of nozzles (which are difficult to check) is essential.
2. The formation of nitrous gases due to an excess of nitrite can be avoided by accurate metering of the reaction compounds.

13141Date Unknown

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

In the exhaust air system of a laboratory building with many animal rooms, massive deposits had formed in the duct work and especially on the rotor of the central exhaust blower. To facilitate a clean-out, the blower was switched off and an opening cut into its housing using a 'sabre saw'. This started a fire within the blower, which spread quickly through the plastic ductwork and developed into a major blaze. Damage caused by smoke was very high.
[animal products, maintenance, cleaning, fire - consequence, solids deposition, cleaning inadequate, ducting, blower, nitrate]

Lessons

The suction grills in the animal rooms were not fitted with dust filters, and organic material like animal hair, dried excrement etc was sucked up and formed deposits in the ventilation system. The system had not been cleaned during 12 years of operation. To prevent the emission of bad odours, ozone was dosed into the system, causing the formation of nitrates in the organic material.
When the 'sabre saw' was used, it produced hot cuttings, which ignited the readily combustible deposits. Melted, burning, polypropylene dropped through vertical ducting and spread the fire throughout the building.

9 Date Unknown

Source : JOURNAL OF LOSS PREVENTION IN THE PROCESS INDUSTRIES, 1989, OCT.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A 30% solution of potassium cyanide placed in a high density polyethylene drum at 50 degrees C began venting gas immediately. 1/2 hour later the drum exploded.
[explosion, storage, runaway reaction]

Lessons

[None Reported]

11849Date Unknown

Source : ICHEME
Location : , USA

Injured : 0 **Dead :** 0

Abstract

On a catalytic reforming unit a charge/effluent heat exchanger tube sheet gasket failed. The failure was probably due to over tightening the joint. Inspection of replacement gaskets in store showed that the surface of the 5% chrome jackets was corroded. This rough gasket surface was the probable cause of the overtightening. These exchangers had a history of minor joint leaks.
[naphtha, hydrogen, heat transfer, shell and tube heat exchanger, gasket, blowout, fire - consequence, corrosion, gasket failure, inspection inadequate, incorrect material of construction]

Lessons

1. The quality of replacement parts should be checked before they are used.
2. In the present case the 5% chrome jackets were replaced by 316 or 347 stainless steel to avoid deterioration in storage.
3. Where repetitive problems of any kind occur a search should be made for the faulty part with one which is the same.

11183Date Unknown

Source : ICHEME
Location : ,

Injured : 2 **Dead :** 0

Abstract

Two operators were burned by an explosion in a furfural unit extract vacuum flash heater following a surge of gas into the firebox.
The investigation showed that a reduction in the load on the burner heater had resulted in the closure of the fuel gas controller, which had jammed in the closed position due to the presence of ammonium chloride deposit and did not respond until the signal pressure was near maximum: in addition, the pilot burners were fouled with ammonium chloride. The source of ammonium chloride was the excessive carry-over of liquid into the fuel gas system from the ferrofiner knock-out drum.
[processing, heater, solids deposition, explosion, burns, ammonium chloride, injury]

Lessons

[None Reported]

11913Date Unknown

Source : ICHEME
Location : , USA

Injured : 0 **Dead :** 0

Abstract

A hydrotreater unit was shutdown to regenerate the catalyst by burning off coke deposits. The reactor was first to be evacuated and purged with nitrogen to remove combustible vapours. However, despite checks to ensure against air in leakage, the temperature at the top of the catalyst bed rose from 320 degrees C to 780 degrees C in the course of four nitrogen purges. Only then was the quality of the nitrogen supplied by a contractor, checked and found to be mainly compressed air.
[nitrogen, air, purging, catalyst, reaction vessel, near miss, oxygen enrichment, inspection inadequate, faulty instructions]

Lessons

[None Reported]

11912Date Unknown

Source : ICHEME
Location : , USA

Injured : 0 **Dead :** 0

Abstract

During commissioning of a catalytic cracking unit, it had to be shutdown and steamed out for minor modifications. On restarting the diaphragm loaded pilot operated relief valves on the wet gas compressor suction leaked. It was found that the steam out temperature had damaged the rubber diaphragms and o rings on these valves. Fortunately the leak did not ignite.
[steam, safety relief valve, gas / vapour release, near miss, thermal degradation, design inadequate, incorrect material of construction]

Lessons

1. During commissioning a close watch should be kept on new plant to detect faults before damage occurs.
2. When setting equipment design specifications allowance must be made for abnormal conditions such as those during star-ups and shutdowns.

11906Date Unknown

Source : ICHEME
Location : , USA

Injured : 0 **Dead :** 0

Abstract

A gasoline leak occurred in piping close to a tetraethyl lead (T.E.L.) weigh tank. This was ignited by unknown means. The fire heated 1.5 tonnes of T.E.L, left in the weigh tank, so its spontaneous decomposition temperature. The vessel exploded and ruptured a second tank also containing T.E.L. It took 5 weeks to clean up the area so that it was safe and free of T.E.L.
[normal operations, pressure vessel, rupture, fire - consequence, runaway reaction]

Lessons

There are a substantial number of unstable chemicals in use, many of which do not have such a high profile as say actetylenes. All hazard reviews should consider whether any are present.

11891Date Unknown

Source : ICHEME
Location : , USA

Injured : 0 **Dead :** 0

Abstract

In a thermal reformer heater the replaceable seat of a return header box failed. On inspection it was found to be mild steel rather than the 9% chrome steel specified. As a result, it had corroded five times faster than the correct material and failed well before the next inspection was due. The resulting fire was well controlled and did not cause major damage.
[naphtha, normal operations, furnace tube, blowout, fire - consequence, incorrect material of construction, inspection inadequate]

Lessons

Quality control of spare parts is as important as that on the original equipment.

11890Date Unknown

Source : ICHEME
Location : , USA

Injured : 0 **Dead :** 0

Abstract

A unit processing tar from a catalytic cracking unit shut down. While an operator was diverting the tar to storage, the hot tar line failed. Inspection showed the failure was due to corrosion by sulphur compounds.
However, inspection 3 months earlier had not shown dangerous levels of corrosion. The only difference in operation in the last 3 months was a drop in temperature of about 15 degrees C and the absence of insulation on short sections of the line.
[sulphur compounds, tar, cracking, pipe, rupture, corrosion, incorrect temperature, incorrect material of construction]

Lessons

[None Reported]

11861Date Unknown

Source : ICHEME
Location : , USA

Injured : 0 **Dead :** 0

Abstract

Hydrocarbon solvent was treated with a mixture of caustic soda and chlorine in a line mixer. The caustic solution was then settled out in a separator and recirculated to the mixer. The chlorine was added to the caustic recirculation line in batches of 7.5kg using welch scales. Operating procedures had recently been changed so that the caustic circulation was shutdown while injecting the chlorine was added an explosion occurred when caustic flow was restarted.
[chlorine, hydrocarbon, caustic soda, batch reaction, modification, mixer, pipe, explosion, fire - consequence, runaway reaction, modification procedures inadequate]

Lessons

1. It is known that runaway reactions can occur between hydrocarbons and chlorine.
2. The probable explanation is that the introduction of the chlorine as a slug rather than dissolved in a stream of caustic soda triggered this runaway.
3. For even minor changes to operating procedures a safety evaluation is required before implementation.
4. In this case the use of chlorine has discontinued.

11859Date Unknown

Source : ICHEME
Location : , USA

Injured : 0 **Dead :** 0

Abstract

On a catalytic reforming unit the 460mm pipe from a reactor to a reheat furnace ruptured due to high temperature hydrogen attack.
The carbon 1.5 % moly steel used was not adequate to resist this attack at the 450 degrees C and 25 bar hydrogen attack was found in a reactor charge effluent exchanger and the first reactor inlet line.
[hydrogen, continuous reaction, pipe, shell and tube heat exchanger, rupture, fire - consequence, damage to equipment, incorrect material of construction, inspection inadequate, hydrogen embrittlement]

Lessons

1. The affected heat exchanger shell and all the piping in high temperature hydrogen service were replaced in 1.5 % chrome .5% moly steel.
2. Hydrogen attack frequently causes blistering well before failure. Thus adequate inspection might have prevented this incident.
3. Inspection of units on their first planned shutdown should be particularly thorough.

11857Date Unknown

Source : ICHEME
Location : , USA

Injured : 0 **Dead :** 0

Abstract

In a catalytic reformer annular reactor the deflector plate over the top of the catalyst bed failed. The reactor inlet flow then impinged on the top of the bed displaline some catalytic behind the annular screen. This created an area of low LHSV in the catalyst bed where highly exothermic hydrocracking reactions could take hold. Luckily this was detected by multiple skin thermocouples on the vessel shell before it ruptured. The unit was shutdown.
[naphtha, hydrogen, continuous reaction, reaction vessel, near miss, flow rate too low, runaway reaction, design inadequate]

Lessons

1. In a location with low LHSV there is time for the hydrocracker reactions to develop and insufficient flow to carry - way the heavy produced. This results in a spiralling increase in temperature.
2. To counter this problem:-
- Reactor internals must firmly secure. In another case the annular screen came lose again allowing catalytic to get behind it.
- As the area of low LHSV is usually small multiple thermocouples are required to detect it. The reactor outlet temperatures may only rise slightly.

11854Date Unknown

Source : ICHEME
Location : , USA

Injured : 0 **Dead :** 0

Abstract

A naphtha hydrosulphuriser started to have serious heat exchanger fouling when charging naphtha which had been in contact with air in storage. It is thought that because of a partial shutdown the deposits slowed off the heat exchanger and ended up preferentially in one of the two tube passes of the reactor charge furnace. The furnace then had to be fired harder and harder to maintain the combined outlet temperature. After 7 months operation a furnace tube ruptured. That tube pass was then found to be particularly plugged.
[naphtha, oxygen, heating, furnace tube, rupture, fire - consequence, oxygen enrichment, blockage by polymer, design inadequate]

Lessons

1. Individual pass outlet temperature points or flow meters would have detected the problem before tube failure.
2. In the present case multiple furnace tube skin thermocouples were installed on each pass. This is the most direct method of deterlting the cause of the failure - overheating of the tubes.
3. An oxygen stripper was installed on the naphtha feed which greatly required the fouling.

11851Date Unknown

Source : ICHEME
Location : , USA

Injured : 0 **Dead :** 0

Abstract

Catalyst in catalytic reformer units was reactivated by burning off coke deposits. The burn started with 2% oxygen and ended with 10% giving 2 bar partial pressure.
After the realtivation a lear was found in the cold end feed effluent heat exchanger. The cause was found to be combustion of an oily pyrophoric iron sulphide deposit in the tubes which had melted them. Due to problems elsewhere the unit charge had, had a higher than normal sulphur conduct for the proceeding month.
[iron sulphide, hydrocarbon, oxygen, catalyst regeneration, shell and tube heat exchanger, damage to equipment, plant shutdown, spontaneous combustion, incorrect chemical present]

Lessons

1. It is wise to analyse the potential consequences of any abnormal operation on a plant before proceeding with it. However it has to be said that in this particular case it would have been hard to predict what happened.
2. If there had been a temperature point in the exchanger train it could have picked up what was happening.

11846Date Unknown

Source : ICHEME
Location : , USA

Injured : 0 **Dead :** 0

Abstract

An aluminised carbon steel reactor feed line on a hydodesulphurisation unit ruptured without warning after 3 years service. Autoignition and a severe fire followed. The cause was corrosion of the carbon steel by high sulphur content oil at discontinuities in the aluminium coating. Several areas of corrosion were found in the line and these were worst adjacent in welded joints. The welding apparently destroyed the integrity of the coating.
[hydrocarbons, hydrogen, continuous reaction, pipe, rupture, fire - consequence, corrosion, material of construction failure]

Lessons

1. Aluminised piping should not be used under conditions where the base metal would be subject to rapid corrosion. 100% inspection to allow detection of all discontinuities in the coating is not really practical. Three months previously spot checks using an ultrasonic thickness gauge had shown no loss of metal.
2. In this case the piping was replaced in 5% chrome alloy.

11840Date Unknown

Source : ICHEME
Location : , USA

Injured : 0 **Dead :** 0

Abstract

On commissioning a unit to saturate 10% of diolefins in an aromatic feed stock a runaway reaction occurred with a peak temperature of 650 degrees C in the nickel catalyst bed. A large excess of hydrogen was used. At the feed temperature of 150% the initial reaction of the diolefins heated the bed to a point where the aromatics were hydrogenated to naphthenes. This raised the temperature above 260 degrees C at which point hydrocracking of any hydrocarbon to methane caused an exothermic reaction.
[nickel, reaction vessel, near miss, overheating, design inadequate, safety procedures inadequate]

Lessons

1. Small scale pilot plant reactor trails tend to operate closer to isothermal rather than adiabatic conditions. Thus the potential for runaway reactions may be missed.
2. Nickel catalysts are extremely active for hydrogenation at low temperatures.
3. In this case the problem was solved by:-
· The reactor inlet temperature was lowered.
· The excess hydrogen was reduced to about 75%.
· Extra thermocouples were placed in the catalyst bed.
· Means were installed to rapidly depressure the reactor.

11809Date Unknown

Source : ICHEME
Location : , USA

Injured : 0 **Dead :** 0

Abstract

During a catalytic cracker shutdown several pressure relief valves discharging to flare were removed for servicing whilst the diethanolamine treater connected to the flare header was still operating. The valves were removed under controlled conditions and the connections to flare immediately blinded. However, in one case where the blind was in place and the gasket was being installed, ignition occurred. It was determined that this was due to the presence of pyrophoric iron sulphide.
On many previous occasions, although, some vapour hydrocarbon had been released there had been no ignition.
[blowout, fire - consequence, spontaneous combustion, safety procedures inadequate]

Lessons

[None Reported]

11774Date Unknown

Source : ICHEME
Location : , USA

Injured : 0 **Dead :** 0

Abstract

A small leak occurred in the return header box of a furnace, on a crude oil distillation unit, which had been in service for four years.
A steam purge put out the fire but the leak increased and after none months the plant had to be shut down. The leak was found to be due to severe corrosion in one return bend. This was due to the bend being made of mild steel rather 9% chrome alloy specified.
[heating, furnace tube, plant shutdown, corrosion, incorrect material of construction, inspection inadequate]

Lessons

[None Reported]

11767Date Unknown

Source : ICHEME
Location : , USA

Injured : 0 **Dead :** 0

Abstract

The level indicator controller and gauge glass in a HF (hydrofluoric acid) acid boot on a depropaniser over head receiver both failed. As a result the boot over flowed and HF acid was pumped to the HF stripper. This overloaded and HF flowed to the bottom of the solid KOH (potassium hydroxide) neutraliser. When acid built up to the level of the bottom of the KOH bed the reaction caused a almost instant mixing of the KOH and HF inventory. The resulting sudden vaporisation ruptured the vessel.
[control failure, settling, level control, instrument/controller, explosion, rupture, fire - consequence, safety procedures inadequate, runaway reaction]

Lessons

[None Reported]

11273Date Unknown

Source : INSTITUTE OF GAS ENGINEERS, COMMUNICATION 451, UNUSUAL INCIDENTS AT GAS WORKS AND THEIR LESSONS, PART 2, 28 SEP, 1954.
Location : , UK

Injured : 5 **Dead :** 0

Abstract

An explosion occurred in a gas purifier box within a gas production works during cleandown and inspection following identification of a fault. Careful precautions were taken prior to inspection to cool the oxide bed within the box using water sprays. The purifier box was left for several days to cool down. The box was carefully vented before opening, and appropriate emergency response equipment was placed in the work area.When the oxide bed was disturbed, it ignited giving off sparks which led to an explosion. The fire was quickly brought under control, but five personnel were slightly injured.
[decommissioning, gas, purifier, autoignition, injury]

Lessons

The following recommendations were made:

1. Difficult to determine whether incomplete reaction in the purifier box might lead to self-ignition on decommissioning.
2. Require to pass large volumes of clean gas through the purifier box to remove the retained heat prior to opening.

7782 Date Unknown

Source : BARTON J AND ROGERS R, CHEMICAL REACTION HAZARDS, 2ND EDITION, ICHEME, 1997, APPENDIX 1, 180.
Location : ,

Injured : 0 **Dead :** 0

Abstract

3-nitro-p-cresol was manufactured from nitric acid and p-toluidine. An incident occurred when one carboy of nitric acid was charged into the reaction vessel, followed by a second carboy. Unfortunately, it transpired that this second carboy contained oleyl chloride and not nitric acid. The vessel ruptured and a fire occurred.
[charging reactor, fire - consequence, incorrect chemical present, chemicals added incorrectly]

Lessons

[None Reported]

7445 Date Unknown

Source : LOSS PREVENTION BULLETIN, 115, 13.
Location : ,

Injured : 0 **Dead :** 1

Abstract

An operator went down into a pit to open a steam valve that was rarely operated and had been closed for 9 months. Attempts to open the valve with a reach rod, 8 metres long had been unsuccessful. The pit was recognised as a confined space and so the atmosphere was tested, the operator wore a rescue harness and a stand-by man was on duty outside. The steam main was up to pressure on both sides of the valve and the gauge pressure was 120 p.s.i (8.3 bar) on the upstream side, 115 p.s.i (7.9 bar) on the downstream side. There was a stream trap on the downstream side of the valve but not in the upstream side and as the valve was on the lowest part of the system about 5 tonnes of cold condensate had accumulated on the upstream side.
The operators took about 1-2 minutes to open the valve halfway. Very soon afterwards there was a loud bang as a 6 inch (15 cm) cast iron valve on a branch, an unused and blanked branch, failed as a result of water hammer.
After investigation the following conclusion was made, the accident would not have occurred if:
1. Cast iron had not been used. It is brittle and therefore not a suitable material of construction for steam valves which are always liable to be affected by water hammer.
2. There was a steam trap upstream of the valve.
3. The valve had been located in more accessible place.
Fatality.
[valve failure, incorrect material of construction]

Lessons

[None Reported]

7168 Date Unknown

Source : LOSS PREVENTION BULLETIN, 048, 28.
Location : ,

Injured : 0 **Dead :** 0

Abstract

Incomplete detontamination. A heat exchanger was received from an ethylene dichloride plant and some of the tubes were blanked off. These tubes were opened by drilling with a compressed air drill. A liquid escaped which contained two phases. On analysis the liquids were shown to be water and ethylene dichloride.
[spill, cleaning inadequate]

Lessons

[None Reported]

7169 Date Unknown

Source : LOSS PREVENTION BULLETIN, 048, 28
Location : ,

Injured : 0 **Dead :** 0

Abstract

Incomplete decontamination. A de-gasser was received from another plant, and some of the tubes were blanked off. When they were opened using a hand grinder, a liquid escaped which was later analysed as monochlorobenzene.
[cleaning inadequate]

Lessons

[None Reported]

7175 Date Unknown

Source : LOSS PREVENTION BULLETIN, 030, 159.
Location : ,

Injured : 0 **Dead :** 0

Abstract

The main reaction mass had to be kept at 160 degrees C for 24 hours to remove water by distillation. In the course of the first batch, after holding for 22 hours the temperature started to rise slowly and then with increasing rapidity. Decomposition gases containing SO2 (sulphur dioxide) and SO3 (sulphur trioxide) escaped. The nearby public road had to be blocked off. The very poor heat dissipation from the steam heated reaction kettle could not be removed the heat generated by the decomposition. The decomposition temperature was later found to be lowered by the presence of catalytic impurities.
[runaway reaction, batch reaction]

Lessons

[None Reported]

7192 Date Unknown

Source : LOSS PREVENTION BULLETIN, 051, 16.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A fire occurred recently on lagging surrounding pipework containing molten petroleum jelly. The pipework was lagged with non-asbestos magnesia based lagging and the pipework was stream-traced. The maximum temperature of the lagging was 150 degrees C, and the flash-point of the petroleum jelly being 204 degrees C.
The lagging appeared to have been soaked with petroleum jelly for some time and presumably a slow pyrolysis of the petroleum jelly had been taking place which ultimately resulted in conditions which lead to the autoignition of the petroleum jelly. The fire was then supported by additional petroleum jelly being drawn out of the open cell structure of the lagging. This process is known as wicking.
[lagging fire, fire - consequence]

Lessons

There are available types of lagging which have a closed cell structure and are thus not susceptible to the wicking process. These lagging types are recommended for installations where lagging is likely to be subject to spillages of oil or materials with similar properties.

7245 Date Unknown

Source : LOSS PREVENTION BULLETIN, 070, 13-14.

Location : ,

Injured : 0 **Dead :** 0

Abstract

A steam leak developed at a pair of flanges in a non-isolatable steam main having a nominal 44 bar (640 lbf/in2) line pressure. The gasket was of the spiral wound type. The area of the leak was so constricted that a special three part clamp had to be designed. The clamp was made and inspected before fitting. Shortly after fitting, the clamp split gently into two 18 degree segments.
On investigation, it was found that the clamp had failed because the cap screws used to assemble the three parts were in the wrong material, mild steel rather than B7 material as specified.
[incorrect material of construction, flange leak]

Lessons

[None Reported]

7271 Date Unknown

Source : LOSS PREVENTION BULLETIN, 083, 25-26.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A reactor was overpressured due to a faulty pressure regulator which caused the safety relief valves on the reactor to lift and the discharge autoignited. The reactor unit was shut down, but the safety valves failed to reseat and the discharge continued to burn until the reactor was depressurised. The main fire from the safety valve vent piping did no damage, but a secondary fire developed around the safety valve flanges which damaged some pipework, insulation and electrical equipment. The secondary fire was caused by the location drain holes in the safety valve riser piping which resulted in flame impingement on flanges. The flanges opened up and released additional fuel to the fire.
This was not a large loss fire, but it clearly points out the need to examine safety valve discharge piping to establish that drain holes are correctly located. Sometimes a short nipple and elbow are required to direct potential flames to a safe area. The location of bellows vent piping has been given considerable attention lately and rightly so. However, the drain in safety valve risers to the atmosphere are just as important.
[reactors and reaction equipment, overpressurisation, autoignition, fire - consequence]

Lessons

[None Reported]

7409 Date Unknown

Source : LOSS PREVENTION BULLETIN, 024, 167.

Location : ,

Injured : 0 **Dead :** 0

Abstract

Explosion in measuring vessel. Two measuring vessels were connected to a reactor R by a common pipeline. One measuring vessel (M1) served to charge concentrated sulphuric acid, the second (M2) to charge acrylonitrile.

Due to an operating error or to leaking valves, acrylonitrile penetrated from M2 into M1 (hydrostatic pressure difference).

The uncontrollable reaction between acrylonitrile and concentrated sulphuric acid accelerated into an explosion that ruptured the vessel M1 (a 1000 L kettle) into two parts.

[uncontrolled reaction, reactors and reaction equipment, charging reactor]

Lessons

1. Hazard analysis must also include the operation of measuring vessels, charge tanks, receivers and associated piping.
2. In the course of hazard analysis, special consideration should be given to possible cross contamination and its effect on the chemicals involved.
3. In case of alterations to production equipment involving measuring vessels and feed lines, the possibility of hazardous interactions between chemicals should be investigated by hazard analysis.
4. Even very small quantities of reactive chemicals may trigger uncontrollable decomposition reactions with devastating consequences.
5. Possible interactions of chemicals should be considered in the course of hazard analysis.
6. Each measuring vessel should be fitted with a separate feed line. If this is not possible, e.g. due to limited space, the piece of common line should be kept as short as possible and no valves should be installed in the common line.
7. Different reactants should not pass through the same charge tank and measuring vessel.
8. When production is changed, measuring vessels and feed lines have to be cleaned following a procedure to be indicated by the plant chemist in charge.
9. When new measuring vessels are installed, especially in multipurpose plant, proper provisions for cleaning must be made.
10. The possibility of measuring vessels being overfilled must be considered. If necessary, level indicators and safeguards against overfilling have to be installed, e.g. standpipes.
11. For each feed line, the need for flow control had to be considered. In critical cases, the maximum flow rate has to be limited.
12. If chemicals have to be fed through dip pipes or into a pressurised vessel, it may be necessary to install safeguards against backflow.

7411 Date Unknown

Source : LOSS PREVENTION BULLETIN, 024, 169-170.
Location : ,

Injured : 0 **Dead :** 0

Abstract

In this process the reaction kettle R was normally used for nitration reactions with nitration acid being fed from the measuring vessel M. This vessel was vented via a glass line E.
When the production programme changed, the measuring vessel M, empty but without being cleaned thoroughly, was used to charge ethylbenzylaniline.
As soon as 2 to 3 litres of ethylbenzylaniline had been pumped into the measuring vessel M, a vigorous reaction with development of gases started which caused the glass vent line E to burst.
[uncontrolled reaction, damage to equipment, cleaning inadequate]

Lessons

1. Hazard analysis must also include the operation of measuring vessels, charge tanks, receivers and associated piping.
2. In the course of hazard analysis, special consideration should be given to possible cross contamination and its effected on the chemicals involved.
3. In case of alterations to production equipment involved measuring vessels and feed lines, the possibility of hazardous interactions between chemicals should be investigated by hazard analysis.
4. Even very small quantities of reactive chemicals may trigger uncontrollable decomposition reactions with devastating consequences.
5. Possible interactions of chemicals should be considered in the course of hazard analysis.
6. Each measuring vessel should be fitted with a separate feed line. If this is not possible, e.g. due to limited space, the piece of common line should be kept as short as possible and no valves should be installed in the common line.
7. Different reactants should not pass through the same charge tank and measuring vessel.
8. When production is changed, measuring vessels and feed lines have to be cleaned following a procedure to be indicated by the plant chemist in charge.
9. When new measuring vessels are installed, especially in multipurpose plant, proper provisions for cleaning must be made.
10. The possibility of measuring vessels being overfilled must be considered. If necessary, level indicators and safeguards against overfilling have to be installed, e.g. standpipes.
11. For each feed line, the need for flow control had to be considered. In critical cases, the maximum flow rate has to be limited.
12. If chemicals have to be fed through dip pipes or into a pressurised vessel, it may be necessary to install safeguards against backflow.

7424 Date Unknown

Source : LOSS PREVENTION BULLETIN, 038, 27.
Location : ,

Injured : 1 **Dead :** 0

Abstract

Phosphorus oxychloride was being sucked from a drum into a measure vessel. When some 10 kg of the material was sucked in, a violent explosion ruptured the vessel and hurled it through a window. The operator who was wearing a gas mask sustained minor chemical burns to the head and had to be treated for severe shock.
It can be assumed that the measure vessel contained a certain quantity of water. It was a current practice to flush the vessel thoroughly with water at the end of each week and the water allowed to drain over the weekend. Possibly the drain line had become plugged by a sediment and some water remained in the vessel. The explosion occurred during the first operation after the weekend. In future the oxychloride will be pumped directly into the reactor.
[cleaning inadequate, cleaning]

Lessons

1. When a plant cleaning is completed, the equipment should be inspected and tested to ensure that it is in a satisfactory condition for subsequent use of plant.
2. Testing for combustible material using a detector may not be adequate when heavy oils or solid material may be present.
3. When a burning or welding operation is to be carried out, the equipment should be purged with an inert gas and tested for oxygen. Alternatively, fire fighting foam gasified with an inert gas could be employed.
4. Testing for flammable or toxic atmosphere should be carried out immediately before the work is to be undertaken.
5. It a plant cannot be inspected it should be assumed that it is contaminated and that appropriate measures have been taken to ensure it is safe.

7441 Date Unknown

Source : LOSS PREVENTION BULETIN, 113, 14.
Location : ,

Injured : 1   **Dead :** 0

Abstract

An air receiver 1.8m long and 45cm in diameter had been installed in a factory.
One morning, while the plant was running normally, the air receiver exploded. The dished end of the receiver was forced outwards and then blown off. It broke through a 0.5 m thick wall and struck a woman, fracturing her leg. The body of the receiver broke loose from its mounting on the floor, shot across the workshop and collided with a lathe which was moved by the force of impact. Several workers in the shop received minor injuries from flying glass and one was grazed on the leg by the body of the receiver.
After examination of the inside of the receiver and the pipes from the compressor, after the explosion, revealed considerable deposits of carbon. Also an excessive amount of crankcase oil was getting past the piston rings and into the cylinder and receiver. When solid carbon is allowed to accumulate in the delivery passages from a compressor, it will become incandescent while the compressor is running, so that any oil mist will readily ignite. It was found that the explosion was caused by the ignition of oil vapour.
[pressure vessel failure, solids deposition, injury]

Lessons

[None Reported]

7165 Date Unknown

Source : LOSS PREVENTION BULLETIN, 048, 27-28.
Location : ,

Injured : 1 **Dead :** 0

Abstract

A batch reactor was overpressured due to a runaway reaction and the subsequent emission seriously injured an operator.
The trouble started when the operator set the temperature control on "60". The required set point was 60 degrees C. The scale, in fact, was 0 to 100% of a temperature range 0 to 200 degrees C. The setting therefore was at 120 degrees C. This caused runaway reaction temperatures and consequently high pressure.
[batch reaction, overpressurisation, reactors and reaction equipment, injury]

Lessons

[None Reported]

7462 Date Unknown

Source : LOSS PREVENTION BULLETIN, 094, 25.
Location : ,

Injured : 0 **Dead :** 0

Abstract

Some months after installing a biocide dosing system on a cooling water unit, one of the dosing tanks overpressurised and ruptured, ejecting its contents some 20 ft in the air. The unusually warm temperature of the tank contents prior to the rupture suggested some form of chemical reaction could have occurred, causing the pressure to rise in the tank.
Following the tank rupture, the area was well ventilated throughout the day, before being shut down for the weekend. On the following Monday, workers entering the building noticed a "chlorine like smell", and closer inspection revealed a liquid deposit on much of the equipment or evidence of a corrosive attack. In particular a large number of electronic components and circuit boards were damaged.
The analysis of gas and liquid samples taken at the time suggested chlorine (Cl2), bromine
(Br2), hydrogen chloride (HCl) and hydrogen bromide (HBr) may have been released following the explosion of the biocide unit.
It was known that the biocide in use could breakdown in the presence of strong alkalies, organics or other oxidisable materials, but no problems had been identified during the commissioning of the system. However, the water was found to contain around 14% ethylene glycol (antifreeze). Tests were initiated to see if a reaction between the biocide and the antifreeze was possible. The results showed that following a "dormant" period of several days, the biocide and ethylene glycol mixture suddenly increased in temperature, releasing bromine gas. A similar reaction could be obtained by heating the mixture to around 60 degrees C. This evidence points to a reaction between the biocide and the ethylene glycol with the evolution of bromine and heat. This reaction was probably responsible for the biocide tank overpressurisation and subsequent release.
The tank concerned was connected to a cooling tower system that had not been run since the commissioning of the biocide system. This had resulted in a stagnant mixture of biocide and water in the tank.
It is believed that this stagnation resulted in conditions favourable to the glycol/biocide reaction. Certainly, if the water had been recirculating through the cooling tower the temperature would have remained low preventing the runaway reaction.
Several other factors were thought to have contributed to the incident, including the unusually high ambient temperatures over the period.
[overpressurisation, spill]

Lessons

The example highlights the need for caution in any design where potentially toxic or harmful chemicals or their by-products are used.

7472 Date Unknown

Source : LOSS PREVENTION BULLETIN, 091, 15.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A chemistry laboratory experienced a violent rupture of a 5 gallon plastic container inside a lab fume hood. The container was used for storage of waste organic slops, monomerics. The lab was preparing for a shutdown, and was collecting samples from refrigerators and elsewhere, and pouring them into their respective waste containers.
TBPO (t-butylperoctoate) was added to the monomerics slops container. Within 25 minutes, a runaway polymerisation occurred. The cap was on the bottle, so there was no relief available and the container ruptured across its seam. The fume hood sash was open.
Polymer shot out of the bottle into the doorways of two adjacent offices. Other glass bottles shot out of the hood, some containing cyanide. No one was injured, there was no fire.
[laboratory work, labelling incorrect]

Lessons

1. Improve labelling of waste containers to detail exactly which chemical wastes are allowed to be put in the container.
2. Segregation of non-compatible waste containers.
3. Instructions to keep fume hood sash down when not in use.
4. Education of laboratory personnel.
5. Periodic follow-up to enforce this procedure.

7477 Date Unknown

Source : LOSS PREVENTION BULLETIN, 091, LOSS PREVENTION BULLETIN, 091, 22.
Location : ,

Injured : 0   **Dead :** 0

Abstract

An operator opened a full drum of sodium hydrosulphite (sodium dithionite) and removed a small quantity for a batch charge. When he returned to the area where the drum was stored he found that the contents of the drum were ablaze. The fire was tackled with dry chemical fire extinguishers and the drum was transported to a safety shower where the contents were deluged with water. After the fire was extinguished, the remaining material was dissolved and dropped to the sewer.
Examination of the drum and review of the incident with the operator did not reveal an explanation of the incident. Further discussion with another site revealed that the material is very sensitive to moisture. (Drops of sweat are sufficient to start a reaction resulting in a fire.)
After investigation these conclusions were made of the causes:
1. Fit of lid on opened drum.
2. Moisture in storage area (humidity).
3. Scoop laid on surrounding surface allowing a contaminated/wet scoop.
4. Dilution tank being cleaned nearby allowing water to splash in the area.
5. Drum lid placed on surrounding surface.
6. Drum stored in unobserved area.
7. Not fully recognising moisture hazard/sensitivity.
[charging reactor, fire - consequence, spontaneous combustion]

Lessons

The lesson to be re-learned here is the moisture sensitivity of the material.
Small amounts of water or contact with a highly humid atmosphere in the presence of air may cause a fire or ignite nearby combustible materials.

7504 Date Unknown

Source : LOSS PREVENTION BULLETIN, 120, 9-10.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A combustion in the vapour space of a 1300 litre chlorination kettle resulted in the rupture of a bursting disc and the release of black smoke outside the production building. Another combustion occurred about 15 minutes later just after the feeds to the reactor had been shut off. There were no injuries or equipment damage and no material release other than the smoke. The combustion resulted from a mixture of chlorine gas and ethyl acetate vapour in the head space of the kettle.
After investigation a follow up literature review showed that chlorine/organic systems can have very low autoignition temperatures. With pure oxygen, organic vapour explosions are extremely violent, and may detonate. Air/vapour explosions are usually more vigorous than chlorine/vapour ones, but not grossly so. In this example the explosion seems to have been mild.
The procedures for check-out of equipment prior to start-up were also reviewed.
1. A fundamental review of the process determined that the ethyl acetate flush procedure could be eliminated altogether. The line was blanked.
2. A reactant weight-loss cross check and lack-of-reaction checks, based on colour change and exotherm rate were added to the operating instructions.

Lessons

Two major recommendations for the chlorination process were:
1. A better inerting procedure (although oxygen did not appear to be involved).
2. Feed control and interlocks based on reactant feed which were considered inherently safer than those based on chlorine feed.

7557 Date Unknown

Source : LOSS PREVENTION BULLETIN, 091, 12.
Location : ,

Injured : 1   **Dead :** 0

Abstract

Two operators had been called to change a filter on a plant. One donned an air-fed hood and the other self-contained breathing apparatus. Both felt the air supply to be only just adequate. Shortly, the operator wearing the hood felt uncomfortable and removed it. He immediately inhaled a very high concentration of methylene chloride, methanol vapour and collapsed. His companion removed his own breathing set to drag him away, a third man was summoned and first-aid was given. The affected man recovered consciousness and was given medical attention. On investigation it was revealed that the hood had not received the normal cleaning treatment after use, had not been disinfected and had not been inspected and placed in a protective polythene bag. The silencer in the air supply was blocked with rust and there was a defective regulator on the compressed air system.
[maintenance, cleaning inadequate]

Lessons

[None Reported]

7565 Date Unknown

Source : LOSS PREVENTION BULLETIN, 097, 9.
Location : ,

Injured : 0 **Dead :** 0

Abstract

During start-up of a new process, leaks occurred at two valve flanges due to the use of titanium gaskets. Titanium reacts vigorously with dry chlorine. These gaskets were improperly identified by a supplier and sent in error.
Due to prompt shutdown action by the plant operators, the release was minor and there were no injuries.
Five gaskets were removed from the chlorine line and sent to the corrosion laboratory for analysis. It was determined that three out of the five gaskets were made of titanium. Titanium ignites in the presence of liquid chlorine.
[testing inadequate, identification inadequate, incorrect material of construction, near miss, gas / vapour release]

Lessons

The following recommendations were made:
All the gaskets in the chlorine line were removed. All gaskets to be used in future chlorine service at the semi-works should be tested for positive identification of their materials of construction. This should be evolved into a system to test all materials, i.e. valves, lines, etc., that will be used in chlorine service for positive identification of their materials of construction.

7595 Date Unknown

Source : LOSS PREVENTION BULLETIN, 127, 17-18.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A tank explosion occurred at a printing ink factory early in the morning. The lid of the tank was thrown through the air, landing around 30 m away, narrowly missing employees arriving for work. The contents of the tank caught fire, but the fire was extinguished promptly with foam.
The tank was around 4.5 m diameter and 12 m high. It was nearly empty, with the depth of the ink being around 1 m. The roof was fitted with a 50 mm vent. Printers ink is thixotropic, that is, it sets to a gel unless it is continually worked. The contents of the tank were continuously recycled by the 15 kW delivery pump. To keep the ink mobile in the vicinity of the pump suction, there were three electric heaters, two 3000 W and one 750 W attached to the outside of the wall of the tank near the base. The recycled ink ran down the wall directly over the surface heated by the 750 W heater.
After investigation it was found that:
There appeared to have been an overheating of the 750 W heater and its supply cables where they were attached to the outer surface of the tank directly above the heater. This had damaged its thermostat bellows which were permanently distorted into the open position. The other heaters appeared in good condition. All the heaters were set to control between 70 - 90 degrees C. The heating coils were not attached directly to the tank, but to a stainless steel backing plate which was in turn attached to the tank.
At first it was suspected that overheating of the surface of the tank by loss of temperature control of the 750 W heater had led to vaporisation and auto-ignition of the ink.
It was recognised that the recirculation pipeline entered the tank directly over the suction line, and that the bulk of the ink was not mixed by the recirculation, and that only a very small volume was being rapidly recycled. It is now suspected that this ink was absorbing the friction heat of the pump, and being heated sufficiently to generate vapour and autoignite. A simple temperature rise calculation confirmed the adequacy of the friction energy to heat the small recirculating volume of the ink to autoignition temperature.
There were ash deposits around the recycle return to the tank, consistent with local overheating and combustion of this stream before the explosion.
It was learned during the investigation that there had been several 'pops' heard at this tank, and others, in the past, but that they had not ruptured the tanks.

Lessons

Preventative measures which should be taken include:
1. Take care when recirculating a pump delivery line to its suction. Ensure that there is sufficient cooling.
2. Where re-circulation is intended to promote mixing, ensure that the design is adequate for this to occur.
3. Investigate unusual occurrences, so that any lessons can be learned and action taken before a serious accident occurs.
4. Protective measures which should be taken include:
5. Nitrogen blanket the tank.
6. Put a high temperature sensor cut out in the recycle line to measure energy input from the heaters and the pump itself.

7708 Date Unknown

Source : SAFER PIPING, ICHEME, SAFETY TRAINING PACKAGE, 012, 4.74.

Location : ,

Injured : 0 **Dead :** 0

Abstract

A fire occurred in a large petrochemical/refinery, atmospheric distillation section. The fire was caused by a pipe rupture (guillotine failure) of a 100 mm, 68 kg 4 inch, 150 lbs carbon steel line containing a light liquid of hydrocarbon product (initial boiling point, 20 degrees C, 68 degrees F, final boiling point 180 degrees C, 356 degrees F). Most probably the product autoignited at the hot parts of the distillation tower, which operates, in the lower part, at temperatures of over 300 degrees C (572 degrees F). The failure of the 100 mm pipe was at the tie-in to a larger 400 mm (16 inch) pipe. The latter sagged downwards because of pipe support failure. The design of the pipe support was inadequate, yet sufficient to last seven years without failure. Additional dynamic load caused by sudden flow changes in the 400 mm piping system, due to a control valve failure, eventually over stressed the pipe support of the column and lasted two hours. The damage was quite extensive but fortunately the large distillation tower did not require replacement.
[autoignition, pipeline failure, design inadequate, fire - consequence, damage to equipment]

Lessons

[None Reported]

7719 Date Unknown

Source : SAFE USE OF CHEMICAL ADDITIVES, ICHEME, SAFETY TRAINING PACKAGE, 018, 3.2.; LOSS PREVENTION BULLETIN, 065, 25.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A two compartment tank was used for making blends of styrene. One compartment was full but the other was empty and was being steamed out prior to entry. Steaming had been in progress for two days when there was a jet of styrene liquid and gas with polymer ejected from the dip hatch of the other compartment. The cause of the incident was, steaming of one compartment causing the heating up of the styrene which assisted the polymerisation.
[spill, mixing, cleaning]

Lessons

Polymer formation in styrene is avoided by keeping it cool and by inhibition. If, however, the temperature rises, polymerisation can be initiated with considerable evolution of heat. In this case the styrene in the compartment was heated up by the steaming of the other compartment. This initiated the polymerisation with radicals already present and overcame the inhibitor. Styrene should be stored at as low a temperature as is economical, but should not be allowed to exceed 30 degreesC.

7720 Date Unknown

Source : SAFE USE OF CHEMICAL ADDITIVES, ICHEME, SAFETY TRAINING PACKAGE, 018, 3.2.; LOSS PREVENTION BULLETIN, 065, 26.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A storage drum of methyl methacrylate was subject to overpressurisation and sheared at the base. The drum was propelled into the roof of the building and polymerised material was scattered around.
It was not possible to determine the cause of the polymerisation but it was probably due to rust in the drum.
[rusting, drums, rupture]

Lessons

The levels of inhibitor added to the product are based on normal amounts of impurities expected when clean equipment is used. If there are impurities present the inhibitor is overwhelmed and polymerisation will occur. The heat of polymerisation results in the drum being overpressured followed by rupture.

7722 Date Unknown

Source : SAFE USE OF CHEMICAL ADDITIVES, ICHEME, SAFETY TRAINING PACKAGE, 018, 3.6.
Location : ,

Injured : 0   **Dead :** 0

Abstract

A violent polymerisation occurred in one of six horizontal storage tanks of 246 m3 capacity containing acrolein resulting in an explosion.
1,700 residents in the area of 13 square kilometres were evacuated due to damage to adjacent tanks. Debris from the explosion travelled 150 metres. Four tanks were lost in the subsequent fire.
It was believed that the polymerisation was initiated by radicals which were picked up by the acrolein from a leak when it passed through a heat exchanger cooled by river water.
[fire - consequence, evacuation, contamination, damage to equipment]

Lessons

Radicals which cause the polymerisation may be picked up from many sources and therefore it is important to identify the possible sources of contamination at the design stage. Levels of inhibitors in the product must take into account the contamination that may occur in normal operation.

6941 Date Unknown

Source : LOSS PREVENTION BULLETIN, 026, 31-38.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A tank in a compound of six identical tanks was found to have totally collapsed with loss of its contents, 70 tonnes of phosphoric acid. In collapsing, it pulled down some of the elevated walkways connecting the tanks and also damaging the side of another tank. The tanks were in an unbunded compound, and the spilled acid entered the works drainage system where the effluent pH detector closed the system outlet enabling the acid to be neutralised before discharging to the local authority sewer.
The tanks were manufactured from glass fibre/resin layer to which P.V.C. was bonded, comprising chopped strand glass and glass filament windings in the 'hoop' direction set in resin. Thus the strength of this material was highly 'biased' in the hoop direction. Additionally, the tanks had a built-in layer of 1 inch thick polyurethane insulation to their sides and underside of base secured by a further outer cladding of GRP.
The following conditions were drawn after investigation:
1. The nature and analysis of the materials involved rule out chemical attack as making any significant contribution.
2. It is possible that a combination of stress factors derived from the construction and foundation of the tank and the cracking of the P.V.C. liner lead to its failure.
3. It is considered that a major factor in the widespread cracking of the P.V.C. liner in some of the other tanks was use of extruded P.V.C.
4. It is considered that a good P.V.C./resin bonding reduces the tendency of the P.V.C. liner to crack.
5. None of the remaining tanks on this installation are considered suitable for further service on this duty.
[incorrect material of construction]

Lessons

The following recommendations were made:
1. If a thermoplastic liner construction is considered for similar chemical duties, the liner selected must be of a crack resistant nature.
2. The reinforcing laminate fibres should be laid in a spiral, cross bias or woven mode.
3. The tanks should be located on a firm rigid base.
4. Tanks in line GRP handling corrosive or hazardous chemicals should be subject to regular and detailed internal inspection.

6825 Date Unknown

Source : LOSS PREVENTION BULLETIN, 003, 11.
Location : ,

Injured : 0 **Dead :** 1

Abstract

Continuous diazotisation was carried out in a rubber lined vat. The agitator drive had to be changed because of mechanical failure. The vat was cleaned with hot water in preparation for repairs. A fitter entered the vat, supported the agitator with wooden wedges and disconnected the motor and drive mechanisms. When the replacement gear was being fitted on the next day, it was observed that the agitator had to be lifted in order to couple with the drive. The fitter entered the vat and attempted to raise the agitator by hammering on the wedges. On the first blow an explosion occurred in the vessel. The unprotected fitter had to be dragged out of the vat by the Works Fire Brigade and taken to hospital.
The causes of this accident were:
1. Crusts of dried diazonium salt present in the vat ignited by friction of the wedges supporting the agitator when these were hammered. The presence of material, which is flammable and explodes on impact, was due to inadequate cleaning of the vessel.
2. The regulations concerning the entry permit to vessels were disregarded. The Plant Manager was unaware of the intended entry into the vessel. The main objective of completing the form "Permit To Work Inside of Vessels" is to ensure that the manager considers all the hazards involved and takes all the necessary steps to eliminate them.
[cleaning inadequate, friction heat, fatality, continuous reaction, mechanical equipment failure]

Lessons

[None Reported]

6835 Date Unknown

Source : LOSS PREVENTION BULLETIN, 003, 3.

Location : ,

Injured : 0 **Dead :** 0

Abstract

Ethylbenzylaniline had to be charged to a stainless steel measuring vessel before beginning the first batch of a production campaign. Immediately after the first 2-3 litres had been pumped in a violent reaction occurred in the measuring vessel. The pressure in the vessel rose, resulting in rupture of the glass vent line. The measuring vessel is normally used for containing nitrating acid. Apparently the vessel was not cleaned before use, so that it still contained residual mixed acid which reacted with the ethylbenzylaniline.
[contamination, cleaning inadequate, charging reactor, reaction vessel]

Lessons

[None Reported]

6837 Date Unknown

Source : ICHEME
Location : ,
Injured : 0 **Dead :** 0

Abstract

In the manufacture of 2-chloro-5-nitrobenzenesulphonic acid, chloro-4-nitrobenzene is added to 20% oleum. In a closed batch reactor with an empty heating jacket the temperature will rise to 120-125 degrees C within an hour. To complete the reaction, this temperature is held for several hours by heating with 2 bar steam.
The incident batch had first been 'stabilised' at 125 degrees C by cooling for a short time. Subsequently, no further attention was paid to temperature. Within the next two hours, the temperature rose steadily.
When the recorder registered 138 degrees C a violent explosion occurred. The kettle was forced down from the mezzanine floor and the top was blown out through the roof.
[4-chloronitrobenzene, batch reaction, damage to equipment, overheating, runaway reaction, auto decomposition, design or procedure error, explosion / pressure release, batch reactor]

Lessons

Investigation showed that, just above the intended reaction temperature, a highly exothermic, formally autocatalytic decomposition reaction occurs. Above 130 degrees C this reaction will be particularly fast and violent if the reactor is closed.

6858 Date Unknown

Source : LOSS PREVENTION BULLETIN, 001, 1.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A section of 2 inch diameter 18' 8 Ti line carrying 55% nitric acid was replaced by a 3 inch diameter line. Two hours after the plant operation was re-established the new line collapsed but fortunately no one was injured.
The new flanges were found to be severely corroded and investigation revealed that they were fabricated of Monel and not of stainless steel. Visually it is difficult to detect the difference between stainless steal and Monel, the plumber welder was not aware of the differences in the materials. Further there was no clear marking on the supposedly separate storage bins in the engineering stores.
[corrosion, incorrect material of construction

Lessons

[None Reported]

6888 Date Unknown

Source : LOSS PREVENTION BULLETIN, 006, 14.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A gasket failure on the top cover of a hydrotreater cold separator drum released hydrogen which was ignited from the plant furnace. The resulting fire was quickly extinguished and damage was minor. The gasket failed as a result of overpressure, estimated at 50 kg/cm2, compared with 38.7 kg/cm2 design pressure of the drum.
The overpressure resulted from solid ammonium chloride deposits which plugged the crinkled wire mesh screen installed in the drum up-stream of the vapour outlet connection. This caused the screen to be forced up into the vapour outlet piping, essentially blocking it. The pressure control valve and safety valve protecting the drum were located in the vapour outlet piping downstream of the screen, and were thus unable to relieve the pressure in the drum.
[overpressurisation, fire - consequence, solids deposition, separation]

Lessons

This incident demonstrates that a crinkled wire mesh screen must not be installed between a safety valve and the equipment it is protecting. This case, the safety valve should have been installed directly on the drum, upstream of the screen, rather than on the outlet piping.

6898 Date Unknown

Source : LOSS PREVENTION BULLETIN, 007,4-5.
Location : ,

Injured : 0 **Dead :** 0

Abstract

An incident occurred when somebody isolated the instrument air to a plant in error. It was not immediately obvious what was wrong because the low pressure alarm on the instrument air supply had been installed before the isolation valve. The pressures in the plant were upset and the hydrogen flow to a reactor was isolated by hand. The valve did not give complete isolation and hydrogen continued to leak in, causing a runaway reaction.
[operator error, isolation inadequate, instrumentation failure, reactors and reaction equipment]

Lessons

In a case like this, when effective isolation is very important, double block and bleed valves should be installed. The position of the LPA (instrument air) should also be checked to ensure that it cannot be isolated from the plant instrument air supply.
The specific recommendations and measurements taken as a result of the incidents described are as follows:
1. Design Philosophy and Procedures
(a) There should be a clear design philosophy for the specification of instrumentation, control and projective systems.
(b) There should be a through Hazard and Operability analysis carried out on the plant design to ensure that all possible eventualities which could lead to a hazardous condition have been eliminated.
(c) The reliability of the instrumentation should be assessed quantitatively whenever possible.

2. Design Principles
a) Generally, the process parameters of direct interest should be measured, and displayed in the right places.
b) The same measurement should not be used for control and protection.
c) The possibility of instrument failure must be fully taken into account. It should be ensured that failure of instruments does not produce hazardous conditions.
d) The action of control loops should be to fail safe.
e) Instrumentation designed to deal with a fault must not be disabled by the fault itself.
f) The system must be designed for abnormal as well as normal operating conditions, e.g. start-up and shut-down.
g) Steam tracing to be provided for instruments liable to freeze.

3. Inspection
All instruments, systems and alarms and trips should be regularly checked under real life conditions. Adequate test facilities should also be incorporated in the system at the design/construction stage.

4. Operators
a) A process operator has a finite error rate. This can and should be reduced by good ergonomics, but cannot be eliminated.
b) A process operator should not be used instead of a trip system.
c) The instrument system should not be allowed to degrade even if the operator seems to compensate for this.

6913 Date Unknown

Source : LOSS PREVENTION BULLETIN, 008, 17.

Location : ,

Injured : 0 **Dead :** 0

Abstract

During the maintenance of a spray drier for dairy products, the atomiser was given too much lubricating oil. The oil soaked into powder deposited on the underside of the roof of the drier and during subsequent operation, the oil-soaked powder spontaneously ignited. The burning material fell to the bottom of the drier, but fortunately no explosion occurred. However, the entire batch of product had to be discarded.
[spontaneous combustion, fire - consequence]

Lessons

There was insufficient supervision of the maintenance staff, who were unaware of the potentially serious consequences of an apparently slight mishap.

6922 Date Unknown

Source : LOSS PREVENTION BULLETIN, 012, 14-15.
Location : ,

Injured : 0 **Dead :** 0

Abstract

This incident involved the sulphonation of 4-chloronitrobenzene with 65% oleum. A runaway reaction took place from an operating temperature of 115 degrees F, blowing the pan cover off and leaving a glowing reaction mass.
This was not a new process but had been changed a few years earlier from the original 20% oleum process. Retrospective work showed that the process was more sensitive to heating and temperature than had been realised. The author concludes that the process was not properly developed and the available information that the process was potentially dangerous above 120 degrees F, was not applied.
[design inadequate]

Lessons

There are obvious lessons to be learned from this. The accident happened because the process and plant were designed with insufficient data. An extensive research work and investigation of the process had to be carried out after the accidents to elucidate their causes, work which should have been conducted before the design was undertaken.
To design a safe plant it is essential to:
1. Identify all components present in the process streams including all minor impurities which do not normally appear on the flowsheet.
2. Determine all the relevant physical and chemical properties of all the material and impurities.
3. Establish the reaction mechanisms and determine the kinetic and thermal data for all the reactions likely to occur.
4. Identify toxic, flammable and explosive hazards.
5. Explore the conditions well outside the normal operating range of concentration, temperature and pressure.

6930 Date Unknown

Source : LOSS PREVENTION BULLETIN, 012, 5-6.
Location : ,

Injured : 0 **Dead :** 0

Abstract

An explosion and fire occurred in a refinery floating roof naphtha storage tank while being prepared for cleaning. The cause was believed to have been ignition of naphtha vapours by pyrophoric iron sulphide formed on the underside of the roof.
The tank was of the floating roof type, 5000 m3 capacity, with internal polyurethane coating of shell and floor. The tank service was naphtha feed to the feed hydrofiner of a catalytic reformer, consisting of heavy virgin naphtha plus some by-product streams from other process plants (solvent distillation overheads and bottoms, and wild naphtha from a diesel hydrofiner). H2S content of the wild naphtha varied between 50 and 2000 ppm.
The floating roof and tank bottom were sufficiently damaged that replacement was necessary. Extensive repairs to platforms, ladders and other auxiliary equipment were also required. There were no casualties.
The fire resulted from the ignition of a flammable naphtha vapour/air mixture formed below the roof after it had landed. The source of ignition is believed to have been pyrophoric iron sulphide formed on the un-coated underside of the roof by the high H2S concentration of the naphtha contents.
As a result of this incident the refinery modified their procedure for emptying floating roof tanks. Before the roof is landed, water is injected and the remaining oil is pumped out from an elevated nozzle on the side of the tank.
[floating roof tank, spontaneous combustion, fire - consequence, damage to equipment]

Lessons

[None Reported]

7160 Date Unknown

Source : LOSS PREVENTION BULLETIN, 047, 23-25.
Location : ,

Injured : 0 **Dead :** 0

Abstract

This incident occurred on a distillation column, normally in hydrocarbon service, while welding during a shutdown. A minor explosion occurred which dislodged the trays. There was no subsequent fire and no injuries.
The column had been shutdown, isolated by spading or disconnection and steamed preparatory to installing a new 40 mm (1 and a half inch) connection in the 200 mm (8 inch) liquid line to the reboiler. The line was then high pressure water jetted. The column was tested by a gas detector and by visual inspection before a Fire Risk Permit was issued. The hole for the new nozzle was flame cut and a heavy smoke was noticed coming out of the top column manhole when the cut was near completion. Before the work could be stopped however there was a minor explosion within the column with a jet of flame reported from the bottom column manhole. There was no sign of an internal fire but the column was purged with steam for a period before cooling and inspection.
The following points emerged from the investigation:
1. The line being cut was coated internally with a layer of hard carbon-like material which had not been removed by the high pressure water jetting.
2. A period of about two hours elapsed between issuing the permit and the job being started. During this time the reboiler had been coated with an antifoulant preparatory to start-up. (The liquid inlet to the reboiler remained disconnected and blanked).
Subsequent testing of the antifoulant showed it most unlikely to have provided fuel for the explosion and that the cause of the incident was due to the creation of a heavy smoke containing sufficient carbon to eventually ignite.
[cleaning inadequate]

Lessons

Site procedures have been modified to:
1. Minimise the extent of plant and equipment which could possibly give rise to such an explosion by isolating the smallest item (in this case the shortest length of pipe), that will allow the maintenance job to be undertaken.
2. Minimise any delay between issuing a permit and the job commencing.

6975 Date Unknown

Source : LOSS PREVENTION BULLETIN, 012, 2-3.
Location : ,

Injured : 0 **Dead :** 0

Abstract

The practice in this refinery was to continuously blanket asphalt tanks with steam, to eliminate the possibility of flammable hydrocarbon/air concentrations in the vapour space.
Three men were working on the roof of one of these tanks (cone roof type, 10,000 m3 capacity), repairing insulation. The tank was about half full of asphalt at 172 degrees C.
Two days prior to the incident, the blanketing steam to this tank was shut off to avoid overheating the roof, following a complaint from the workers. Two hours before the incident, 3000 m3 of product was pumped out of the tank for shipping.
While the three men were on the roof, an internal explosion occurred which ruptured the weak roof seam along one third of the circumference on the opposite side from the stairway. Fortunately the men were near the stairway and were able to escape without injury. The incident is believed to have been an example of pyrophoric ignition. Pyrophoric iron sulphide or pyrophoric coke deposits would have formed during normal tank operation when air was excluded by the blanketing steam. Shutting off the blanketing steam and lowering the liquid level would result in air entry through the vent, and exothermic oxidation of pyrophoric deposits would then cause localised heating up to a temperature sufficient to ignite flammable vapours present in the tank.
[spontaneous combustion, refining]

Lessons

[None Reported]

6976 Date Unknown

Source : LOSS PREVENTION BULLETIN, 012, 3.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A minor fire occurred during the cleaning of a storage drum which had contained sour propane. Scaffolding planks just outside the manhead were ignited by pyrophoric scale which had been removed from the vessel.
[spontaneous combustion, fire - consequence]

Lessons

[None Reported]

6980 Date Unknown

Source : LOSS PREVENTION BULLETIN, 016, 7.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A caustic soda storage tank started to leak seriously. Facilities existed for pumping the tank contents into another tank in the event of an emergency. Attempts to do so failed however, since the valve leading to the transfer line was jammed. The bottom run-off valve could no longer be opened, since the pneumatic activator had been destroyed by the leaking caustic soda. Attempts to use immersion pumps were only partially successful, since they were made unusable in as short time by the caustic soda. In the end, an open plastic container was placed under the tank, and the caustic soda allowed to flow into it. From there, the solution was pumped into the second tank.
It was found that the original tank was constructed in a low carbon (mild) steel suitable for low pressure applications. It had been overlooked that this material is only resistant to corrosion caused by caustic soda if it has been annealed.
[incorrect material of construction, storage tanks]

Lessons

[None Reported]

6998 Date Unknown

Source : LOSS PREVENTION BULLETIN, 015, 7.
Location : ,

Injured : 0 **Dead :** 0

Abstract

Hot hydrogen leaking to atmosphere through a stress corrosion crack in the weld of the stainless body of the hydrogen purifying unit ignited spontaneously. The only damage was to the cotton wrapped glass fibre insulation. The leak which caused the fire was indicated by the baseline displacement it caused on the chromatograms, the gas chromatographs being optimised for parts per million determinations, and subsequently the smell of burning insulation.
The power was switched off, the hydrogen supply shut off and nitrogen turned on. The unit was taken off line and examined and a small leak found in a weld joint. The leak could only be detected by pressurising the unit with hydrogen and using the hydrogen detector.
The unit was returned to the supplier for investigation and repair.
The supplier reported the cause of the crack to be chloride resulting in stress corrosion cracking of the stainless steel.
Subsequently analysis of the hydrogen gave results of up to 2 ppm chlorine despite the suppliers specification that chlorides were not detectable.
On a subsequent occasion 1 gram of chloride (salt) was washed out of the purifying cell.
[weld failure, spontaneous combustion, fire - consequence, purification]

Lessons

The following corrective action was taken.
A filter containing lime and alumina impregnated with silver metal (via silver nitrate) was installed in the hydrogen feed line.
The purifying units are rinsed out to remove chloride before installation and quarterly thereafter. The stainless steel welding flux contains 50-60 ppm chloride and should therefore be removed.
Every cylinder of hydrogen is being analysed for chloride content for the time being.
Because hydrogen has a very low viscosity and high diffusivity, it is necessary to use either hydrogen, or a gas with similar properties, such as helium, for leak-testing hydrogen systems.

7003 Date Unknown

Source : LOSS PREVENTION BULLETIN, 015, 7-8.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A road transportation incident. A truck mounted, detachable container contained a mixture of highly flammable solvent and sludge. An electric agitator was permanently mounted on the container and was used to keep the sludge in suspension. While the container was emptied at the incinerator, using 20 p.s.i.g (1.4 bar gauge) of nitrogen pressure, the operator noticed that material was leaking from the packing around the agitator shaft. Later, after re-mounting on a truck and while driving it to the production building, the operator noticed in his rear-view mirror that the container was on fire. He immediately dropped the container on the road and notified the fire section. No injuries occurred, and there was minor damage to the container.
Some of the material had not only leaked from the packing, but had also soaked into the insulation under the metal shielding of the container. It ignited by spontaneous combustion while the emptied container was in transit.
[fire - consequence]

Lessons

The following recommendations were made:
1. All insulated, detachable containers to be inspected and any damage to the metal shielding which might allow chemicals to enter the insulation will be repaired.
2. Any container without fully-enclosed shielding around the insulation will be taken out of service until the insulation is fully enclosed.

7008 Date Unknown

Source : LOSS PREVENTION BULLETIN, 017, 8.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A man left his donkey jacket on a steam pipe for a couple of hours. When he returned only the collar was left, the rest had smouldered away.
The steam pipe was covered with temporary lagging only and the heat was sufficient to set fire to some oil on the jacket. Oily clothing or other fabrics can catch fire at quite low temperatures in the same way that lagging can. Spontaneous ignition of heaps of oil rags is a well-known hazard.
[spontaneous combustion]

Lessons

[None Reported]

7062 Date Unknown

Source : LOSS PREVENTION BULLETIN, 021, 78-79.
Location : ,

Injured : 0 **Dead :** 0

Abstract

Incident during start-up of a reactor. It was filled with reaction mixture from another reactor which was already on line and the panel operator started to add fresh feed, gradually increasing the flow while he watched the temperature on a recorder conveniently situated at eye level. He intended to start a flow of cooling water to the reactor cooler as soon as the temperature started to rise, the usual method.
Unfortunately, there was a fault on the temperature recorder and although the temperature actually rose this was not indicated. Resulting in a runaway reaction.
The rise in temperature was, however, indicated on a six point temperature recorder at a lower level on the panel, but the operator did not notice this.
Fortunately the runaway was not serious because a high temperature alarm on the six point recorder alerted the operator before the temperature got dangerously high.
[temperature meter/control, instrumentation failure]

Lessons

[None Reported]

7117 Date Unknown

Source : LOSS PREVENTION BULLETIN, 037, 13-14.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A group of four tanks provided rundown storage for liquor produced when several vacuum crystallisers are boiled out. The crystallisers are part of a plant producing a high boiling point acid intermediate to fibres production. All the tanks are stainless steel 4.3 m diameter by 9 m high. Each has a 50 mm vent and a low pressure stream coil in the bottom.
In the incident, a solid layer formed in one of the tanks. When some liquid was pumped out of the tank a space was left underneath the solid. Later more liquid was added on top of the solid. The solid gave way the liquid on top drained so rapidly into the space below that the vent pipe could not let air in sufficiently quickly and the tank collapsed.
According to the level gauge, one of the tanks was empty and had been for 4 days. Fifty tonnes of liquor was run into it, the temperature of the rundown being not more than 50 degrees C at first. Shortly afterwards the sides of the tank started to cave in. Several wrinkles developed which were sufficiently large to prevent it being used without repair.
The vent was seen to be quite clear. But when the manhole, on the tank roof, was removed, the bottom of the tank could not be seen at all. The view was obscured by a raft of solidified acid, stretching right across the tank, and whose top was thought to be about 2m above the tank base. Hot condensate was pumped in and circulated to remove the deposit. Two days later, much of it remained despite the intensive washing.
The collapse of the tank was due to a pressure difference and a number of possibilities were explored, for instance, condensation of vapours when liquor at 30 degrees C was pumped in. The only plausible explanation was that the liquor was pumped in and rested on the raft. It was known that, from time to time, boil out liquor contained lumps of solid acid, so if the raft was not complete at the beginning of the transfer, any lumps in the liquor would fill the holes. Liquor thus built up on the raft until this cracked and collapsed, allowing the liquor to drain through, and suddenly creating a gravity drainage condition, with which the vent was not designed to cope. It was estimated that a vacuum of 15 m bar (6 in wg) would have been generated, more than enough to start collapsing the tank. It was also thought that the raft was quite thick, flat on top, convex under and resting on the tank bottom. Of course, as liquor drained, air under the raft was displaced to the upper part of the tank, so the collapse was only partial.
[solids deposition, design or procedure error]

Lessons

After the incident the storage procedures were amended, the tanks were taken out of service regularly, and washed to avoid thick rafts of solid acid building up. In addition, the upper manholes were left open to provide more venting capacity. This illustrates the possibilities for unexpected incidents when solids can form in a tank.

7149 Date Unknown

Source : LOSS PREVENTION BULLETIN, 031, 23-25.
Location : ,

Injured : 0 **Dead :** 0

Abstract

Reports from the engineers that some mono-pumps when opened up contained a material which ignited on exposure to air resulted in some of the ignited material being sent for analysis in the laboratory. It was found to be finely powdered stainless steel worn from an internal coupling which obviously rapidly oxidised when opened and exposed to air.
[spontaneous combustion]

Lessons

[None Reported]

7159 Date Unknown

Source : LOSS PREVENTION BULLETIN, 047, 21-23.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A new product was being investigated at pilot level. Laboratory work had shown that the material could be produced by an isomerisation reaction in the presence of a catalyst. The reaction was rapid and strongly exothermic. To maintain control in a larger reaction volume the feed was to be introduced in small amounts after the initial volume charged had reacted.
The vessel was charged with 5 litres of reactant to a level just above the glass beads and catalyst was added. The lowest zone of the isomantle was switched on and warm up commenced. Due to the low level used the thermocouple was reading the vapour temperature. Warm up proceeded with no apparent effect until 60 degrees C was reached in the vapour space. Then, without warning, the contents of the vapour space ignited producing an orange flash and pushing apart the base flange of the reactor. The electricity supply to the isomantle was isolated and the system allowed to cool. On inspection the vessel was found to be intact apart from the loosened flange.
The following findings were made:
1. The material in the vessel was analysed and found to be un-reacted feed.
2. The reactor was filled to the same level with water and the heating switched on. After only 10 minutes the glass surface temperature above the liquid level against the isomantle had reached a temperature of 250 degrees C.
3. Contact with the isomantle manufacturers confirms that the mantles will easily provide surface temperatures of 300 degrees C. The high temperature cut on the element is usually set at 350 degrees C.
4. The incident is believed to have been caused by autoignition of the vapour by the hot surface above the liquid level.
[reactors and reaction equipment]

Lessons

The following recommendations were made and actions were taken:
1. The liquid level must completely cover the isomantle zones in use.
2. Use of a heel to provide the necessary level.
3. The glass beads should be removed and the stirrer run.
4. The thermocouple should monitor liquid temperature.
5. Using the above method the product has since been successfully prepared.

10648Date Unknown

Source : ICHEME
Location : ,

Injured : 2 **Dead :** 0

Abstract

A flare line had been kept in service during refinery maintenance. A number of relief valves on various vessels were to be removed and blind flanges installed. Over a period of four days, using breathing masks, a number of relief valves had been removed without incident. A few minutes before the accident, two men had successfully completed the same operation on a nearby vessel.
The accident occurred when working on a 1.2m dia by 6m high vertical drum used for mixing gasoline inhibitor. When the two men swung the relief valve away from a 150mm flare header flange, a large cloud of black dust escaped from the opening, partially enveloped the men, then floated away. The blind flange was quickly slid into position and secured with several studs and nuts, then slightly parted again to insert a gasket. At this point ignition of the escaping flare gas occurred immediately. The two men sustained second and third degree burns whilst trying to escape.
It was believed that the dusty material was pyrophoric, and this caused ignition of the escaping flare gas.
[line break, flare header piping, fire - consequence, gas / vapour release, spontaneous combustion, isolation inadequate]

Lessons

It was recommended that in future, unless some emergency dictated otherwise, the flare line was to be isolated, depressured and steamed before connections to it were broken

7925 Date Unknown

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

An accident, which occurred within a contractor's compound, when a contractor's employee welded one of the product nozzles of a vacuum road tanker without first ensuring that the tank was free from flammable vapours. The full diameter end cover of the tank was blown a distance of about 12 metres by the force of the explosion.
It became apparent during the investigation of the accident that, despite the careful vetting and selection of the cleaning contractor, the induction training given by the refinery to all the individuals involved, most of whom had had three or four years experience on site, the regular participation of the contractor's representative in refinery organised safety meetings on site and the written instructions to the contractor which required an additional Hot Work Permit for the type of work which caused the accident, those involved neither recognized the hazards they were facing nor the need for an additional Hot Work Permit to cover the work.
[cleaning inadequate, permit to work system inadequate, safety procedures inadequate]

Lessons

In the light of the tragic experience, it was recommended that blanket Hot Work Permits covering workshop areas should explicitly prohibit the entrance of equipment contaminated with flammable liquids or vapours. It was also recommended that consideration should be given to providing each cleaning vehicle with a document, akin to a Transmittal Permit, to apply for as long as it is on site or likely to be contaminated. This would state the vehicle's limits of access, the standards to which it must be maintained for safety in hazardous areas and the precautions necessary before carrying out any hot work in its vicinity.

7848 Date Unknown

Source : MANAGING FOR SAFETY, ICHEME, TRAINING PACKAGES, 017, 4.67.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A 1.3 m3 dosing vessel was supposedly filled with methanol, which is used as an initiator for the reaction of ethylene and propylene oxide. The reaction product is used as a diluent for the manufacture of brake fluid.
Upon addition of potassium hydroxide flakes, which are used to catalyse the reaction, the vessel exploded.
The most probable cause is that propylene oxide entered the vessel inadvertently. Addition of the hydroxide flakes caused the oxide to polymerise uncontrollably, resulting in an excessive pressure build up.
[high pressure, polymerisation, explosion, reaction vessel]

Lessons

The following recommendations were made:
1. Plant changes on process installations should be thought through thoroughly on all possible health, safety and environmental aspects and challenged by appropriate and independent specialists. In this case this should have resulted in the installation of a separate independent feedline for either MEG or methanol, equipped with its own dedicated flow counter.
2. Operating instructions should be precise in defining required manipulations in batch processes. A check list could be used as a help.
3. Procedures need to be discussed with operating personnel to make sure that they are fully understood.

7855 Date Unknown

Source : DUST EXPLOSION HAZARDS, ICHEME, TRAINING PACKAGES, 022, 4.13.
Location : ,

Injured : 0   **Dead :** 0

Abstract

A filter unit in a plant processing polymer crumb suffered a major explosion. The force blew out the 4 rupture panels on the dirty side and 2 of the 3 discs on the roof of the filter unit. A serious fire ensued in the filter and around the plant due to ejected burning product. The fires were soon brought under control and extinguished without further incident.
The following conclusions were made:
It was clear from the damage that the explosion had originated in the lower half of the collector, beneath the grid. The most likely source of ignition was an electrostatic spark. The metal grid was loose fitting and not bonded to the earthed body of the dust collector. The powder had a high resistivity and deposits on both the grid and supports may have caused the grid to become isolated from earth. The mechanism for charge generation was the pneumatic transfer of material through pipework to the unit. Highly charged powder could raise the potential of the isolated metal until a spark occurred between the grid and the earthed filter body.
[lack of earthing, solids deposition]

Lessons

The following recommendations were made:
The primary recommendation was to secure the metal grid which separates the bag section from the lower plenum. It may be possible to remove the grid completely as its only function was to prevent fouling of the rotary valve in the event of a bag being detached. The grid mesh had to be widely spaced otherwise it would cause a restriction and impede flow to the explosion panels, in the event of ignition in the bottom plenum.
Tests needed:
1. MIE to evaluate electrostatic risk.
2. MIT to determine sensitivity of dust cloud.
3. Thermal stability tests to examine behaviour when heated.
4. 20 litre sphere test for explosion relief design.
5. Train firing tests for assessment of fire/flame propagation (in the clean air ducting where deposition may occur due to seepage of dust).

7857 Date Unknown

Source : DUST EXPLOSION HAZARDS, ICHEME, TRAINING PACKAGES, 022, 4.23.
Location : ,

Injured : 0 **Dead :** 0

Abstract

Within one year, two explosions occurred in a large spray drier handling dairy products. The incidents caused both fire and explosion damage. Explosion relief vents at the top of the drier opened into the building causing fire damage to nearby instrumentation. Burnt material also spread to associated fluidised beds and cyclones.
An investigation was made and it appeared that excessive deposits of process material had collected on the walls and roof of the spray drier and had self-heated until combustion occurred spontaneously. Although flammable dust clouds are normally only found in the lower section of co-current driers, the burning fragments at the top (hotter section) may have caused ignition directly when falling through the cloud or by starting a fire in the hopper section.
The following conclusions was made:
Laboratory data after the event indicated that the product being dried was capable of self-heating to a level at which spontaneous combustion occurred, when exposed to temperatures similar to the drier (hot air) inlet.
[fire - consequence, solids deposition, explosion suppression, heating,]

Lessons

The following recommendations were made:
The disruption to the plant was severe and resulted in closure for a considerable period. When the plant was rebuilt, an explosion suppression system was installed to provide the necessary level of protection and overcome the problem of venting inside the building. A study of the thermal decomposition behaviour of the range of products was also required in order to specify safe drying conditions (in terms of temperature and exposure period).
Test needed:
1. MIE (minimum ignition energy) to evaluate electrostatic risk, e.g. (discharge risk from highly charged powder).
2. MIT (minimum ignition temperature) to determine sensitivity of dust cloud to hot surfaces.
3. Thermal stability to examine behaviour when heated.
4. 20 litter sphere test for explosion relief design.
5. Train firing tests for assessment of flame propagation risks from layers o f material within the system.
6. Test powder for resistivity and charge decay time.

7858 Date Unknown

Source : DUST EXPLOSION HAZARDS, ICHEME, TRAINING PACKAGES, 022, 4.27.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A wet type dust collector was located in the open air and was used to filter aluminium dust from a finishing machine. The water level in the collector had been reduced to prevent water splashing from the lid of the machine. An explosion occurred immediately the fan motor was started after maintenance causing burn injuries to the engineers standing by the open front of the unit.
The following conclusions were made:
Thermite sparks of the type produced when both aluminium and rust are involved are extremely energetic. The exothermic reaction initiated by the heat from the impact can raise the spark temperature to several thousand degrees Centigrade. Such sparks therefore are capable of igniting many dusts.
The sensitivity of powders to these sparks is difficult to determine. There is evidence to suggest that the ignition sensitivity of dust clouds to a variety of sparks (e.g. single impacts, grinding, flintstone etc.) can be predicted from both the MIT value and MIE value. However, great care is needed when applying these assumptions as anomalies have been found.
[thermite reaction]

Lessons

The following recommendations were made:
Recommended safety measures included resetting the water level to the required level to ensure that dust capture was more effective. The mild steel fan blades were also replaced with a non-sparking type. Procedures were instigated to clean the inside of the filter unit regularly, to avoid accumulation of aluminium dust. Steps were taken, additionally, to ensure that hydrogen would not accumulate within the filter unit.
Test needed:
1. MIE to evaluate electrostatic risk.
2. MIT to determine sensitivity of dust cloud.
3. 20 litre sphere test for explosion relief design.
4. Train firing test is not necessary as finely divided metals are known to be pyrophoric when moist.
5. Gas evolution test to define ventilation rates.

7859 Date Unknown

Source : DUST EXPLOSION HAZARDS, ICHEME, TRAINING PACKAGES, 022, 4.33.
Location : ,

Injured : 0 **Dead :** 0

Abstract

Explosion in cereal processing plant. An incident occurred which caused a suppression system to operate. The explosion in the filter unit caused the inspection door frame to open which allowed the release of flame into the workspace along with unburnt dust and suppressant.
The cause of ignition was identified as the milled material binding on the screen of the mill which, through self-heating, began to decompose and smoulder. [decomposition, solids deposition]

Lessons

Tests needed:
1. MIE (minimum ignition energy) to evaluate electrostatic risk, e.g. (discharge from highly charged powder).
2. MIT (minimum ignition temperature) to determine sensitivity of dust cloud to hot surface ignitions.
3. Thermal stability tests to examine behaviour, e.g. (gas generation when heated).
4. 20 litter sphere test for explosion protection design.
5. Train firing tests for assessment of flame propagation risks from deposits of material in pipework etc.

7865 Date Unknown

Source : DUST EXPLOSION HAZARDS, ICHEME, TRAINING PACKAGES, 022, 4.52.
Location : ,

Injured : 0 **Dead :** 0

Abstract

Over lubrication caused spontaneous ignition. During maintenance of a spray drier for dairy products the atomizer was given too much lubricating oil. The oil soaked into powder deposited on the underside of the roof of the drier. During subsequent operation the oil-soaked powder ignited spontaneously. The burning material fell to the bottom of the drier, but fortunately no explosion occurred. However, the entire batch of product had to be discarded.
[spontaneous combustion]

Lessons

[None Reported]

7867 Date Unknown

Source : DUST EXPLOSION HAZARDS, ICHEME, TRAINING PACKAGES, 022, 4.52.

Location : ,

Injured : 0 **Dead :** 0

Abstract

An explosion occurred during commissioning of fluid bed coal drier. Commissioning of a 4.3m diameter fluidised bed coal drier was plagued by a series of fires in the bed. The cause was traced to non-uniform fluidisation leading to pockets of unfluidised material resting on the hot distributor plate. The distributor was made of steel and had 9% open area and a pressure drop of about 0.012 bar. At higher than normal temperatures, which were encountered when the feed rate rose above the design value, the plate buckled slightly and the refractory seal around the circumference was broken.
[incorrect material of construction, design inadequate]

Lessons

The steel distributor was replaced by a ceramic plate with 4.5% open area and 0.043 bar pressure drop. This completely eliminated the fires.

7868 Date Unknown

Source : DUST EXPLOSION HAZARDS, ICHEME, TRAINING PACKAGES, 022, 4.53.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A milk powder plant explosion. Fires occurred within a set of four interconnected fluid bed driers in a milk powder plant. The fires, which were believed to be due to self-heating of the powder, were swiftly controlled by the internal water spray systems. However, further smouldering became evident in the almost horizontal sections of the exhaust bunking to the cyclone, and it was some hours before this was extinguished. Considerable deposits of powder had accumulated in this bunking.
This incident shows the need to reduce the length of horizontal bunking on drier exhausts to a minimum. If this is not possible, access doors should be provided for regular cleaning and the air velocity should be kept as high as possible.
[fire - consequence, solids deposition]

Lessons

[None Reported]

7870 Date Unknown

Source : LOSS PREVENTION BULLETIN, 107, 23-24.
Location : ,

Injured : 0 **Dead :** 1

Abstract

An explosion in a flare stack during maintenance. At a site, four flares, each with their own knock out vessel and seal vessel, were connected to a flare header. The procedure for decommissioning an individual system was to close the hydrogen sulphide valve, to close the butterfly valve and to open the nitrogen valves. Once the flame on the flare was extinguished, the nitrogen purge was changed to a steam purge, via a valve. Before starting to turn the spectacle blind, the vessels were pumped out and drained. It had been recognised that some hydrocarbon sludge deposits would remain in the knock out vessel. Since the steam purge gave problems to the fitters changing the spectacle blind, it was replaced by a nitrogen purge about an hour before the work started.
Work proceeded to the point at which the spectacle blind had been removed and there was a space of approximately 50 mm between the flanges of the 900 mm line into the knock out vessel. At this stage there was a rumble in the pipe system followed by an emission of gas and soot from the open joint. Nothing further was heard and it was decided to insert the isolating blank and bolt up as quickly as possible. While this was being done a second rumble occurred followed by a loud explosion with a violent expansion of gases through the joint, which was in the process of being bolted up. The force of the explosion blew one of the men, who was directly in line with the flange, over the platform guard-rails to the ground 8 metres below. He subsequently died from his injuries.
The reasons for the explosion were concluded to be:
1. Steam at 13 tonnes/day had been entering the system for about 16 hours. It had been replaced by nitrogen, approximately two hours before the incident. Calculations showed that nitrogen at a rate of 40 tonnes/day would have been required to replace this quantity of condensing steam. However, only 10 tonnes/day was available, so in order to re-establish equilibrium, air would have been sucked in via the flare stack.
2. This air mixed with hydrocarbons accumulated in the seal vessel during steaming.
3. The flammable mixture then moved up to the top of the flare and was ignited by the pilot at the top of the stack, which was still alight.
4. The flame propagated down the flare stack and there was a pressure surge back to where the men were working.
[cleaning inadequate, fatality]

Lessons

The procedure now specifies that only nitrogen purging is to be used and that both seal vessel and knock out vessel are to be filled with water. Any hydrocarbons present are to be floated off before the line is broken, to change the spectacle blind.

7889 Date Unknown

Source : LOSS PREVENTION BULLETIN, 090, 5-7.
Location : ,

Injured : 0 **Dead :** 0

Abstract

An organic salt was prepared by a several stage synthesis on a pilot plant and centrifuged. After acetone and water washing the resulting cake was separated.
A 600 litre ss vessel equipped with steam/water jacket, 3 fixed baffles, a turbine mixer and an extraction system was charged with water. With the mixer on, 46 kg of polyacrylic acid was added and the mixture heated to 70 degrees C. The salt was added manually over a period of 20 minutes. When the temperature was then raised to 80 degrees C, bubbles were observed on the liquid surface so the heating was switched off and 6 kg of cold water was added.
When a solution of sodium sulphate was introduced the reaction erupted violently with 2/3 of the contents boiling over.
Fortunately, the operators managed to step clear.
One hypothesis was that the accident resulted from the presence of acetone. Worst case calculations based on analysis of the cake suggested that the acetone content would produce a mixture of b.pt of 85 degrees C, i.e. in excess of the process temperature . Furthermore, laboratory experiments on the cake failed to reproduce a boilover. The favoured theory was that the cause could be attributed to the inadvertent use of sodium carbonate rather than sodium sulphate, a hypothesis sustained by laboratory trials.
[chemicals added incorrectly, reactors and reaction equipment]

Lessons

[None Reported]

7838 Date Unknown

Source : MANAGING FOR SAFETY, ICHEME, TRAINING PACKAGES, 017, 4.13.
Location : ,

Injured : 0 **Dead :** 0

Abstract

Runaway exothermic reaction. A fire occurred in an electrical substation of a large chemical works. This resulted in loss of power to most of the manufacturing units and gave rise to many problems over the site. Eleven hours later during the afternoon of the same day there was an explosion in a reaction vessel, in which a reaction involving an aromatic nitro compound was being carried out. A secondary explosion and subsequent fires were the result of a release of flammable vapours from the reactor. There were no serious injuries. Property and consequential losses were very high.
[fire - consequence, runaway reaction, power supply failure, fire - consequence, processing]

Lessons

[None Reported]

7939 Date Unknown

Source : ICHEME
Location : ,

Injured : 1 **Dead :** 0

Abstract

A contractor was employed to increase the size of the vent on an overhead tank from 25mm to 65mm diameter. The tank had previously contained kerosene and prior to the work commencing the sub-contractor, to whom the job was given, had attempted to steam-clean the tank for about an hour using a small portable steam generator.
When the man commenced work on the tank using an oxy/acetylene cutter there was an explosion which blew both ends out of the tank and caused it to be dislodged from its stand. The fitter was thrown off and suffered a suspected fractured skull, two broken arms and a broken leg.
Subsequent to the incident it was found that the sub-contractor had not removed all the fittings from the tank while attempting to steam it out and also he had not brought a flammable vapour detector to the site.
A permit to work system was not in force and although there had been some discussion about working methods, a misunderstanding appears to have arisen about exactly how the cleaning was to be carried out. In fact the steaming equipment was totally inadequate to clean the tank properly and the fact that there was no manhole through which the tank could have been visually inspected compounded the problem. In this situation a flammable vapour detector would have been of very limited use anyway.
A safer way would have been to fill the tank with water, if this were possible, although disposal of the contaminated water may have been difficult.
[hot work, cleaning inadequate]

Lessons

This incident highlights the need for careful selection of contractors, proper control of sub-contracted work and the further need for a permit to work system whereby experienced and knowledgeable personnel can decide on an appropriate and safe method of work.

7971 Date Unknown

Source : ICHEME
Location : ,
Injured : 0 **Dead :** 0

Abstract

A serious release of LPG gas occurred on an HF (hydrogen fluoride) Alkylation Unit in a refinery.
The gas was released over a period of one and a half hours and required the attendance of the refinery and local authority fire services. Fortunately the gas cloud did not ignite. There were no injuries to personnel inside or outside the refinery.
An investigation into the incident concluded that the LPG gas had been released from a hole caused by excessive localised internal corrosion of the outlet pipework of one of the two parallel isobutane recycle heat exchangers. A build up of iron fluoride deposits over a period of time in the outlet pipework had set up an environment which had allowed rapid localised corrosion to take place which had not been identified as a problem.
The investigation highlighted several factors which were believed to have contributed to the incident:
1. Inadequate engineering design and installation features that encouraged the build up of iron fluoride deposits, i.e.
2. The exchangers were designed to operate with shells in parallel and with an extremely low pressure drop (0.01 bar) which encouraged the deposition of sludge deposits in the shell sides of the exchanger.
3. The exchanger outlet pipework being the low point on the recycle loop encouraged the collection of deposits from the process stream.
4. Operating techniques and practices adopted following several start up and shut down situations, during previous months, had dislodged scale and corrosion products which accumulated in the recycle exchanger outlet pipework.
5. The corrosion inspection programme in force was not sufficiently comprehensive in that it failed to identify the area of severe localised corrosion.
[design inadequate, installation inadequate, solids deposition, inspection inadequate, gas / vapour release, refining]

Lessons

[None Reported]

8784 Date Unknown

Source : STATESIR W.A, EXPLOSIVE REACTIVITY OF ORGANICS AND CHLORINE, LOSS PREVENTION VOL 7, AICHE, 1973, 114-120.
Location : ,

Injured : 4 **Dead :** 0

Abstract

A filter in liquid chlorine service violently exploded and propelled shrapnel up to 50 feet away. About 160 lb of chlorine were released to the atmosphere, exposing four employees to chlorine fumes.
Liquid chlorine was to be fed from a ton cylinder through a polypropylene cartridge type filter at ambient temperature to a positive displacement pump, and then through a steam-heated vaporizer to a process. Prior to the explosion, new polypropylene filter elements had been installed. At 2.30pm the filter exploded releasing a white cloud (probably HCl) followed by a large evolution of chlorine gas. Steel shrapnel from the exploding filter case caused varying degrees of damage to nearby equipment and building facilities. Chlorine was shut off at the ton cylinder by two men wearing breathing apparatus. Inspection of the area revealed significant amounts of carbon residue on the pieces of shrapnel and on the concrete floor in the nearby vicinity of the filter.
[gas / vapour release, processing, runaway reaction]

Lessons

The following conclusions were drawn and recommendations made:
1. In the opinion of the explosion experts who examined the pieces of shrapnel and evidence of carbon, the explosion was determined to have been a high level deflagration, not a detonation.
2. The explosion may have developed up to 10,000 lb/sq in. in order to cause rupture to the filter.
3. The explosion was a result of a runaway chemical reaction between chlorine and the polypropylene filter element. The reaction was probably initiated by Zinc Chloride. Analysis of the filter core indicated a high concentration of Zinc Oxide present as a filler in the polypropylene which had apparently chlorinated to Zinc Chloride. Furthermore the polypropylene was found to contain traces of many other metal elements which could have contributed to catalyzing the explosive reaction.
4. Chlorine feed system materials of construction to be restricted to steel, stainless steel, nickel alloy, polymerised tetrafluoroethylene and glass. Chlorinatable organics, including partially chlorinated hydrocarbons and moat polymers, must not be used for chlorine service.
5. Although the single diaphragm positive displacement pump was determined to be in proper operating condition and did not contribute to the cause of the incident, the investigation revealed that a double diaphragm pump with an inert fluid between the process and the oil to be specified for this system to prevent possible reaction of chlorine with the hydrocarbon oil used in the pump.

8947 Date Unknown

Source : CHEMICAL HAZARDS IN INDUSTRY, 1997, JUL.

Location : ,

Injured : 0 **Dead :** 0

Abstract

A fire in a first stage pygas (pyrolysis gasoline) hydrogenation of a naphtha cracker was caused by escape of a mixture of gasoline, hydrogen and nickel catalyst through a crack in the wall of the reactor. Investigation showed that the crack was caused by a brief local temperature excursion, explained by a local disturbance and heat removal, attributed to a runaway reaction during the start-up (7 days previously) initiated by sudden increase in fresh feed added to the reactor. Excessive formation of carbon-like products impeded the liquid distribution.
[fire - consequence, leak, reactors and reaction equipment]

Lessons

[None Reported]

9485 Date Unknown

Source : ICHEME
Location : , UK

Injured : 1 **Dead :** 0

Abstract

Maintenance work was being carried out in the top of a furnace using pneumatic tools supplied by an air hose. The end of the hose blew off the coupling and struck the chargehand. The hose had been serviced to the coupling by means of a crimped brass ring. This ring when examined by the works metallurgist appeared to have failed due to stress corrosion cracking due to contact with ammonium salts.
It is likely that the hose had been used in a building where di-ammonium phosphate or ammonium sulphate was used.
[tools & access equipment, incorrect material of construction]

Lessons

The crimped rings used to secure the air hose to couplings should be made from a material which is unlikely to be present.
Austenitic stainless steel would probably be the most suitable material in this case.

9654 Date Unknown

Source : LOSS PREVENTION IN THE PROCESS INDUSTRIES, F. LEES.

Location : ,

Injured : 0 **Dead :** 0

Abstract

Cold liquid was pumped into a storage tank containing hot liquid. The liquid in the tank was cooled, the vapour pressure fell and the tank collapsed inwards.
[storage tanks, thermite reaction]

Lessons

[None Reported]

9661 Date Unknown

Source : LOSS PREVENTION IN THE PROCESS INDUSTRIES, F. LEES.

Location : ,

Injured : 0 **Dead :** 0

Abstract

Pressure relief on a low pressure refrigerated ethylene tank was provided by a relief valve set at about 1.5psig and discharging to a vent stack. When the design had been completed, it was realised that if the wind speed was low, cold gas coming out of the stack would drift down and might then ignite. The stack would drift down and might then ignite. The stack was not strong enough to be extended and was too low to use as a flare stack. It was suggested that steam be put up the stack to disperse the cold vapour and this suggestion was adopted. The result was that condensate running down the stack met cold vapour flowing up, frozen and completely blocked the 8 inch pipe. The tank was overpressured and it burst. Fortunately the rupture was a small one, the ethylene leak did not ignite and was dispersed with steam while the tank was emptied.
[design or procedure error, thermite reaction, overpressurisation, gas / vapour release]

Lessons

[None Reported]

10023Date Unknown

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 2

Abstract

In order to replace the gasket of a road vehicle tank manhole, the driver and a mechanic were attempting to remove the manhole cover. Considerable force, which may have involved a hammer, was apparently applied to loosen one of the retaining bolts. At this moment an explosion took place inside the tank compartment which killed both men, destroyed the vehicle, extensively damaged the workshop and shattered windows in nearby offices. Apparently the tank, which had previously carried gasoline, had not been cleaned or gas freed since no 'hot' work was to be done.
[cleaning inadequate, friction spark, gasoline, road tanker, operation omitted, explosion, fatality]

Lessons

This incident was unusual as research has shown that the hand held tools used were not capable of creating an incendive spark when impacting steel. However, it is possible that there may have been a chip of silica or some other hard material such as flint embedded in the head of the hammer which caused the friction spark.
Vehicles to be gas freed before any maintenance is carried out on the tank involving the use of major force.

10179Date Unknown

Source : ICHEME
Location : ,

Injured : 0 **Dead :** 0

Abstract

A rail tanker used for the transportation of dibromoethane (DBE) was being cleaned in preparation for inspection and maintenance. The tank was emptied via a dip leg, which left a small 'heel' of DBE in the bottom of the tank. The vessel was then partially filled with water, and a steam lance inserted through an open manhole to heat the water to boiling.
After several hours, the tank contents erupted discharging a column of boiling water 6 to 8 feet high into the air. Nobody was injured and the tank was undamaged.
[dibromoethane, water, cleaning, rail tanker, explosion, accidental mixing]

Lessons

DBE is a dense liquid immiscible with water and which has a significant vapour pressure at 100 degrees C. It is likely that the steam lance was only inserted into the water layer and only an upper water layer was heated whilst the lower DBE remained relatively cool and undisturbed. As the water was heated, boiling eventually occurred at the DBE/water interface resulting in instability. When the DBE mixed with the heated upper water layer, the temperature of the water was then such that the combination of the vapour pressures of the water and DBE exceeded atmospheric and violent boiling ensued.
It has been recommended that:

1. Where possible, no heel of heavy organic material should be left in such vessels
2. Ensure that steam is injected at the bottom of the vessel and into the lower organic layer so that there is proper mixing and uniform heating of any possible two-phase system.

10327Date Unknown

Source : SEDGWICK, LOSS CONTROL NEWSLETTER, 1991, PAGE 8-9.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A runaway reaction occurred in a small shell and tube heat exchanger upstream in the hydrogen methanator reactor associated with an ethylene unit. This resulted in the rupture of the exchanger shell.
The incident occurred about one week after initial start-up with the operation still being debugged. With no warning, the exchanger shell ruptured, releasing gas at 450 psig with ignited. The methanator trip system was initiated manually which successfully isolated and depressurised the equipment involved. Flames initially estimated at about 30 feet high, died to 3 feet within 5 minutes. The equipment was finally isolated manually and the fire put out. There were no injuries and damage was limited to the exchanger and some minor overhead cable trays.
An investigation revealed that level instrumentation malfunctioned on an upstream separator drum and allowed ethylene-rich liquid into the hydrogen vapour stream, despite there being three separator level instruments shared a common impulse line and liquid accumulation had created a false reading in all instruments. Modification and procedures were implemented to resolve the problems.
Although the separator overfilled the exothermic reaction would not have been expected
[reactors and reaction equipment, gas / vapour release, fire - consequence]

Lessons

This incident indicates an accumulation of rust is capable of catalysing ethylene and possible other exothermic hydrogenation reactions. These reactions have the potential for high-temperature excursions at locations not anticipated in the design and thereby instigating a failure.
Not only should this potential be evaluated in the design and start-up preparations of new plant but also precautions should be taken in the restart of significant accumulation of rust.
The incident also clearly demonstrates:
1. The need for redundancy and diversity in critical instrument design.
2. The value of trip systems that automatically isolated and depressure sections of plant.

7729 Date Unknown

Source : LEARNING FROM ACCIDENTS, ICHEME, SAFETY TRAINING PACKAGE, 020, 43.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A tray drying oven, of type commonly used in the pharmaceutical and fine chemicals industries, was used to evaporate methanol from a crystalline powder which was spread out in a number of trays in the oven. The oven was heated by drawing hot air through it by means of an induced draught fan. The air was heated by passing it over a number of steam heated finned tube heat exchangers which comprised one side of the oven. These were not, however, visible, being covered with a steel sheet which formed the outer wall of the oven. The heated air had two purposes, (a) to provide latent heat of evaporation of the methanol and (b) to dilute the methanol vapour to a safe concentration, below the lower flammable limit. The oven had been operated safely for a number of years, but one day it blew up unexpectedly and caused serious damage to the process building.
Examination of the oven and associated equipment revealed that, over a long period of time, various chemical powders had been drawn on to, and accumulated on, the fins of the heat exchangers. This deposit had built up and hardened and had virtually completely blocked the spaces between the fins. This caused,
1. The total air flow through the oven to be diminished until it was no longer sufficient to dilute the methanol vapour to a safe level and
2. The solid deposits prevented heat from leaving, gradually heating up the deposits, leading to decomposition, smouldering and eventually fire, thus igniting the methanol vapour. The explosion then occurred.
[solids deposition, cleaning inadequate, solids deposition]

Lessons

The finned tube heat exchangers were inside the structure of the oven and not easily visible. The vital dismantling and cleaning had apparently not been carried out for a considerable period of time.

7796 Date Unknown

Source : BARTON J AND ROGERS R, CHEMICAL REACTION HAZARDS, 2ND EDITION, ICHEME, 1997, APPENDIX 1, 184.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A reactor erupted during the oxidation of 2-methyl-2-prentenal with sodium dichromate to produce 2-methyl-2-pentenoic acid. The process consisted of first pumping acetic acid into the reactor followed by the addition of all the solid sodium dichromate. The temperature of the contents was raised to 323 K and then the 2-methyl-2-pentenal was added over about half and hour, applying a partial vacuum and sucking in the aldehyde. There was no flow meter. The normal operator went for a break after starting a batch, handing over control of the process to an operator who was working on an adjacent plant. Excessive fumes were noticed and part of the plant shattered. It was concluded that the aldehyde must have been added too quickly into the oxidising mixture in the reactor and that the cooling provided was unable to prevent a runaway reaction.
[batch reaction, charging reactor, reactors and reaction equipment, rupture]

Lessons

[None Reported]

7747 Date Unknown

Source : BARTON J AND ROGERS R, CHEMICAL REACTION HAZARDS, 2ND EDITION, ICHEME, 1997, APPENDIX 1, 163.

Location : ,

Injured : 0 **Dead :** 0

Abstract

The first stage of the synthesis of the ketone p-nitroacetophenone had been carried out a number of times when it was noticed that some of the catalyst from each charge was remaining behind, stuck to the walls of the reactor. This build-up was considered unimportant because it was felt that the catalyst would quickly become inactivated. However, an incident occurred in the form of an instantaneous, uncontrollable runaway reaction. The reactor was pressurised beyond the capacity of its safety valve.

[reactors and reaction equipment]

Lessons

[None Reported]

7767 Date Unknown

Source : BARTON J AND ROGERS R, CHEMICAL REACTION HAZARDS, 2ND EDITION, ICHEME, 1997, APPENDIX 1, 166.

Location : ,

Injured : 0 **Dead :** 0

Abstract

A series of exotherms occurred in the production of anisylacetate from the addition of acetic anhydride to anisyl alcohol. An investigation revealed that traces of sulphuric acid were present in the mixture. The acid had come from the weighing tank, that is, acid was weighed just before the anhydride. It was later found that sulphuric acid catalysed an exothermic polymerisation.
[contamination]

Lessons

[None Reported]

7776 Date Unknown

Source : BARTON J AND ROGERS R, CHEMICAL REACTION HAZARDS, 2ND EDITION, ICHEME, 1997, APPENDIX 1, 178.
Location : ,

Injured : 0 **Dead :** 0

Abstract

The non-flammable plasticiser trichlorethylphosphate was manufactured in a stirred, water cooled, lead-lined reactor by admitting phosphorus oxychloride, with 1% aluminium chloride as a catalyst in a continuous stream in liquid form. Ethylene oxide was admitted in the vapour phase and the reaction rate was governed by the rate at which ethylene oxide was absorbed by the charge. On one occasion, the temperature within the reactor was allowed to fall too low. This reduced the reaction rate whilst increasing the rate of absorption of the ethylene oxide, the net effect being to produce a substantial quantity of unreacted mixture. When the reaction recommenced a runaway occurred. The relief valve could not cope and ethylene oxide vapour escaped and found an ignition source.
[runaway reaction, low temperature, gas / vapour release, reactors and reaction equipment, continuous reaction]

Lessons

[None Reported]

7779 Date Unknown

Source : BARTON J AND ROGERS R, CHEMICAL REACTION HAZARDS, 2ND EDITION, ICHEME, 1997, APPENDIX 1, 179.

Location : ,

Injured : 4 **Dead :** 0

Abstract

An explosion occurred in a 1250 litre stainless reaction vessel, used for the distillation of crude o-nitrobenzaldehyde (ONBALD). The main pilot plant laboratory was completely destroyed and four shift workers leaving the building caught the blast.
The explosion occurred due to the convergence of several events, a dangerous material (o-nitribenzylnitrate) developed whilst the ONBALD was left in store (the drums of ONBALD had been stored for eight months), the use of different test tubes in the thermal stability test actually invalidated the test results, when the runaway did occur, the temperature set point of the automatic quench system was too high and manual override did not work.
[runaway reaction, laboratory work]

Lessons

[None Reported]

7781 Date Unknown

Source : BARTON J AND ROGERS R, CHEMICAL REACTION HAZARDS, 2ND EDITION, ICHEME, 1997, APPENDIX 1, 180.

Location : ,

Injured : 0 **Dead :** 0

Abstract

Organic material was introduced accidentally to a stirred reaction vessel mixing nitric acid and sulphuric acid. There was a violent explosion with extensive off site damage.
[accidental mixing, incorrect chemical present, damage to equipment]

Lessons

[None Reported]

7783 Date Unknown

Source : BARTON J AND ROGERS R, CHEMICAL REACTION HAZARDS, 2ND EDITION, ICHEME, 1997, APPENDIX 1, 181.

Location : ,

Injured : 0 **Dead :** 0

Abstract

In the manufacture of an alkyd resin, 2.5 m3 of linseed oil and 367 kg of soya oil were charged into a reactor and heated to 423 K. 525 kg of trimethylol propane was added and the mix heated to 503 K, when 0.4 kg of lithium acetate was added and the mix heated to 503 K. When the reaction was complete 775 kg isophthalic acid and 8.5 kg of triphenylphosphite were added and the mixture heated to 533 K until the further reaction was complete. The product was then cooled. The whole reaction sequence was carried out under a blanket of carbon dioxide. On the day of the incident, the reaction had been completed in half the normal time, however, no significance was attached to this fact. The temperature of the mix continued to rise, full cooling water flow was applied and the mix diluted with linseed oil when it reached 553 K. At this point, the mix erupted out of the unbolted chargehole cover, ignited and a large fire occurred. The investigation revealed that insufficient linseed oil had been charged initially, the gross concentration imbalance giving rise to a highly exothermic polymerisation reaction.

[charging reactor, exothermic reaction, reactors and reaction equipment, chemicals added incorrectly]

Lessons

[None Reported]

7787 Date Unknown

Source : BARTON J AND ROGERS R, CHEMICAL REACTION HAZARDS, 2ND EDITION, ICHEME, 1997, APPENDIX 1, 182.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A runaway exotherm occurred because of gross misproportionation of reactants, an aniline stock tank had not been drained of water and the aniline fed to the reactor consisted largely of water. The 25 mm thick top of the reactor was shattered, the stirrer was ejected and a hole was blown in the roof of the building. Fortunately there were no injuries.
[runaway reaction, chemicals added incorrectly, rupture, reactors and reaction equipment]

Lessons

[None Reported]

7788 Date Unknown

Source : BARTON J AND ROGERS R, CHEMICAL REACTION HAZARDS, 2ND EDITION, ICHEME, 1997, APPENDIX 1, 182.
Location : ,

Injured : 1 **Dead :** 0

Abstract

Dimethylamine was pumped into a weight tank containing epichlorohydrin because of confusion with the colours of drums. A violent exotherm in the weight tank blew the bottom off and propelled the tank up to the roof of the building. On falling it struck a maintenance engineer, a fire occurred.
[chemicals added incorrectly, rupture, material transfer]

Lessons

[None Reported]

7789 Date Unknown

Source : BARTON J AND ROGERS R, CHEMICAL REACTION HAZARDS, 2ND EDITION, ICHEME, 1997, APPENDIX 1, 182.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A large release of solvent through the condenser of a reactor occurred due to a runaway exothermic reaction resulting from mischarging of two reactants. A massive explosion followed. The quantities of reactants should have been 17.5 and 155 gallons, but these quantities were transposed in error. A poor process instruction sheet may have contributed to the error. The operator was not clear what to do when the reactor temperature rise was noted.
[runaway reaction, charging reactor, document errors, reactors and reaction equipment]

Lessons

[None Reported]

7836 Date Unknown

Source : MANAGING FOR SAFETY, ICHEME, TRAINING PACKAGES, 017, 4.5.

Location : ,

Injured : 0 **Dead :** 0

Abstract

Runaway reaction in a polymerisation reactor resulting with a rupture of a water settler drum.
A polymerisation plant was running with reduced capacity because of difficulties to remove the heat of reaction via the reactor cooling system. The refrigeration compressor was running flat out and the operations management team, who had never experienced this severe cooling problem before, decided to take action. They had been ensured that the limitation was the poor heat transfer in the pump around the exchanger, due to fouling polymer deposits.
The plan was to empty the reactor, shut down the refrigeration compressor and fill the reactor with pure olefinic reactant (C-4 olefins). It was believed that the warm olefin product would dissolve the polymer deposits while being circulated through the reactor cooling system and the plant could then be quickly restarted.
After the olefinic reaction reactant had been circulating for a while, the pressure in the reactor rose quickly. The emergency high pressure alarm when off and the safety valve started to blow into a closed blow down system. The pressure recorder in the control centre went off scale and outside a loud noise was heard.
The emergency drill was initiated and response teams set up a water curtain to disperse the C-4 hydrocarbon vapour cloud.
No further consequences resulted from the incident as the drum was isolated from the flare.
[reactors and reaction equipment]

Lessons

The following recommendations were made:
1. Plant and technology groups should be involved prior to establishing new process conditions to ensure that known process hazards are dealt with.
2. Any process modification must undergo a formal, systematic and critical hazard assessment study. Plant management should be made aware of the main hazards of new operations.
3. Plant documentation needs to be updated and operator training should be carried out prior to modification implementation.
4. Release rates of plant safety valves should always be kept updated when the process conditions are changing.
5. Safety valve collection system capacity should always be kept updated when process conditions are changing.
6. Safety valve collection system capacity should be reviewed on a frequent basis (biannually).
7. A formal proof testing programme should be established for all safety critical instruments. The proof testing must be recorded. Frequencies of the proof testing intervals should be adjusted based on the results of the proof test.
8. Management systems and organisational structures should be implemented to ensure that the above recommendations are implemented and become a plant culture.

7803 Date Unknown

Source : BARTON J AND ROGERS R, CHEMICAL REACTION HAZARDS, 2ND EDITION, ICHEME, 1997, APPENDIX 1, 185.

Location : ,

Injured : 0 **Dead :** 0

Abstract

A malfunction on a heating oil cut-out caused overheating of a resin reactor and runaway. Flanges and joints failed and the plant area was covered in polymer. An emergency relief venting system was provided but the bursting discs were mounted wrongly.

[runaway reaction, flange failure, joint failure, installation inadequate, spill, reactors and reaction equipment]

Lessons

[None Reported]

7812 Date Unknown

Source : BARTON J AND ROGERS R, CHEMICAL REACTION HAZARDS, 2ND EDITION, ICHEME, 1997, APPENDIX 1, 187.

Location : ,

Injured : 0 **Dead :** 0

Abstract

A runaway reaction vented safely but there was no catchpot and a noxious yellow substance was deposited over an extensive area. The water charge had been omitted from the batch and the practice of dipping the reactor at each stage of charging had fallen into disuse, the process instructions were not being followed.
[spill, charging reactor, chemicals added incorrectly, reactors and reaction equipment]

Lessons

[None Reported]

7813 Date Unknown

Source : BARTON J AND ROGERS R, CHEMICAL REACTION HAZARDS, 2ND EDITION, ICHEME, 1997, APPENDIX 1, 187.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A resin based on rosin was manufactured by an en masse reaction. Only a small exotherm was involved. In an attempt to keep the product mobile for ease of transfer and handling, the reactor was heated above the unknown autoignition temperature of the flammable vapours in the ullage space. Autoignition occurred, there was an explosion and a fire.
[fire - consequence, reactors and reaction equipment]

Lessons

[None Reported]

7814 Date Unknown

Source : BARTON J AND ROGERS R, CHEMICAL REACTION HAZARDS, 2ND EDITION, ICHEME, 1997, APPENDIX 1, 188.
Location : ,

Injured : 15 **Dead :** 1

Abstract

Styrene a peroxide catalyst were held in a preheater vessel for a considerable time. Polymerisation occurred and released flammable vapours into the workroom, which ignited and exploded. One person was killed by falling masonry and 15 others were injured by flying debris. Fatality.
[reaction vessel, gas / vapour release, explosion, injury]

Lessons

[None Reported]

7815 Date Unknown

Source : BARTON J AND ROGERS R, CHEMICAL REACTION HAZARDS, 2ND EDITION, ICHEME, 1997, APPENDIX 1, 188.

Location : ,

Injured : 0 **Dead :** 0

Abstract

A reaction was slow, so extra catalyst was added. A vigorous reaction ensued. Flammable vapours, released through the loose chargehole cover, ignited.
[fire - consequence, chemicals added incorrectly, reactors and reaction equipment]

Lessons

[None Reported]

7819 Date Unknown

Source : BARTON J AND ROGERS R, CHEMICAL REACTION HAZARDS, 2ND EDITION, ICHEME, 1997, APPENDIX 1, 189.
Location : ,

Injured : 0 **Dead :** 0

Abstract

In the manufacture of polyurethane prepolymer, toluene diisocyanate (TDI) at 293 K was charged into an 8 tonne reactor at night. The following day 1700 kg of polyol was added over 20 minutes and the temperature rose to and was maintained at about 400 K to complete the preparation. On the occasion of the incident the reagents had been added and the temperature maintained at 403 K but after 35 minutes the temperature increased to 443 K. The stirrer stopped working and could not be restarted. The temperature rose to 473 K and the pressure rose to 3.4 bar g. The reactor ejected its batch.
The TDI being used was from a new supplier. Benzoyl chloride was added to the TDI by the old supplier as a reaction moderator. The new supplier did not add the moderator and hence it should have been added during the formulation of the pre-polymer. The absence of the moderator led to a runaway exothermic reaction in which solidification of the product caused agitator failure and gases formed causing the pressure and failure of the reactor.
[charging reactor, agitation failure, chemical missing, reactors and reaction equipment, rupture, runaway reaction]

Lessons

[None Reported]

7822 Date Unknown

Source : BARTON J AND ROGERS R, CHEMICAL REACTION HAZARDS, 2ND EDITION, ICHEME, 1997, APPENDIX 1, 190.
Location : ,

Injured : 0 **Dead :** 0

Abstract

A production plant had always received from the warehouse benzyl chloride which the supplier had stabilised with aqueous caustic soda. After an interruption of 3 months, 270 kg of benzyl chloride were to be separated as usual from the caustic soda in a 1 m3 glass lined reaction vessel. The operator had sucked the benzyl chloride into the vessel and opened the vessel ventilation line. Immediately, the benzyl chloride started to polymerise with formation of fumes and hydrochloric acid. The valve in the ventilation line was closed but the safety valve lifted. The temperature in the vessel rose to 328 K. An investigation showed that the benzyl chloride charged to the vessel had no longer been stabilised by the supplier but had been delivered in drums with polypropylene liners. The benzyl chloride, when charged to the vessel, was already acidified by hydrochloric acid (moisture, leaky polypropylene liner). It is believed that when the ventilation line was opened, rust or iron particles could have entered the vessel and formed the metal chloride which acted as a catalyst. Polymerisation started and caused the incident. A defect in the glass lining of the vessel could have led to the same incident.
[spill, gas / vapour release]

Lessons

[None Reported]

7828 Date Unknown

Source : BARTON J AND ROGERS R, CHEMICAL REACTION HAZARDS, 2ND EDITION, ICHEME, 1997, APPENDIX 1, 192.
Location : ,

Injured : 0 **Dead :** 0

Abstract

An exotherm occurred during the production of an alkyd resin in a 5 tonne reactor. The contents spilled out of the chargehole and ignited. Inadvertent polymerisation occurred due to a gross imbalance of reactants. It is likely that an insufficient amount of one reactant was added due to a metering fault. The operator in charge did not know what to do when he saw the temperature rising, and a more experienced operator did not recognise the fact that the reaction was proceeding much faster than normal was a matter for concern.
[chemicals added incorrectly, fire - consequence, training inadequate, instrumentation failure, reactors and reaction equipment]

Lessons

[None Reported]

7829 Date Unknown

Source : BARTON J AND ROGERS R, CHEMICAL REACTION HAZARDS, 2ND EDITION, ICHEME, 1997, APPENDIX 1, 192.
Location : ,

Injured : 0 **Dead :** 8

Abstract

A chlorinator exploded. The accident occurred in the chlorination step during methyl parathion production. The temperature was controlled automatically, on this occasion, however, the thermocouple output was very low. A leak in the thermowell was discovered and an instrument mechanic was called to carry out repairs. Chlorine was added faster than normal due to the fault. The agitator and brine cooling were stopped while the faulty thermowell was being replaced. [cooling equipment, explosion, temperature meter/control, instrumentation failure, chemicals added incorrectly, fatality]

Lessons

[None Reported]

7833 Date Unknown

Source : BARTON J AND ROGERS R, CHEMICAL REACTION HAZARDS, 2ND EDITION, ICHEME, 1997, APPENDIX 1, 193.

Location : ,

Injured : 0 **Dead :** 0

Abstract

During vacuum distillation an exothermic decomposition of dimethyl sulphoxide (DMSO) occurred, blowing the chargehole cover off the reaction vessel. The flammable contents released and ignited causing a second explosion which extensively damaged the building. The still had been shut-down to attend to a minor leak but the steam heating had been left on in error. The contents of the still were contaminated by accumulation residues from previous batches and the poor cleaning of the plant catalysed the exothermic decomposition of DMSO. The vessel had not vent.

[cleaning inadequate, design inadequate]

Lessons

[None Reported]