Chemical fumes were released during a mixing process in a vat whilst making an epoxy product. The building and nearby businesses were evacuated. Four people were injured in the incident.

Lessons

[None Reported]
A fire and explosion occurred three days after an explosion that injured two people. Three workers suffered serious burns. The incident occurred, as workers were mixing chemicals in a large vat. The force of the explosion blew out a cement wall and caused a fire, which was quickly extinguished. Damage is estimated at more than $1 million (2000). It is thought that sparks from a passing forlift truck triggered the explosion.

[fire - consequence, unknown chemicals, injury]

Lessons

[None Reported]
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.

Lessons
[None Reported]
A fire occurred during start-up of a cold section of a gas-cracker with imported ethylene causing deep cracks to appear in the top 25 m of an ethylene cracker.

Lessons
[None Reported]
Abstract
Three explosions occurred at a chemical plant, which caused a natural gas leak and blew out a cloud of sodium hydroxide and bauxite ore, a caustic chemical from which aluminium is obtained, into the air.
The explosion occurred in a part of the plant where electricity is generated and where the bauxite ore and liquid sodium hydroxide are mixed. Twenty-one workers were injured in the blast, two critically. Injuries ranged from severe burns, breathing difficulties and eye irritation. Nearby residents were also treated for nausea and respiratory problems.
An investigation into the incident found that the cause was due to power failure at the plant. The power to a vat holding chemicals failed. The material was supposed to move from the vat to another part of the plant, but the pressure built up after pumps failed, causing the explosion that destroyed approximately 25 percent of the plant.
The company was fined $533,000 (2000).

Lessons
[None Reported]
Abstract
A fire occurred on a unit making kerosene and gas oil at a refinery. The hydrocracker where the fire occurred used fuel oil to make middle distillates and had a desulphuriser which made low sulphur fuel oil. The fire was brought under control within two hours.
At least three people were injured.
At the time of the incident the refinery was operating normally.
[fire - consequence, processing, injury]

Lessons
[None Reported]
An explosion and fire occurred on a hydrocracker unit at a refinery. There were no injuries and the fire was controlled within two hours.

Lessons

[None Reported]
An explosion occurred on a hydrocracking unit at a refinery sending towering flames and thick black smoke billowing into the atmosphere. The explosion occurred in the isomax unit, which processes heavy fuels into gasoline and jet fuel. Nearby residents were warned to stay inside their homes as fire fighters struggled to control the fire.

Lessons

[None Reported]
Source: IChemE
Location: , GERMANY
Injured: 0  Dead: 0

Abstract
During the filling out of paint an explosion occurred in a mixing vessel. No one was injured and no environmental damage occurred. The mixing vessel was damaged though.

[mixer, damage to equipment, near miss]

Lessons
[None Reported]
Abstract

A second plug inserted into a "U" tube reactor blew out while the shell side of the Alkylation Unit's "Exchanger/Reactor" was pressurised with nitrogen at 50 psi to detect leaking tubes. The plug blew out as the craftsmen were about to drive it in, spraying a mist of liquid on to the face shield of one of the craftsmen. The reactor had been prepared in accordance with the procedure to test for leaking tubes. The reactor had been blocked in, depressurised and drained. The shell side had been caustic washed to neutralize any alkylation acid and the reactor was blinded off from the acid settler. When the front cover plate was removed, some residual liquid was found in the bottom of the channel head and fire water was used to flush the channel head and tube sheet area. Dry nitrogen at 50 psig was then used to pressure up the shell side of the exchanger in order to find the leaking tubes. As this is a "U" tube bundle, the bottom leaking tube is usually found to dribble liquid out with the nitrogen. When a plug is driven in this end, then the top end of the leaking tube has to be found by detecting the escape of nitrogen. The top plug was put in place with the nitrogen pressure still applied on the shell side and tapped into place. The craftsmen were then preparing to drive the plug in completely when it blew out, spraying a mist of liquid on to the face shield of one of the craftsmen.

There is no written maintenance procedure specifically for repairing a leaking "U" tube in the reactors at Alkylation Unit. There is a Job Aid for repairing a leaking exchanger tube and the most significant difference between the Job Aid and the typical practice at the Alkylation 2 is that the Job Aid calls for water to be used to fill up the shell side of the exchanger and then this is pressured up (if necessary) to detect tube leaks. The investigation team discussed this at length and agreed that the use of nitrogen for the Alkylation Unit's reactor/exchanger is acceptable and can be done safely. The Job Aid, however, does specifically call for the shell side to be depressurised and drained before tube plugs are installed. Plugging a reactor tube while there is still nitrogen pressure on the exchanger shell was not typical practice. Nitrogen is normally blocked in and allowed to depressure first. The craftsman alleges that he was directed to attempt to plug the leaking tube while nitrogen pressure was still on the shell. The technique of inserting and driving home a plug does not require the craftsmen to enter the channel head area, as he uses an extension piece to reach into the tube sheet and insert the plug. This means a confined entry permit is not required. However, to detect which tube is leaking requires the inspectors to use a portable instrument which detects the sound of a leak. To use this instrument they must climb into the channel head, following the issue of an entry permit by the safety inspector. The safety inspector had been called for a confined space entry permit, and was present when the plug blew out. He had refused to issue the confined spaced entry permit, advising the operator that the nitrogen had to be blocked out and the shell depressurised.

A safety inspector will not issue a confined space entry permit until the nitrogen is disconnected from the reactor shell. However, the corrosion inspector must have the nitrogen connected and under pressure for the instrument to "hear" the leak. Accordingly, the typical practice is for the nitrogen to be disconnected from the shell, have the shell depressurized and obtain a confined space entry permit. After this, pressurise the shell and enter the channel head area to use the instrument to detect the leak. The investigating team agreed that this was an unacceptable practice, because as soon as nitrogen is used to repressurize the shell the conditions of the confined space entry permit are invalid.

Lessons

The following recommendations were made:
1. Failure to have a detailed procedure with a task analysis and periodic observations for unusual jobs will lead to attempts to short cut normal practices.
2. Gas under pressure has a great deal of potential energy waiting to be released. Plugs under pressure whether in heat exchanger tubes or furnace tubes present a potential hazards.
3. A robust permit to work system is essential to prevent accidents.
An explosion occurred when unauthorised welding set fire to a vat of paint. A large tank of chemically polluted water also exploded.

[fire - consequence, human causes]

Lessons
[None Reported]
Abstract
Approximately 210 kgs of dope (composition approximately 27% acetate and 73% acetone) was spilt when a joint line failed. The spilt dope was recovered and put into a mixer for reuse.

Lessons
[None Reported]
Fumes were released when a leak occurred from a vat of organic solvents, resulting in the surrounding area being sealed off to traffic. The situation was brought under control within 2 hours.

Lessons

[None Reported]
Abstract
An explosion and fire occurred on a cracker causing the shut down of a 860,000 tonne/year plant for months. Damage was caused to the compressor, furnace, purification train and cooling tower.

Lessons
[None Reported]
Abstract
A night shift was converting bright dope into matt dope using a mixer by adding titanium paste. When the operator went to discharge the mixer he opened the wrong valves. The dope was discharged to old pipework which at the time was being decommissioned and had an open end. Approximately 2000 kilograms of matt dope was released. The dope was approximately 73% acetone and 27% acetate.

Lessons
[None Reported]
A fire occurred in a platinum reformer resulting from a leak of gasoline at a pump. Plant back on line within a week.

[fire - consequence, processing]

[None Reported]
Abstract
One of two catalytic crackers was damaged due to an overpressurisation incident that ruptured some piping and damaged a waste heat boiler.
[damage to equipment, cracking]

Lessons
[None Reported]
An explosion on No.3 cracker occurred during the start-up of the plant after unplanned maintenance.

Lessons

[None Reported]
Abstract
Hydrotreater recycle hydrogen line failure at a refinery.
Localised corrosion of a FCCU (Fluid Catalytic Cracking Unit) feed hydrotreater recycle hydrogen line by-pass around a hydrogen pre-heat exchanger led to an explosion and fire. The failed part of the line had been identified by inspection as a dead leg. After investigation it was found that the mechanism of corrosion was ammonium chloride under deposit corrosion. The source of chloride has not been traced, but hydrogen from the catalytic reformer was strongly suspected. Inspection inadequate of the dead leg was identified as the cause of this incident. There was damage to equipment, material loss and product loss.

Lessons
Localised corrosion mechanisms are difficult to detect with fixed point UT, and dead leg corrosion can have several different corrosion mechanisms.
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<tr>
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**Abstract**

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

**Lessons**

[None Reported]
The feed effluent exchangers of a reformer suddenly caught fire. The fire was extinguished in 5 minutes and the unit safely shut down. The precise cause of the sudden fire is not known. An estimate of the total cost of the incident is $311,000 (£177,000) (1996), including $154,000 (£88,000) (1996) in production lost and $154,000 (£88,000) (1996) for labour and materials.

The FCC1 operator reported seeing smoke in the direction of the reformer. Upon arrival of operators and supervisors to the scene, the feed effluent exchangers were fully involved in fire. The fire was extinguished within about five minutes, and the unit was safely shut down. There were no injuries as the result of this incident. Due to liquid carryover to the DHT make-up gas knock out drum, both DHT compressors were shut down. The unit operator at the time of the incident stated that he had just been in the area of the 4 exchangers, and that he had not observed leakage of products. Shortly after returning to the control room, he was informed that the exchangers were on fire. He estimated the elapsed time between walking through the area and being informed of the fire was approximately 5 minutes. He indicated that when he arrived at the scene, the most intense burning seemed to occur around the lower portion of the two stacked feed/effluent exchangers.

The immediate cause of the fire was leaking reformer reactor effluent released to atmosphere above its auto-ignition temperature from either one of the bolted channel covers, channel head flanges, ring jointed piping connection or a threaded plug in the channel head cover. The basic cause has not been determined, but seems likely to be either incorrect tightening of the heat exchanger covers, piping joints or threaded plug.

Lessons

The following corrective actions were taken:
1. Although an improper tensioning procedure was an unlikely cause, it is recommended that in the future all assemblies requiring hydraulic bolting be supervised by technical personnel familiar with the procedures including lubricated studs and extensiometer readings to assure proper bolt tightening.
2. If possible, all threaded plugs in critical or corrosive services (elevated temperature, hydrogen, hot oil service, etc.) should be replaced with welded connections. At a minimum, a thread gauge must be used to assure proper thread engagement during turnarounds.
3. Consider installation of a water deluge system over the feed/effluent exchangers.
4. Consider fireproofing of cable trays in overhead pipe racks where damage occurred.
Fatality during maintenance on Fluid Catalytic Cracker Unit (FCCU) heat exchanger.

During steaming of heat exchanger shell covers, to facilitate removal, the lower cover blew off, striking an operator. The tight fit between the shell cover and floating head restricted the path of steam flow, creating an overpressurisation. This was due to the minimum clearance between the shell cover and floating head being less than that required by design.

Lessons

When using steam for heating equipment for disassembly, a free path to vents must be available and maintained; e.g., not blocked by sludge. Personnel need to be aware of the potential force of steam, nitrogen, air, used as a maintenance aid and not build up uncontrolled pressure in equipment.
Abstract
Infringement of work permit system. During a shut-down of the high pressure hydrogenation unit to change-out catalyst, checking of and maintenance on valves in the high pressure loops was to be carried out as well. When work on the first valve had just begun, the operating authority, who happened to be passing by, stopped the work. Pressurised airline masks had been specified for removal of the valve bonnets, but the contractor supervisor had not communicated this to his crew. In addition the contractor supervisor had not posted a work permit at the work site, which was required by the permit-to-work system.

[permit to work system inadequate, near miss]

Lessons
Specifications for use of airline breathing masks when breaking lines must be complied with in order to provide protection to the individuals doing the work.
A contractor had been carrying out the work of moving catalyst drums. Upon entering the storage area, the unloaded forklift truck collided with a lamp post and knocked it down. The operator was thrown from the vehicle; but the vehicle overturned, trapping him between the safety roof and the ground. It was found that blind spots obstructed clear vision of the lamp post in the work area. The basic cause was overconfidence with regard to repetitive, routine work, without apparent risk and insufficient awareness in attitude toward safety.

Lessons
Even trained and experienced forklift truck operators have serious accidents, most likely through complacency. Emphasis must be placed on maintaining an AWARENESS of good safety practice.
Abstract
Small fire occurred in the furnace area of the catalytic reformer unit and was quickly extinguished.

Lessons
None Reported
Abstract
One of three operating crackers was shut-down following a fire and minor damage to two of the plants twelve furnaces.
[fire - consequence, damage to equipment, cracking]

Lessons
[None Reported]
Abstract
A fire broke out in a four storey catalytic cracker unit. 600 evacuated.

Lessons
[None Reported]
<table>
<thead>
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<th>Injured</th>
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**Abstract**

Incident started as a small local fire in the fluid catalytic cracker unit. Fire was attacked using a local monitor. Firewater was contaminated with gasoline which led to fire escalation.

**Lessons**

[None Reported]
Abstract
Oil leaking from a catalytic cracker led to an explosion and fire. Interruption expected to last 13 days.
[fire - consequence, cracking]

Lessons
[None Reported]
Residue hydrocracker fire. A 6 inch schedule 40, carbon steel elbow ruptured; and a fire resulted. It was found that the pipe failed due to erosion/corrosion. The cause was due to failure to apply management of change procedures to the decanted oil injection that identified erosion as a possible consequence of the decanted oil injection. No metallurgy upgrades or additional inspections were recommended as a result.

Loses $2.5 million (1995) (£1.59 million) (1995), including damage to equipment.

[fire - consequence, cracking, management system inadequate]

Lessons

The cumulative impact on the materials of construction from gradual changes in process conditions, e.g., flow rate, temperature, sulphur content, can, unfortunately, be overlooked if the threshold valves are not established to provide a base line for comparison.
Abstract
A fire occurred on a mixer handling cellulose acetate and acetone. The cellulose acetate was in the form of waste produced during the process and was being recovered by adding to the acetone prior to charging fresh flake. This requires removal of the man lids on the charging chute. It is carried out under a positive pressure of inert gas and with vapour extraction. The fire was extinguished by refitting the man-lids and suffocating it.
The waste is in bale form and passes over a wetted earth-bonded roller prior to addition via the earth-bonded chute.

[fire - consequence, mixing]

Lessons
The investigation concluded that:
1. The cause of the incident was static discharge from inadequately discharged waste and oxygen from air entrained in the waste.
2. Under the then current operating procedure, avoidance of localised pockets of flammable vapour in the mixer could not be guaranteed.
3. The systems for discharge of static electricity were inadequate.
The main recommendations were:-
1. Improve the wetting of the waste as it enters the system in the short term.
2. Investigate an automatic waste addition system in the medium term.
Abstract
Drain line failure on catalytic reformer on a refinery. During the application of a temporary clamp over a pin-hole leak, a drain line from the level switch bridle on the catalytic reformer compressor dry drum failed catastrophically. There was a gas release; but it, fortunately, did not ignite. There was damage to equipment and product loss.
It was found that the wrong type of sleeve was fitted to the line, and that excessive tensile load was applied to line during injection of compound. The basic cause was that the sleeve was not approved prior to installation as required by procedure.
The procedures did not specifically address the possibility of over stressing from hydraulic effects.
[gas / vapour release, installation inadequate]

Lessons
The task of temporary repair to pipework using the "Furmanite" injection technique is a highly technical one which requires a sophisticated level of control to avoid disasters.
Injured: 2  Dead: 0

**Abstract**
A new compressor on the isocracker unit of this refinery was destroyed by an explosion. The ensuing fire was rapidly extinguished. Damage was anticipated to require 6 months to repair although the unit was started within a month.

Lessons
[None Reported]
Abstract
Isocracker explosion at a refinery. While pressure testing discharge valves on an out-of-service reciprocating compressor, 2100 psig process pressure blew out a gasket at the blinded flange in the system. A vapour cloud was released and subsequently ignited. It was found that the temporary compressor side blank failed due to pressure above its design capability. Operations personnel conducting the pressure testing were not familiar with the pressure limitations of the blind that was in place.

Lessons
Need to ensure that correct blinding is always used to meet the maximum pressure capability of the system. Need to ensure that Operations personnel are knowledgeable of the application limitations of various blinding systems which may be used.
Explosion at the ethylene cracker which did not affect production.

Lessons
[None Reported]
Abstract
Isocracker heat exchanger flange leak at a refinery. An Isocracker Unit was shutdown due to a small pinhole leak found in the first stage feed/effluent exchanger outlet piping. After disassembly of the piping system, the flange revealed extensive cracking.
Losses including damage to equipment, product loss, and materials and labour amounted to $1.3 million (1995). It was found that chloride stress corrosion cracking caused the incident. All four criteria for chloride stress corrosion cracking were present: Material of cracked flange was austenitic type stainless steel, known to be vulnerable to chloride cracking. Flanges were overcompressed and the joints had not been hydraulically torqued during previous turnaround. Even low overall concentration of chlorides got into grooves and pits during cycling and went undetected for many years/cycles.

Lessons
Chloride stress corrosion cracking propagates during start-up and shutdown periods, even in low overall concentrations of chloride, concentrating in grooves and pits.
Injured : 1    Dead : 2

Abstract
Gas release from a pump on the catalytic cracking unit of this refinery. Fatality.
[catalytic cracker, gas / vapour release, refining]

Lessons
[None Reported]
Abstract
Reformer extended outage on a refinery. During a planned shut-down to regenerate catalyst, internal damage and a loss of catalyst containment occurred within the reactor system. It was found that the catalyst beds were disturbed and the seal at top of reactors lost allowing the catalyst to migrate out of reactors. The cause was due to the current regeneration procedure not adequately alerting personnel to problems during the regeneration process. Current data and tracking capabilities did not indicate any potential problems within the reactors.
Loss including $3.5 million (1995) and £2.1 million (1995) in lost opportunity.
[damage to equipment, product loss, reactors and reaction equipment, safety procedures inadequate]

Lessons
Procedures acceptable over many years still need review when operating parameters are changed e.g., feed rates, feed quality, and severity of operation.
Abstract
A small dust explosion occurred as naphthol powder was poured from metal container into blender. The stirrer was not working at the time of the incident. The cause of the incident is not known but is thought that an electrostatic spark may have ignited the dust. One worker suffered 10% burns and another suffered slight injuries.

Lessons
[None Reported]
A fire and explosion occurred at a facility involving water reactive materials, mixed in a blender with a water-cooled seal, in a room with other water supplies.

[fire - consequence, design or procedure error]

Lessons
[None Reported]
Abstract
A fire on one of two naphtha crackers reduced ethylene production by 40% for two weeks. The fire was brief but intense, following a release of naphtha, hydrogen and catalyst. Damage is estimated at US$570,000 (1994).

[fire - consequence, damage to equipment, cracking]

Lessons
[None Reported]
Abstract
Small fire in hydrocraker at a refinery resulting from gasket failure in lubricating oil system.

Lessons
[None Reported]
Abstract
Fire at plastics plant caused evacuation of 3000 people. Liquid blowing agent left in mixer, where it suffered a decomposition, overheated and burned.

Lessons
[None Reported]
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<th>Source</th>
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**Abstract**

Explosion and fire in 50 m high vessel at a 300,000 tpy naphtha cracker. Plastics production restricted. False readings on controls suspected after weekend power cut.

[fire - consequence, power supply failure, cracking]

**Lessons**

[None Reported]
Abstract
Catalytic cracker vapour line deformation. During start-up of the reduced crude conversion unit (a heavy oil cracker), the reactor vapour line was heated up to a temperature sufficient to ignite coke in the line, resulting in overheating and deformation of the line. There was damage to equipment.
It was found that the line was heated beyond it's maximum capability. The cause was due to inadequate instructions, concerning operating limits, in the start-up procedure for the operators. In addition an air line heater outlet temperature indicator was not properly calibrated to read above the maximum allowable temperature.

Lessons
Start-up procedures should include consequences of deviation as well as procedural steps to take to control temperatures and quench the reactor.
Explosion in fluid bed catalytic cracker during start-up operations after a one week repair. Fatality.

[cracking]

[None Reported]
Location: Rayong, THAILAND
Injured: 3  Dead: 3

Abstract
Explosion outside cracking furnace during commissioning test run by contractors. Fire spread in open drainage channels. Fire attributed to accumulation of naphtha in oil/water drainage system. Vapour cloud formed when hot water discharged into system. Ignition of vapour occurred at the high pressure steam main. Fatality.

Lessons
[None Reported]
Location: Port Sulphur, Louisiana, USA
Injured: 0  Dead: 0

Abstract
400 m strip of sulphur burnt for 4 hours on the edge of a solid sulphur vat.

[fire - consequence, storage]

Lessons
[None Reported]
Catalytic reformer shut-down due to coking at a refinery. Thermal sensitive paint alerted to hot spots in third reactor. After shut down and coke burn, all three reactors were opened for inspection, at which time the third reactor was found to have sustained considerable damage. Oxidation led to creation of hot spots, which further led to catalyst destruction, contributing towards equipment destruction.

The cause of this incident was a lack of facility for measuring catalyst bed temperatures or monitoring oxygen levels in the reactors.

Lessons
All modifications to plant, or changes in procedures, must be subject to the formal review procedure, taking account of designers/licensers information and/or approval.
Abstract
Small fire on hydrocracker.
[fire - consequence, cracking]

Lessons
[None Reported]
Abstract
Ruptured pipes in one report but leaking ducts in another, on ethylene catalytic cracker plant caused small explosion and fire.

Lessons
[None Reported]
Explosion and fire in ethylene catalytic cracker unit at chemical plant burnt for 3 days.

[fire - consequence, cracking]

Lessons

[None Reported]
Abstract
3 alarm fire at refinery in the reformer unit where gasoline is boosted in octane.
[fire - consequence, refining]

Lessons
[None Reported]
Source: OIL AND GAS JOURNAL, 1994, 25 JUL.
Location: Cinizia; Gallup, New Mexico, USA
Injured: 2    Dead: 0

Abstract
Pressure vessel used to treat propane failed in an alkylation unit.
[vessel failure, rupture, gas / vapour release, processing]

Lessons
[None Reported]
Injured: 5  Dead: 4

Abstract
Explosion in furnace of the catalytic reforming unit of an oil refinery during maintenance work. Fatality.

Lessons
[None Reported]
<table>
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<tr>
<th><strong>Injured</strong></th>
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**Abstract**
Explosion on a catalytic cracker following the failure of a hydraulic supply to a control valve, regenerator/reactor equilibrium was lost and oil impregnated catalyst entered the regenerator.

**Lessons**
[None Reported]
Abstract

Fire occurred when a pump seal failed on a catalytic cracker and was rapidly extinguished. Crude unit also shut down.

Lessons

[None Reported]
Abstract
Fire on a cracker in a furnace and was put out in 5 minutes. Caused thought to be due to cracked furnace tube. Substance involved naphtha.

Lessons
[None Reported]
Injured: 0  Dead: 0

Abstract
Fire in cracker at a refinery.

[fire - consequence, refining, cracking]

Lessons
[None Reported]
Abstract
Fire broke out when flying sparks from a welding torch ignited a small vat of dichloronitrobenzene.

Lessons
[None Reported]
Abstract
A FCC (Fluid Catalytic Cracker) bottoms pump fire. While maintenance work was being carried out on the already isolated bottoms reflux pump, there was a release of catalyst and fractionator bottoms which formed a cloud. There was no check made to assure the system was depressured. Catalyst had plugged the discharge valve seat, preventing complete closure of the discharge block valve. The cause was due to the Lock Out/Tag Out system being unclear as to whether isolation and depressuring should be verified before the release of equipment to maintenance, and the location of pumps encouraged catalyst laydown in piping. Fatality.

Lessons
In isolating, as well as de-isolating, adequate checks are essential before opening flangers or removing end blanks, to ensure that pressure has not built up by leakage through the valves.
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.

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.
Injured: 0  Dead: 0

**Abstract**
Fire at refinery damaged electrical cables and equipment. Hydrocracker plant shutdown for 3 weeks. Substance involved gas.

**Lessons**
[None Reported]
Abstract
An explosion occurred during cleaning of a vat of slightly radioactive sodium. Fatality.

Lessons
[None Reported]
Source: "LLOYDS LIST, 1994, 10 MAR.
Location: Coryton, UK
Injured: 1  Dead: 0

Abstract
Fire involving packing rings on a crude pressure vessel.
[fire - consequence, processing]

Lessons
[None Reported]
Abstract
Fire engulfed fluid catalytic cracker unit from leaking diesel fuel/gasoline.

Lessons
[None Reported]
Naphthol powder was being emptied from a metal container into a blender when the dust ignited. The stirrer was not working at the time. Electrostatic spark considered to be the ignition source.

[fire - consequence, dust explosion, charging reactor, naphthol]

Lessons

[None Reported]
Abstract
Electrical power outage at a refinery. A major refinery power outage occurred, causing shutdown of the FCC (Fluid catalytic Cracker), Alky, and Coker units, and the once through cooling water system which supplies the surface condenser on the turbine. The operations supervisor opened isolating switch for the wrong 34.5 KV oil circuit breaker. The basic cause was a lack of written procedure for de-energising 34.5 KV loop. The procedure had become too routine and the incorrect switch was pulled out of habit rather than according to procedure. The procedure for using two people to re-energise the loop had been recently altered to allow one person to do this alone, due to manpower limitations.
Losses: estimated $142,000 (1994), $122,000 (1994) the result of 10 hours’ lost throughput, and $20,000 (1994) for maintenance on the unit.

Lessons
1. A written procedure should be prepared and used for each 34.5 KV loop switching.
   Line isolation should be done with two people, one to check the other.
2. Communication between control operator and the supervisor de-energising loop serves to verify the procedures as well as to keep the control operator advised as to what exactly is happening should something go wrong.
<table>
<thead>
<tr>
<th>Source</th>
<th>CHEMICAL HAZARDS IN INDUSTRY, 1995, MAY.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location</td>
<td>France</td>
</tr>
<tr>
<td>Injured</td>
<td>0</td>
</tr>
<tr>
<td>Dead</td>
<td>1</td>
</tr>
</tbody>
</table>

**Abstract**

A warehouse employee was asked to clean out an empty wine vat which had just been emptied. He was later found dead near the manhole at the bottom of the vat. The autopsy found death was due to asphyxiation. Carbon dioxide, sulphur dioxide and hydrogen sulphide had accumulated at the bottom of the vat. Fatality.

[cleaning, warehousing, entry into confined space, testing inadequate]

**Lessons**

[None Reported]
Hydrocracker heat exchanger failure at a refinery.
Two occurrences of tube failures in an exchanger in the reactor effluent circuit each resulted in the hydrocracker being shut down. There was damage to equipment, and product loss. It was found that erosion, corrosion stress was brought on by velocities in the reactor effluent exchangers which were in excess of the licensor's recommendations.
The inadequate identification of both the corrosion risk to reactor effluent circuit exchangers and the appropriate mitigation strategy caused this incident.

Lessons
Management of Change (MOC) techniques could have improved the timeliness of identifying both the corrosion risk to the reactor effluent circuit exchangers and the appropriate strategy to mitigate.
A fire occurred on one of the charge pumps of the debutaniser section of a hydrocracker unit, resulting in severe damage to pumps, heat exchanger, air coolers, surrounding pipework, steel structure and the debutaniser column.

The cause of the fire was attributed to failure of the screwed drain connection of the pump casing.

Fortunately, there were no severe casualties, and only two minor injuries occurred during the fire-fighting operation. Repairs took six months to complete and cost approximately USD 7.5 million (1994).

The cause:
It was found that, in addition to the blown-out pump drain, some process lines had ruptured and a number of flanges had failed. However, since these lines and flanges showed no signs of significant corrosion, it was concluded that their failure was due to the heat of the fire.

Lessons
[None Reported]
<table>
<thead>
<tr>
<th>Source</th>
<th>SEDGWICK LOSS CONTROL NEWSLETTER, 4TH QUARTER, 1993.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location</td>
<td>Convent; Louisiana, USA</td>
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<tr>
<td>Injured</td>
<td>0</td>
</tr>
<tr>
<td>Dead</td>
<td>0</td>
</tr>
</tbody>
</table>

**Abstract**

Fire caused shutdown of residue upgrade unit at refinery. Equipment involved: hydrocracker.

[fire - consequence, plant shutdown, refining, cracking]

**Lessons**

[None Reported]
<table>
<thead>
<tr>
<th>Source</th>
<th>HAZARDOUS CARGO BULLETIN INCIDENT LOG, 1993, DEC.; LLOYDS LIST, 1993, 30 OCT., &amp; 13 NOV.</th>
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<tbody>
<tr>
<td>Location</td>
<td>Tel-Aviv, ISRAEL</td>
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<tr>
<td>Injured</td>
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</tr>
<tr>
<td>Dead</td>
<td>1</td>
</tr>
</tbody>
</table>

**Abstract**

Cause attributed to the leak of acidifier in a storage tank and the chemical reaction of another material. Acid fumes did not spread outside plant. Fire fighter died when he fell into hydrochloric acid vat as they tried to neutralise acid with caustic soda. Fatality.

[unwanted chemical reaction, gas / vapour release]

**Lessons**

[None Reported]
Abstract
Small fire in reformer caused shutdown of unit. Substance involved: xylene.
[fire - consequence, processing]

Lessons
[None Reported]
Abstract
Overfiring in furnace box during maintenance shutdown damaged 3 of 8 furnaces of naphtha cracker on petrochemical complex. Awaiting delivery of furnace tubes.

Lessons
[None Reported]
Cleaning worker died after falling into vat of toxic waste. Second worker overcome by fumes in rescue attempt and fell into vat. Vat turned over to release men. Fatality.

Lessons

[None Reported]
Abstract
Fire in catalytic reforming unit.
[catalytic reformer, fire - consequence]

Lessons
[None Reported]
**Source:** LLOYDS LIST, 1993, 6 AUG.

**Location:** Kaduna,

**Injured:** 0  **Dead:** 0

**Abstract**
Fire destroyed fluid catalytic cracking unit at a refinery. Substance involved gasoline.

**Lessons**
[None Reported]
Source: OIL AND GAS JOURNAL, 1994, 5 SEP.
Location: VENEZUELA
Injured: 0  Dead: 0

Abstract
Accident in refinery caused by human error shut down catalytic cracker
[plant shutdown, operator error, cracking]

Lessons
[None Reported]
| Source | HAZARDOUS CARGO BULLETIN INCIDENT LOG, 1993, JUL.; OIL & GAS JOURNAL, 1993, 31 MAY.; LLOYDS LIST, 1993, 26 MAY. |
| Location | Jubail, SAUDI ARABIA |
| Injured | 0 |
| Dead | 0 |

**Abstract**

Second fire in 3 months to hit refinery. Fire in butane stripping unit of hydrocracker.

[fire - consequence, refining, cracking]

**Lessons**

[None Reported]
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, Health & 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.

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.
Pipe joining 2 vats burst during repairs releasing several tonnes of oleum. A cloud drifted towards a nearby town and airport.

[gas / vapour release, sulphur trioxide, sulphuric acid]

Lessons

[None Reported]
Abstract
A major release of combustible gases and liquids took place on the gasoline treater unit of an ethylene plant. Severe damage occurred to pipework, an 8 inch line positioned underneath two heat exchangers surrounded by a platform ruptured. Ignition occurred after the release of gas, 80% hydrogen and 20% methane causing a massive fire. The radiation from this fire scorched the paint on the flat slab side panels of the cold box on the ethylene cracker. The works fire brigade and public fire services attended with speed and prevented any major escalation of the damage.

Lessons
[None Reported]
Abstract
Isocracker air cooler failure at a refinery. Shortly after discovering a minor tube leak in a tube of an air cooled heat exchanger bundle on the isocracker, the tube ruptured. The tube failed due to acid corrosion.

Due to the collapse of the trays in the Recycle Splitter 12 months previous, the bottoms temperature of the first-stage stripper was lowered by 15-25 degrees F (8-14 degrees C) from its normal operating temperature. This "subtle" change caused an increased water content in the stripper bottoms and, as a consequence, normally dry conditions in the second stage air cooler became wet and accelerated ammonium chloride corrosion.

Losses total of $1.6 million (1993), $1.1 million (1993) in lost opportunity and $0.5 million (1993) in maintenance and repairs.

Lessons
Beware of small changes in operating conditions/modifications to plant, small changes in feedstock composition, etc. can produce accelerated corrosion conditions which may occur between inspection periods.

Regular removal of deposits from air cooled heat exchanger bundles/header boxes is recommended. Ensure any water flushing is done with chloride free water, and the bundle thoroughly air dried before return to service.
Abstract
During the unplugging of a steam mixer with steam (steam purge), the increase in pressure forced the material back up the chute and into the washer. The impact of the expelled material blew off the partial hood of the pulp washer. The hood (approximately weight: 1,000 pounds) landed on a nearby worker and killed him.

Steam mixers are used to increase the effectiveness of bleaching chemicals on pulp by raising its temperature. They are meant to operate at atmospheric pressure.

Lessons
The following recommendations were made:
1. It is recommended that the purging of a plugged steam mixer be done using low-pressure water and/or by physically opening the vessel to manually remove the stock. These methods are currently in use in many mills.
2. If steam is to be used to purge a plugged mixer, all workers to be evacuated from areas at risk of rupture and discharge (e.g. washer and steam mixer areas) to a safe location during a steam purge operation.
3. Although a fully enclosed hood on the washer (as opposed to a partial hood) may not contain a steam purge, it would improve containment of periodic steam "blow-backs" which occur during normal operation when a steam mixer is downstream of a washer.
4. Any opening in the full-enclosure hood (e.g. inspection doors, sampling ports) shall be offset at least 10 feet from the pipe connecting the washer to the steam mixer.
Abstract
Cracking unit kiln temperature excursion at a refinery. Temperature excursion encountered during start-up of a catalytic cracking unit. The investigation team concluded that there were, actually, three separate incidents being realised at the time of the temperature excursion. An immediate and basic cause is provided for each of the three incidents.

Immediate cause
1. Deviation from normal operating procedures during start-up (Operating (equipment) without authority).
2. Leaving plate (blind) in the kiln outlet hopper after maintenance (Failure to secure).
3. Faulty board level instrumentation (Warning system).

Losses: catalyst damage, loss on margins, maintenance, environmental fines, for a total of $3.25 million (1993).

Lessons
1. Clear, written instructions covering all operating phases, operating limits, safety systems and their functions.
2. Safe work practices and mechanical integrity program to assure the integrity of plant and instrumentation prior to start-up.
3. Thorough training of operators.
Source: SEDGWICK LOSS CONTROL NEWSLETTER, 1ST QUARTER, 1993
Location: Naples, ITALY
Injured: 2  Dead: 2

Abstract
Fire during maintenance work on catalytic reformer. Fatality.

[fire - consequence]

Lessons
[None Reported]
Abstract
Workers at a petrochemical facility were carrying out preparatory work for a decoking operation at one of the ethylene cracking furnaces. Decoking is a routine operation to remove the coked layer formed inside reaction tubes under normal operation by burning with high temperature air-steam mixtures. During this operation naphtha leaked from a 3/4 inch (1.9 cm) drain valve installed on a feed line and ignited, causing a fire. The supply of the feed fluid and fuels to the furnace and one of the adjacent furnaces was cut off immediately. The valves located upstream of the feed lines were closed also. It took approximately an hour for fire-fighters to contain the fire. With exception of these two furnaces, operation of other three furnaces in the unit was continued.

[fire - consequence, maintenance]

Lessons
The following recommendations were made:
2. Review and modification of the existing operation manuals and check-list.
3. Thorough training of operators.
Abstract
High pressure drop isocracker reactor. Periodic pressure measurements on the first bed of the second stage reactor revealed pressure drops greater than the maximum allowable. The unit was shutdown ahead of schedule to change the catalyst. A blockage caused by a 4-inch layer of soft crust material, forming a brick-and-mortar pattern between catalyst particles, developed in the reactor causing the high pressure drop. The primary basic cause was corrosion of upstream low-chrome steel plant that had deposited fine iron sulphide particles on the top bed. The secondary cause was that a coarser filter element had recently replaced a fine element on feed stream, allowing more particles to filter through.

Actual Losses

Lessons
Monitoring of systems should detect changes in corrosion rates to allow preventative actions to be taken.
Changing filter element mesh sizes should be subject to technical considerations and approval. Apart from operational problems, different filter mesh sizes may not be adequate.
If too coarse, may produce excessive static electric charge; if too fine, etc.
Source: OIL AND GAS JOURNAL, 1993, 8 MAR.; HAZARDOUS CARGO BULLETIN INCIDENT LOG, 1993, JAN.; LLOYDS LIST, 1992, 10 & 16 NOV.;
THE INDEPENDENT, 1992, 10 NOV.

Location: Marseilles, FRANCE

Injured: 12  Dead: 6

Abstract
Explosion in catalytic cracker in refinery. There was a subsequent fire in a gasoline tank and cryogenic unit involving propane and butane. Cause believed to be due to the rupture of a pipe carrying LPG to a low pressure gas scrubber. The inquiry concluded that 10 tonnes escaped and exploded after leak from pipework in one of the gas plant towers recovering liquified gas produced by the upstream catalytic cracker. The leak was probably caused by corrosion. Fatality.

[refining, cracking]

Lessons
[None Reported]
Abstract
Operations were normal at this 136,000 barrels-per-day refinery when a vapour cloud explosion occurred in the 29,700 barrels-per-day fluid catalytic cracking (FCC) unit. The initial vapour cloud explosion and several subsequent lesser explosions could be heard approximately 18 miles from the refinery. An estimated 5000 kg pounds of light hydrocarbons were involved in the initial explosion. A gas detection system in the FCC unit sounded an alarm, indicating a major gas leak in this unit. While the unit operator was contacting the security service to warn of this situation, the initial explosion occurred. The initial gas released is believed to have resulted from a pipe rupture in the gas plant, which is used to recover butane and propane produced in the FCC unit. The explosions and subsequent fires devastated about two hectares of this refinery, which covers a total area of about 250 hectares. The FCC unit and associated control building were destroyed by this incident. Two new process units under construction, which were scheduled to come into operation in 1993, were seriously damaged. Outside the refinery, roofs were damaged in a nearby town, and windows were broken within a radius of 900 m, with some windows broken up to six miles away. The refinery fire brigade and over 250 firefighters from three neighbouring industrial sites and four nearby towns were used for more than six hours to bring this incident under control. Approximately 140,000 litres of foam concentrate were used during the fire fighting effort. Some fires were intentionally left burning for a few hours after the incident to allow safe depressurising of the process units since the flare system was particularly damaged by the explosions.

Lessons
[None Reported]
A fire in a desulphurisation unit also affected reformer unit. Equipment involved: heat exchanger. Substance involved: naphtha.

[Lessons]
[None Reported]
Hydrocracker reactor effluent pipeline failure and fire at a refinery.
A 6 inch outlet elbow of a first stage reactor effluent air cooler failed, resulting in a fire. There was some damage to equipment. The presence of aqueous ammonium bisulphide resulted in erosion/corrosion that caused the pipeline failure. The cause was inadequate inspection for the detection of general and localised corrosion.

Lessons
An adequate inspection programme to detect general and localised corrosion/erosion attack is essential, coupled with a good recording system for all findings.
Abstract
Power supply failure while adding materials, trimethyl phosphite and methyl chloroacetate, to a vat stopped a mixer and the mixture overheated causing a release of vapours.

Lessons
[None Reported]
Abstract
A fire broke out in a catalytic cracking unit at the refinery. Substance involved: gasoline.

Lessons
[None Reported]
An explosion occurred inside the feed pipe to a catalytic reformer which led to damage and fire. Production cut by 50%. Fatality.

Lessons

[None Reported]
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 proceeded 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.

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 charging 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 as appropriate.
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.
Abstract

During normal operation of this ethylene plant, a leak was detected in the cooling/heating water jacket for the upper zone reactor tubes. The ethylene plant was immediately shut down and the pressure in the reactor was gradually reduced to 25 bar. Water was drained from the jacket and ethylene detectors were inserted to identify the location of the gas leak. Ethylene gas was reintroduced into the system and the pressure was gradually increased to 980 bar. When the source of the leak was detected the operators started to reduce the pressure in the reactor and separators.

As the pressure in the reactor and separators started to decrease, a loud noise was heard in the control room. Operators believed the noise to be a large ethylene leak and actuated the emergency dump system which closed the ethylene and oxygen inlet valves of the reactor, released gas through the reactor vents, and closed the outlet valve of the high pressure separator. Almost immediately after the emergency dump system was actuated, an explosion occurred which was followed by fire.

The explosion caused substantial damage to equipment and buildings within a one-half mile radius of the plant and severely damaged the concrete containment bunker for the reactor and high pressure separator. The walls of the bunker remained standing, secured by the steel reinforcing, but had been bowed outwards. The damage patterns suggest that there were two simultaneous vapour cloud explosions, one within the bunker and one centred above the top of the bunker. The fire following the explosions was extinguished within 10 minutes as the flow of gas was shut off. Fire damage was observed on the top of the high pressure separator and at the bottom valves of the low pressure separator.

The initial release of ethylene gas during testing came from the high pressure separator lid, which was secured to the body by a series of studs and was sealed with a steel ring. The leakage was said to have been caused by differential thermal contraction of the seal and the lid/body assembly following the introduction of cold ethylene gas into the reactor and separators for test purposes. There was no evidence of fracture or mechanical failure on either the seal ring, lid or body of the high pressure separator. Additional ethylene gas was released from the reactor and separators when the emergency dump system was actuated. The source of ignition for the ethylene gas was failure of insulation on electrical wiring for a remote operated dump valve. This valve would have been operated with electrical sparking during the emergency dump system actuation.

Lessons

[None Reported]
Abstract
A fire occurred in a refinery's power plant resulted in the shutdown of a catalytic cracker and other upgrading units. No disruption of crude units.

Lessons
[None Reported]
Abstract

In April 1992, an operator detected two leaking flanges at joints in the overhead transfer line at a catalytic cracker reactor. Measures taken to avoid ignition were successful.

In August 1991, a hydrocarbon leak was detected on the overhead system. The leak was repaired, however, during the installation, thermal lagging was erroneously applied over the flanges and their bolts on the two inlet nozzles of the reactor.

The basic cause for the leakage can be attributed to covering the flanges with thermal insulation. This was done for the whole of the reactor overhead transfer line at the August, 1991, repairs. This allowed the flange bolts to reach temperatures close to the process ones (approximately 515 degrees C), and at this temperature the bolt material of 21CrMoV 57, enters the yielding area (stress relaxation). With increasing service time, material elasticity is lost as follows:

<table>
<thead>
<tr>
<th>Length of exposure</th>
<th>Remaining Tension</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,000 hours of service</td>
<td>50%</td>
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<tr>
<td>10,000 hours of service</td>
<td>25%</td>
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</table>

In this way the flange surface pressure is reduced after a given service time to below-the-design requirements, and a leak will result. In this case the service time was approximately 5,500 hours.

After removing the insulation from the flanges, and successively replacing all the bolts and raising their tension (to about 75% compared to room temperature), both flanged joints became tight again.

Insulation on all flanges in the reactor overhead transfer line, and flange connections to that line, was removed.

Lessons

According to Quantitative Risk Assessment (QRA), flanges in such hot services should not be covered by thermal insulation, because:

1. Bolts can reach temperatures close to the process temperature, with high temperatures increasing the probability of leakage due to bolt stress relaxation.
2. The severity and extent of damage is higher in the case of leakage under thermal insulation, since the leaked product can spread unnoticed and be absorbed by the insulating material.

Heavy oils being transferred in thermal insulated piping presents a very high risk of fire in case of leakage since they flow at temperatures higher than their auto-ignition temperatures (over about 200 degrees C).
10 January 1992

Source: HAZARDOUS CARGO BULLETIN INCIDENT LOG, 1992, MAR.
Location: Newark, New Jersey, USA

Injured: 14  Dead: 0

Abstract
Vat of plastics resin exploded on top floor of 5 floor plant manufacturing resins for paints and varnishes. Extensive fire damage.

Lessons
[None Reported]
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]
Abstract
Three explosions in autoclaves. One report suggests that it was due to the build-up of nitrate.

Lessons
[None Reported]
Abstract
Two fireball explosions ripped through a steel vessel striking the workers carrying out maintenance. The two explosions at this catalytic cracker plant were heard several miles away. The accident occurred when 30 men were working inside the 40 ft diameter regeneration vessel which had been emptied whilst repairs were being carried out. Production not affected.

Lessons
[None Reported]
Abstract
Fire in chemicals warehouse. Stocks of catalyst overheated in raw materials warehouse. Chemical dust was released and reacted with an incompatible chemical.
Fire loss £6 million (1992), significant fines £100,000+ (1992), significant pollution, 400 different chemicals washed out of store went directly into local watercourses or into the sewers.
The following causes were found:
1. Fire hazard. Ignition source not pinpointed.
2. Presence of ammonium persulphate, which reacted with chemical dust.
3. Tools, equipment, materials and chemicals were not stored properly.
[fire - consequence, warehousing, unwanted chemical reaction]

Lessons
Care is needed in storage of chemicals/gas bottles, etc. avoid mixing flammables and oxidizers in adjacent, close locations.
On Saturday, December 21, 1991, a sudden release into an isocracker compressor flare header destroyed a safety relief valve and damaged a sight glass on a liquid collection pot. A release of hydrogen rich vapor to atmosphere occurred, necessitating a shut down of the isocracker. The damage was limited to that previously described, and there were no injuries. The isocracker was returned to service on December 25. The incident cause was an accumulation of liquid in the flare header. The problem was compounded by undersized header and piping, and triggered by unstable operating conditions.

Additionally, deficiencies in the incident response procedures were uncovered. Based on the investigation findings, recommendations have been made to review and revise procedures and to re-engineer the flare header. In this incident the losses are limited to reduced production and repair costs; however, there was a potential threat to life and major equipment.

Lessons
1. Drain drip pots frequently to prevent liquid build-up.
2. Locate source(s) of liquid and remedy now, where possible, or during the shutdown.
3. Ascertain any testing required for individuals exposed to high levels of noise or hazardous vapours.
4. Redesign the liquid removal system to ensure no build-up.
5. Redesign the flare header to reduce velocity and back pressure.
6. Adjust the operating and emergency procedures to reflect the dangers of rapid feed rate changes.
7. Review the maintenance requirements for compressor alarms and trips.
8. Review the refinery quality control procedures for work done in outside workshops.
Location : Scholven; Gelsenkirchen, GERMANY
Injured : 8  Dead : 0

Abstract
An explosion occurred in a hydrocracker complex caused fire.
[fire - consequence, cracking]

Lessons
[None Reported]
Source: HAZARDOUS CARGO BULLETIN INCIDENT LOG, 1992, FEB.
Location: Gwalior, INDIA
Injured: 100  Dead: 9

<table>
<thead>
<tr>
<th>Abstract</th>
</tr>
</thead>
<tbody>
<tr>
<td>Four explosions and fire enveloped vats of petrol, gasoline, and unknown chemicals used in dyeing process in flames. Workers trapped under fallen roof. Fatality.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Lessons</th>
</tr>
</thead>
<tbody>
<tr>
<td>[fire - consequence, injury]</td>
</tr>
<tr>
<td>[None Reported]</td>
</tr>
</tbody>
</table>
A fire occurred on a pump located within a catalytic cracker unit. Substance involved gasoline.

[fire - consequence, cracking]

Lessons

[None Reported]
<table>
<thead>
<tr>
<th>Source</th>
<th>Location</th>
<th>Injured</th>
<th>Dead</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEDGWICK LOSS CONTROL NEWSLETTER, 4TH QUARTER, 1991.</td>
<td>Charleston; South Carolina, USA</td>
<td>33</td>
<td>6</td>
</tr>
</tbody>
</table>

**Abstract**

Unknown chemicals were being mixed in a reactor when there was an explosion. Fatality.

**Lessons**

[None Reported]
A fire occurred on a catalytic cracker which cut gasoline output.

Lessons
[None Reported]
Injured: 12  
Dead: 1

Abstract

Lessons
[None Reported]
<table>
<thead>
<tr>
<th>Source</th>
<th>LLOYDS LIST, 1991, 7 JUN.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location</td>
<td>Jubail, SAUDI ARABIA</td>
</tr>
<tr>
<td>Injured</td>
<td>0</td>
</tr>
<tr>
<td>Dead</td>
<td>0</td>
</tr>
</tbody>
</table>

**Abstract**
A leak and fire occurred in a hydrogen compression section of a hydrocracker.

**Lessons**
[None Reported]
Abstract
A fire occurred in pipe work of a catalytic cracker.
[fire - consequence, cracking]

Lessons
[None Reported]
Abstract
A fire forced shutdown of catalytic cracker and was brought under control in 1 hour.

Lessons
[None Reported]
Abstract
An explosion occurred when one of three catalytic cracker units came back on stream after shutdown for routine maintenance. Steam used at start-up is normally condensed and pumped out of the fractionator into a vessel. The water from the vessel is drained by a valve. This valve was closed and the water could not drain. When hot oil hit the water it vapourised and ruptured the vessel. The hot oil ignited. The relief valve could not cope with the quantity of steam produced. Fatality.
[reactors and reaction equipment, operation inadequate, cracking]

Lessons
[None Reported]
A fire occurred in hydrocracker of refinery.

Lessons
[None Reported]
An explosion and fire occurred in crude unit producing naphtha for adjacent ethylene plant. 11 pumps and cooling water equipment destroyed. Entire electrical system destroyed. Extreme cold and frost led to pipe failure. Cracker to be on stream in one month.

Lessons

[None Reported]
Hydrogen pressure vessel failed causing extensive property damage. Failure was due to peaking in the zone of the longitudinal welds of the pressure vessel and execution of the welding seams - inside weld reinforcement and undercutting in the transitional zone cover pass/base metal, cyclic pressure loading due to discharging and filling operation of the H2 storage tank (in this case about 1500 load cycles) and pure hydrogen.

[Abstract]

[Lessons]

[None Reported]
Abstract
A leak in a LPG pipeline that transports ethane and propane to a gas cracker complex resulted in an explosion at an off-site treatment compression facility. Since the explosion took place outside the complex, the cracker and downstream units were not damaged while the off-site facility experienced significant damage. The cracker was initially shut down due to feedstock supply problems but was later operating on a gas supply directly from the pipeline. Prior to this incident, low density polyethylene (LDPE), linear low density polyethylene (LLDPE), high density polyethylene (HDPE), and polypropylene (PP) units were to be brought on-line within a few months. The commissioning of these units was expected to be delayed between four and 12 months due to this incident. Fatality.

Lessons
[None Reported]
Source: LLOYDS LIST, 1990, 8 NOV.
Location: Chalmette: Louisiana, USA

Injured: 1  Dead: 0

Abstract
An oil cracking tower blew up and caused a fire which was under control within one hour. Fatality.

[fire - consequence]

Lessons
[None Reported]
A vapour cloud explosion occurred in the hydrocracker unit of this 160,000 barrels-per-day refinery. A mechanical equipment failure involving the shell of a heat exchanger in this unit resulted in the formation of a vapour cloud, which was ignited by a heater. The subsequent fires in this unit burned for 10 to 12 hours before they were extinguished by the refinery fire brigade with mutual aid assistance.

As a result of this incident, the hydrocracker unit was shutdown for approximately three months for repair. However, the fire damage was limited to the hydrocracker unit and the refinery was brought back online within one week.

[refining, fire - consequence, damage to equipment, cracking]

Lessons

[None Reported]
An explosion occurred in a refinery hydrocracker due to metal failure. Substance involved: hydrogen.

Lessons

[None Reported]
An ethylene plant was shutdown due to a sequence of events that occurred over a two-day period. Two mechanical problems on ethylene cracker caused the shutdown of the plant for repair. During the process of shutting down the plant, a fire occurred on a furnace which was extinguished by site fire service.

Lessons

[None Reported]
Abstract
An explosion caused a boiler to be destroyed in a refinery Fluid Catalytic Cracker Unit (FCCU) plant. Substance involved: fuel oil. Cause was instrumentation failure and operator error.

Lessons
[None Reported]
<table>
<thead>
<tr>
<th>Source</th>
<th>SEDGWICK LOSS CONTROL NEWSLETTER, 3RD QUARTER, 1990.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location</td>
<td>Benicia; California, USA</td>
</tr>
<tr>
<td>Injured</td>
<td>0</td>
</tr>
<tr>
<td>Dead</td>
<td>0</td>
</tr>
</tbody>
</table>

**Abstract**
A fire led to shutdown of a catalytic cracker. Substance involved: lube oil.

**Lessons**
[None Reported]
Abstract
A fire occurred in a reformer which lasted for four hours. The main crude capacity unaffected.

Lessons
[None Reported]
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.

Lessons
[None Reported]
Leak from high pressure section of hydrocracker led to fire.

[fire - consequence, cracking]

Lessons
[None Reported]
Search results from IChemE's Accident Database. Information from she@icheme.org.uk

Source: LOSS PREVENTION BULLETIN, 129, 8.
Location:
Injured: 0  Dead: 0

Abstract
An operator was draining water from the debutanizer system of the fluid catalytic cracking (FCC) gas plant when liquefied petroleum gas (LPG) was suddenly released. The LPG release continued at this 65,000 barrels-per-day refinery as the operator panicked and left the FCC gas plant. Subsequently, an ignition occurred resulting in an explosion and fire.

[catalytic cracker, refining, fire - consequence, fluid cracker]

Lessons
[None Reported]
Abstract
During the morning shift numerous processing problems were experienced on an ethylene cracker unit at a petrochemical plant. An explosion occurred at 11.45 am and an internal cold box leak was suspected.

Lessons
[None Reported]
<table>
<thead>
<tr>
<th>Injured</th>
<th>Dead</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

**Abstract**
Explosion in chemical mixing building causing toxic emission alarm to be actuated. Explosion caused by a metal-to-metal spark while unblocking magnesium granules in a blending machine ignited the magnesium. Company procedure called for the use of a wooden rod. Fatality.

**Lessons**
[None Reported]
Abstract

Lessons
[None Reported]
<table>
<thead>
<tr>
<th>Source</th>
<th>SEDGWICK LOSS CONTROL NEWSLETTER, 1990, FIRST QUARTER.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location</td>
<td>Philadelphia, USA</td>
</tr>
<tr>
<td>Injured</td>
<td>0</td>
</tr>
<tr>
<td>Dead</td>
<td>0</td>
</tr>
</tbody>
</table>

**Abstract**

A fire occurred in the reformer of a refinery.

**[fire - consequence, refining]**

**Lessons**

[None Reported]
A fire and explosion occurred in an ethylene cracker days before it was due to restart following another accident three months earlier. A blockage occurred in the acetylene heat exchanger, and a valve opened by mistake led to a release of ethylene. This cooled the heat exchanger down to a very low temperature and caused brittle fracture of the heat exchanger. The gas was then ignited. Fatality.

[fire - consequence, gas / vapour release, cracking]

Lessons

[None Reported]
Naphtha reformer damaged when gasoline, leaking from a heat exchanger, ignited and started a fire.

[fire - consequence, damage to equipment]

Lessons

[None Reported]
Abstract
Worker suffered 90% burns while welding in paint vat which was empty but retained sludge and puddles of paint stripper/solvents. Fatality.

Lessons
[None Reported]
Abstract
An explosion occurred in a reformer unit of refinery. The ultra former - 2 unit was sequestrated by investigative magistrate and likely to remain shut until investigation complete.

Lessons
[None Reported]
Source: EASTERN DAILY PRESS, 1989, 9 JUL.
Location: Wymondham, UK
Injured: 0  Dead: 1

Abstract
Welding was taking place in a vat where there were puddles of flammable material, sodium hydroxide and methylene chloride. Fatality.

Lessons
[None Reported]
Abstract
An explosion of a chemical mixing vat. Fatality
[unknown chemicals, unidentified cause, injury]

Lessons
[None Reported]
A fire occurred in a catalytic cracker.

Lessons

[None Reported]
<table>
<thead>
<tr>
<th>Abstract</th>
<th>Lessons</th>
</tr>
</thead>
<tbody>
<tr>
<td>A flash fire occurred in a catalytic cracker.</td>
<td>[None Reported]</td>
</tr>
</tbody>
</table>

**Source**: LLOYDS LIST, 1989, 16 MAY.

**Location**: Warren, Pennsylvania, USA

**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.

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.
Abstract
Mechanical failure led to damage of a turbine at this refinery Fluid Catalytic Cracker Unit (FCCU) plant.
[damage to equipment, mechanical equipment failure, refining, fluid cracker]

Lessons
[None Reported]
Abstract
A 2-inch line carrying hydrogen gas at approximately 2,800 psi failed at a weld, resulting in a high pressure hydrogen fire. The fire resulted in flame impingement on the support of a 100-foot high reactor in a hydrocracker unit. The steel skirt for this reactor, which was 10 to 12 feet in diameter and had a wall thickness of 7 inches, subsequently failed. The collapse of this reactor damaged fin-fan coolers and other processing equipment, greatly increasing the size of the loss. It is believed that at the time of the loss, the hydrocracker unit was in the process of being shut down for maintenance. Therefore, the reactor was in a hydrogen purge cycle. The cause of the initial hydrogen leak is believed to have resulted from the failure of an elbow to reducer weld in the 2-inch hydrogen preheat exchanger bypass line. Fatality.

Lessons
[None Reported]
An explosion occurred in an Fluid Catalytic Cracker Unit (FCCU) plant when plant closed for maintenance.

[fluid cracker]

Lessons
[None Reported]
Abstract
Cracked Fluid Catalytic Cracker Unit (FCCU) reactor vapour line at a refining company. During start-up of the FCCU, and shortly after the introduction of feed, vapour was noticed to be coming from the insulation around the reactor vapour pipeline and support hanger. There was product loss and damage to equipment. Failure of the line was due to thermal fatigue. A contributing factor was inadequate insulation that allowed plates to remain cool and not expand with the line, acting as a restraint. Insufficient maintenance of insulation around the line in recent years was the cause of this incident, in addition to inadequate design of support section.

Lessons
Particular care is needed in regular inspection and necessary repair of plant which is the subject of significant temperature cycles with possibilities of thermal fatigue.
Abstract
An explosion occurred during mixing in a vessel.
The incident occurred whilst making a solution of a metal organic compound in toluene; the powder was manually added to a stirred vessel that was partly filled with toluene. During this manual operation, a slight under-pressure was maintained to avoid dust nuisance for the operator. Approximately 15 minutes after closure of the manhole the explosion occurred.
The report stated the investigations into the cause that found:
A source of flammable atmosphere.
The toluene at 20 degrees C was well above its flash point and, with the sucked-in air, would have produced a flammable atmosphere in the vessel.
Chargeable material.
The conductivity of toluene is typically in the order of 10 pS/m. At this low level, vigorous stirring of two-phase systems may generate hazardous potentials.
Electric charge generation.
During the dissolving process there is a stage at which material is in suspension.
Stirring such a two-phase mixture can generate charge.
Tests showed it reaching a maximum potential some 10 minutes after the start of adding a powder.
At that moment a discharge can occur from the charged suspension to the stirrers, to the tank wall or to inserts, such as instruments.

Lessons
The report stated the following precautions for preventing recurrence:
There are two basic methods for avoiding explosions caused by static electricity discharges in this type of dissolving operation:
Prevent the formation of a flammable atmosphere by inerting the system.
Prevent the build-up of hazardous potentials.
This can be achieved by:
Avoiding vigorous stirring by limiting the power for agitation, and/or
Raising the conductivity of the solvent by adding anti-static additive.
Abstract

Lessons
[None Reported]
<table>
<thead>
<tr>
<th>Source</th>
<th>EUROPEAN CHEMICAL NEWS, 1988, 4 JUL.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location</td>
<td>Port Arthur, Texas, USA</td>
</tr>
<tr>
<td>Injured :</td>
<td>0</td>
</tr>
<tr>
<td>Dead :</td>
<td>0</td>
</tr>
</tbody>
</table>

**Abstract**
Incident at ethylene cracker plant. Explosion damaged steam turbine in a propylene compressor in compressor house from lube oil failure.

**Lessons**
[None Reported]
Abstract
An explosion occurred when mixing explosives in a batch process. Nitroglycerine based explosives were being manufactured at the time of the accident. The most likely cause was contamination of the explosives in the mixers by grit or other hard material. Fatality.

Lessons
A number of technical and equipment changes were made to reduce the possibility of recurrence. The main lesson, however is that overconfident operators must not be allowed to take short cuts to speed up the batch time. This was achieved in two ways.
1. New interlocks and other equipment have been fitted which make it much more difficult to operate the plant while people are present in the mixing area.
2. The role of the supervisor and his supervisory duties in the explosives manufacturing area have been strengthened and clarified and his responsibility to ensure that safe working practices are allowed has been made clear to all. This has meant organisational change and the appointment of people given appropriate skills and authority.
Operations were normal in a 90,000 barrels-per-day fluid catalytic cracking (FCC) unit when internal corrosion caused the failure of the outside radius of an 8-inch carbon steel elbow located 50 feet above ground in the depropaniser column overhead piping system. An estimated 20,000 pounds of propane escaped through the resulting hole, forming a large vapour cloud during the 30 seconds between failure and ignition. Both the depropaniser column and the accumulator depressured through the opening. Ignition of the vapour cloud probably was caused by the FCC charge heater. The initial blast destroyed the FCC control building and toppled the 26-foot-diameter main fractionator from its 15-foot-high concrete pedestal. The column separated from its 10-foot-high skirt before falling. Analysis of bolt stretching of towers in the blast path indicated over-pressures as high as 10 psi. The refinery immediately lost all utilities, including fire water and the four diesel pumps, greatly limiting the fire fighting effort for several hours. Steam pressure dropped abruptly due to severed lines. Twenty major line or vessel failures occurred in the FCC and elsewhere throughout the refinery. Blast damage throughout the plant was extensive, but was most severe in the 300-foot by 600-foot FCC unit.

A preliminary report stated that the failed elbow was located downstream of the injection point where ammoniated water was added to reduce depropaniser condensation or fouling. The elbow was a designated inspection point in the overhead piping system for taking ultrasonic thickness measurements during turnarounds. These inspections had constantly shown the expected corrosion rates of 0.05 miles per year. Measurements taken at the failed elbow and in the downstream piping after the explosion revealed unexpected high localised corrosion rates.

**Lessons**

1. Perform thorough corrosion review as a base case, and update review when operating changes are instituted.
2. Utilize well designed injection systems to avoid corrosion failures; i.e., one with a flanged quill and atomizer to finely distribute the injected product to aid in mixing and to avoid slugging.
3. Monitor not only injection points, but also tees where two streams of potentially different compositions/temperatures join.
Abstract
As a result of a safety relief valve failure during the start-up/commissioning of a second naphtha cracking furnace, “cracked gas condensate” (light hydrocarbons) was able reverse flow through the overpressure relief system, and leak out through an expansion joint. The leaking liquid spilled over a furnace and was ignited. The fire consequences were substantial, involving plant shutdown and major damage to equipment. Although the main fire was extinguished after about 20 minutes, several smaller fires ensued and it was about 1 hour before they were under control. There were no injuries.

Lessons
An inquiry team reported that reverse flow through the relief valves was well known, as there had been a previous incident. The reason why four methods for detecting this relief valve leak had not been carried out was attributed to training inadequate. The procedures were to be revised.
Abstract
A fire occurred involving cracking equipment at a refinery Fluid Catalytic Cracker Unit (FCCU) plant.
[refining, fire - consequence, fluid cracker]

Lessons
[None Reported]
Abstract
A falling liquid level in a fluid catalytic cracker unit (FCCU) resulted in a complete loss of slurry reflux cooling. This in turn led to serious process disturbances on the crude distillation unit (CDU) with temperatures reaching very high levels. The situation was eventually brought under control without a major catastrophe or injuries to personnel.

A routine crude change on CDU 1 was taking place. During this operation there were various interruptions to the crude supply due to intermittent loss of pump suction and the CDU 1/FCCU board operator's attention was focused completely on the crude board. He failed to notice that the change in FCCU feed quality caused a low level in the bottom of the FCCU main fractionator, which in turn caused a complete loss of slurry reflux cooling.

Actions taken by the operators to correct this led to low outlet temperatures on both FCCU risers. These conditions caused feed forward of large quantities of unvaporised oil to the regenerator for nearly an hour.

Limited excess combustion air capacity ensured that the majority of oil entering the regenerator was vaporised, cracked and flowed forward to the main crude pre-heat furnace. Ample excess air in the combustion zone of the furnace allowed combustion of most of this additional fuel. Crude coil and fire box temperatures exceeded 750 degrees C (1400 degrees F) and 1600 degrees C (2900 degrees F) respectively, for a period of 90 minutes. Due to mechanical damage and design restrictions, FCCU flue gas was unable to be fully bypassed around the furnace until 70 minutes after commencement of oil feed forward. Operators did not recognise the FCCU riser feed forward until 60 minutes after commencement of the incident. They initially concluded that a furnace crude tube failure was the source of excess combustion material in the furnace firebox.

Emergency procedures for tube failure were implemented correctly, but this action did not of course address the real problem.

Within 75 to 80 minutes after initial high temperatures were experienced in the furnace and whilst furnace isolation was proceeding, the crude coil failed in two places. During the same period, an LP steam superheat coil in the heater also failed. One crude coil failure released residual oil/steam which combusted with a torch effect destroying approximately 50% of the crude coil. During further isolation activities, the main crude pre-heat furnace boiler feed water (BFW) coil and the BFW coil in the parallel crude furnace were blocked in without by-passes being opened. Total loss of steam generator water supply occurred immediately which resulted in loss of steam drum water levels in all three boilers. Two of the three boilers were manually shut-down within minutes. The remaining boiler stayed on line while the operator re-established water supply. Despite having lost water level, No.1 Generator was not shut-down for 15-20 minutes. As no low level trips are installed on any of the boilers, the latter two in the shut-down sequence sustained damage caused by continued heat input without steam drum water level.

Total steam failure occurred for 25 minutes. Restoration of steam supply on one boiler, albeit at 40% of normal pressure, was secured some 20 minutes after initial loss of supply. At the time of, or subsequent to the loss of the BFW supply to the boilers, the main crude pre-heat furnace water coil failed. After cessation of riser oil feed forward on the FCCU, residual hydrocarbon caused high temperature burns in the regenerator for 90 minutes.

Temperatures in excess of 100 degrees C (1840 degrees F) were observed, while physical evidence indicates that 1100 degrees C (2000 degrees F) was probably achieved.

Unit conditions were secured progressively between 2.5 and 3.5 hours after the initial FCCU incident commenced. Near miss.

Lessons
[None Reported]
Abstract
Gas cloud released from factory affected policemen, firemen and ambulance men. Vat of caustic soda was overheated.

[overheating, gas / vapour release]

Lessons
[None Reported]
Leak of hydrogen from hydrocracker caused a fire in a refinery.

Lessons

[None Reported]
Abstract
A potentially serious incident occurred on a residue cracker resulting in a unit shutdown of 35 minutes duration. An instrumentation problem caused the regenerated catalyst slide valve to shut fully and the resultant loss of catalyst circulation, followed by reduction in reactor temperature allowed unvaporised hydrocarbon to pass to Regen 1. A thick yellow plume of unburnt hydrocarbon mixed with flue gas and some catalyst discharged from Regen 1 stack for approximately 15 minutes, via the carbon monoxide burner.
During the incident the carbon monoxide burner tripped on low steam drum level due to loss of carbon monoxide in flue gas. The sudden increase in steam demand caused problems for the main refinery boilers resulting in prolonged emission of black smoke and shutdown of the solvent de-waxing unit which has a very high steam usage.
When the carbon monoxide burner tripped, a sudden release of flue gas and hydrocarbon occurred from the main seal tank vent at ground level, necessitating sounding of the refinery emergency siren. An operator and a laboratory technician were affected by vapour inhalation when caught in the vapour cloud. No damage was caused to equipment as a result of the incident.
[plant shutdown, instrumentation failure, near miss, gas / vapour release, refining, cracking]

Lessons
This is a good example of how a single equipment item failure which should have been dealt with almost routinely, resulted in a chain of events which uncovered numerous deficiencies in system, design, equipment reliability and operator training.
All these problems, which themselves may have been minor, contributed to a potentially catastrophic situation. All equipment which contributes to the safe operation of the plant must be maintained in good working order, even process water piping.
The possibility of hand radios interfering with process control instrumentation poses problems for refineries.
Abstract

A leak of hydrogen sulphide gas occurred whilst a flange was opened up to remove a spade during the start-up of the catalytic cracker following a scheduled shut down. Four fitters working in the vicinity were overcome by gas, two of whom collapsed. There was no material damage and the unit was started up as scheduled.

The start of the work to withdraw the spades was verbally authorised by the area supervisor to a maintenance supervisor, who initiated the fitters to start work at several locations simultaneously. The gas escape occurred when the flange in the line from the main fractionator overhead receiver to the flare line was opened to remove the 8” spade. The gate valve to the flare was already open, which was not realised by the fitters themselves.

The flange in question is located on a platform which is approximately 8 metres high and the platform is reached by a stairway and access ladder. The fitter working directly over the flange lost consciousness. Three other fitters working in the same area on the removal of other spades tried to rescue the first one.

They also inhaled the escaping gas and a second man collapsed after they had managed to move the first fitter only a short distance. The other two fitters were themselves being affected and had to escape via the access ladder.

The flange was then closed by another fitter wearing breathing apparatus and the fire brigade organised transport of the four fitters to hospital after giving first aid with oxygen.

The precise composition of the flare gases at the time of the incident is not known. However an analysis of the flare gases the following day gave an H2S content of 6.5 ml/100ml. Three men were released from hospital the following day and the fourth man two days later.

An investigation into the incident concluded that it occurred because of the normality of this work, repeatedly performed by the crew without any problems. In this case the situation was different due to the fact that some delay in the start up procedure had caused the work to start during the shift changeover. The fitters were already waiting at the different locations for the sign to start withdrawing the spades. They started working after the verbal authorisation given to them from the maintenance supervisor, without waiting for an operator to come and supervise.

The operator would have checked the valve position and would have closed the valve and depressurised the line, so preventing the incident from taking place.

Lessons

Recommendations and Actions:
1. Authorisation for this special work will in future only be given in written form by a shift foreman.
2. Correct positions of the valves next to the spades to be checked immediately before work authorisation.
3. Work will only be performed under the supervision from unit operators.
4. Work will not be performed during the shift changeover.
5. Small technical modifications for improving identification and accessibility of spades to be carried out.
Abstract
On the morning of the incident the plant foreman on duty had made a maintenance request for a catalyst line to a reactor to be cleaned, following reports by operators that the line was blocked. This was a routine operation which was carried out approximately twice a month.
The operator started work on the catalyst line and removed the catalyst rotameter. He then reported to the workshop foreman that he had found the blockage in the rotameter. The foreman instructed the operator to run water through the catalyst line to check that the rest of the line was clear. This is normally done by running water by gravity from the elevated catalyst tank.
The operator connected the mains (5 to 7 bars pressure) to the open end of the pipeline and attempted to flush the other pipelines connected to the system. He diverted the flow to the emulsion tank system but left the valve immediately downstream of the emulsion tank rotameter (a borosilicate glass tube rated for normal operation of 7.5 bars) closed.
The valve upstream of the rotameter was then opened and the rotameter shattered explosively severing his safety glasses and causing injury. The rotameter burst when the valve upstream was opened, with the valve downstream left closed. This would suggest that the rapid flow of water caused the steel rotameter bobbin to rise rapidly in the tube. This could have caused a crack in the glass. The air behind the water would be compressed to the line pressure of 5 to 7 bars, and be released rapidly when the glass tube cracked, thus causing an explosive shattering effect.

Lessons
It has been suggested that there should have been a protective plate of safety glass mounted in front of the rotameter. Glass is known to be a brittle material and the rotameter was rated for 7 bars. It is designed to be looked at closely and failure in normal service is always possible.
It is uncertain whether a safety glass shield would have been adequate in the circumstances of the accident, but an unshielded piece of glass at 7 bars does present a potential hazard.
A major explosion occurred on a hydrocracker unit. This seriously damaged plant and equipment, completely disintegrating the low pressure (LP) separator vessel with debris being widely scattered. Flames from the ensuing fire reached a height of over 90 m (300 ft) and caused extensive damage to the hydrocracker unit. The hydrocracker unit had been shutdown for maintenance and the day before the accident, the unit was being prepared for recommissioning. Immediately prior to the incident the unit reactor section was on gas circulation at 140 bar (2030 lb/in²). At 07.00 the explosion occurred.

The inquiry team concluded that the incident resulted from severe overpressure of the LP separator designed to operate at 10 bar (140 lb/in²), which caused the vessel to disintegrate and the contents, primarily hydrogen, to be released. A vapour cloud quickly ignited in the form of a fire ball and produced a serious explosion. Although the source of ignition cannot be identified with certainty the three primary considerations are sparks caused by the impact of flying debris, electric wires, light fittings, or ignition of the gas by friction during the failure of the vessel.

Inquiries carried out by the refinery and authorities agreed that disconnection of the trip system had placed too much reliance on operators for safe control of the high pressure/low pressure (HP/LP) interface. Without extra low level protection in the HP separator, the LP vessel was at risk of being overpressurized at any time through human error or level control system failure. The plant was most vulnerable when the level control valve was held on “manual”. Regular testing during start up of alarms and trips was practised on the plant but some, including the HP separator extra low level trip switches were not included on the check list. These systems had been inoperative for some time and were presumed by some operators and maintained staff to be no longer required. Training of new operators by those sharing this belief helped to perpetuate this misconception. Fatality.

**Lessons**

There are three main lessons to be leaned from this tragic and costly accident.

1. Disconnection of trip switches for whatever reasons should only take place after full evaluation of the safety implications as part of standard procedures for reviewing proposed modifications to the process plant. Such changes should be documented and formally brought to the attention of the operations and maintenance.

2. The usefulness of hazard and operability (HAZOP) studies to help identify hazards analyse the causes and effects, assess the risk and make a decision on what action is required is well proven. HAZOP is just as applicable to existing systems as to new plants.

3. The importance of adequate surface drainage on sites. The massive firefighting operation carried out on this occasion produced vast quantities of water which the system could not cope with and resulted in extensive surface flooding. Where it is not feasible to increase existing drainage systems, consideration should be given to directing the flow of excess water to less hazardous areas and the provision of mobile pumps to remove excess water.
A vat of sulphuric acid ruptured releasing a cloud of toxic gas as the result of a fire.

[None Reported]
Phosgene gas was released when a cistern was being attached to a reaction vat. Leak.

Lessons
[None Reported]
Abstract
During the manufacture of an organic compound in a batch reactor, the temperature rose from a control level of 80 degrees C to an actual level of 120 degrees C. It was known that the reactor contents would ignite in the presence of oxygen at elevated temperatures. The reactor was fitted with a nitrogen purge system (including an in-line oxygen analyser for the off-gas). In order to control the situation, the supervisor increased purge rates and this led to odour complaints from local residents. The reactor was brought under control without further incident. Subsequent internal examination of the reactor and product showed no signs of smouldering or combustion.

Lessons
The conflicting evidence prevented a clear analysis of the problem. Improvements in monitoring off-gas temperature and composition were suggested. Off-gas scrubbing was also improved.
Abstract
During a major Fluid Catalytic Cracker Unit (FCCU) overhaul, a four level platform scaffold inside the regenerator vessel collapsed. Although five persons were working on the top platform at the time of the collapse nobody was injured.
The scaffold had been built to allow removal of refractory in the base of the regenerator.
It was meant to be used by five refractory workers and had, accordingly, been designed to a loading of 150kg/m² (about 1200kg in total). A central dump tube was incorporated into the scaffolding to facilitate removal of refractory debris.
At the same time as the refractory was being removed, a group of 15 workers began to remove sleeves from the regenerator standpipes which entered the regenerator vessels immediately above the scaffold. They used the scaffold for access and to support the standpipe sleeves, weighing about 2500kg before they were lifted free of the regenerator. Because the scaffolding platforms were not a close fit against the regenerator wall, displaced refractory was able to fall down and collect on the lower platforms. In any case removal of the standpipe sleeves prevented access to the central dump nozzle.
Some thirteen hours after work began the scaffold collapsed.
This was despite the fact the several persons noticed that some scaffolding tubes had bent during the period between commencement of work and the time of collapse.
It is clear that the scaffold became overloaded by virtue of it having been used to support heavy standpipe sleeves twice the weight of the scaffold design loading plus most of the removed refractory.

Lessons
Overloading of scaffolding is something which can have extremely serious consequences.
It is important that the contractor's supervisors are made fully aware of the dangers of overloading scaffolding and have sufficient scaffolding inspectors to monitor work on scaffolds.
Any departure from the normal, however apparently insignificant, should be immediately reported to supervisors.
Abstract
A fire occurred involving a compressor at a refinery Fluid Catalytic Cracker Unit (FCCU) plant which was caused by mechanical equipment failure.

Lessons
[None Reported]
Abstract
An explosion occurred in the firebox of No. 2 catalytic cracker carbon monoxide boiler. The explosion caused considerable damage, estimated at approximately £200,000 (1986), to the boiler's east wall, roof piping and flue gas and air ducts. There were no injuries to personnel.

An investigation into the incident found that the shut-down procedures in force were not specific enough and merely requested that all fuels to the boiler should be blinded. In addition there were no check-lists in existence. The investigation team recommended that the refinery:

1. Revise the shut down procedure and introduce detailed check-lists for each boiler, specifying the spade isolations required on all gas lines for all occasions when the boiler is taken off-line.
2. Consider the installation of an automatic trip out system to flare on the disulphide off-gas stream to the boiler. This should be linked to the existing heat off system on the boiler.

[damage to equipment, design or procedure error, cracking]

Lessons
1. Review the process control philosophy of foul gas burners, and give consideration to the installation of automatic trip valves in the foul gas streams, linked to the normal heat off system with alternative safe disposal of the foul gas to a safe location e.g. flare.
2. Consider burning foul gas streams in burners equipped with full capacity air registers, with permanent pilot burners.
3. Confirm that the operating procedures associated with the start up, shut down and running modes are comprehensive and up-to-date.
4. Ensure the existence of approved and up-to-date comprehensive check-lists detailing the spade isolation and their sequencing required for all process streams associated with such heaters.
5. Confirm that operating personnel are fully trained and familiar with the procedures and check-lists in force.
Abstract
Ethylene cracker out of action due to fire during routine maintenance work.
[fire - consequence, cracking]

Lessons
[None Reported]
Abstract
A sprinkler alarm of control valve No.1 sounded in the guard house. The shift supervisor, immediately on the site saw a large quantity of smoke coming from the chemical room of the control laboratory. No access was possible. The site firemen entered the room wearing breathing apparatus. Due to absence of visibility, one fireman tried to force one door with his shoulder and was injured. The night operator then came with the firemen and urgency situation was stopped as it was evident that the fire had been detected and extinguished by the sprinkler system.
The cause of the incident is due to the heating not being programmed for 3 litres solution in styrene of rubber on a magnetic agitator equipped with a resistance.

Lessons
[None Reported]
A fire occurred in a hydrocracker due to a joint leak.

[fire - consequence, joint failure, cracking]

Lessons

[None Reported]
Two fires broke out in two refineries. The first fire occurred on a hydrocracker complex causing £55 million (1986) of damage. It is thought that the fire occurred due to a leak from one of the joints in a unit of the complex. The unit was shutdown.

The second is thought to have been caused by traces of oil at the bottom of an empty oil storage tank. No injuries occurred in either incident.

Lessons

[None Reported]
A leak and a subsequent fire occurred at a non-return valve on the debutaniser furnace of a hydrocracker. The unit was immediately shutdown and the fire extinguished. There were no injuries to personnel. Damage to the adjacent equipment was not severe and the unit was only shutdown for some 5 days.

The cause of the leakage on the non-return valve is thought to have stemmed from changes in bolt temperature and line tension during torrential rain at the time. This was an exposed long bolt fitting.

The bolts and flange joints were found to be of the correct material specification. Following the fire one bolt was found broken and two other bolts broke during the process of tightening flanges to facilitate line clearance for inspection.

The non-return valve was of the Duo-check type with 350mm long bolts, the NRV was not insulated, although the pipeline was.

Lessons

[None Reported]
A fire occurred in the cell of a multi-purpose plant. The incident occurred as a batch was being cooled with agitation in a holding tank when the agitation alarm sounded and the operator saw a fire on top of the holding tank. The holding tank dumped due to the action of fire on the dump valve impulse lines and the fire installation was activated. Fortunately no one was injured in the incident and no major damage occurred to equipment.

Lessons

[None Reported]
Abstract
An explosion occurred on a hydrocracker at oil refinery.
[refining, cracking]

Lessons
[None Reported]
Abstract
A leak occurred in the area of the Hydrocracker Unit feed pumps when a weld failed at a "T" piece in the mini-flow pipework associated with one of the feed pumps. Wax at a temperature of 400 degrees F and under 2,000 psig was released and ignited.

The Refinery and Authority Fire Services were in attendance, and the fire was contained with the use of water monitors, water branch pipes and the application of foam (6% fluoroprotein foam concentrate) by foam branchpipe and monitor. The fire started at approximately 1645 hours, and went out with the introduction of nitrogen to the HP Circuit at 1835 hours.

The weld failure occurred in a branch socket on a warm-up line which came off the mini-flow line on one of the feed pumps. There had been vibration on the pipework in this location earlier on the day of the incident.

The branch line was in fact not required for startup and it has subsequently been removed, along with similar unnecessary pipework on the parallel pumps. The failure is put down to excessive vibration, and that the weld throat on the socket was considered by the metallurgists to be undersized.

The fire was substantial in size with flames initially seen above the reactor circuit fin-fans, however it was well contained by the fire service and damage was confined largely to switches, cables and some steelwork. Extensive pipework and metallurgical checking for integrity followed the fire and complete renewal of the fire exposed bolting was required, however the pipeline insulation and fire fighting actions were good enough to protect the pipework and valves in the fire area. Some uninsulated pipework required replacement.

Lessons
The incident re-inforced thinking on:
1. The hazards of pipework and fittings vibrating.
2. The need for good access to valves.
3. The desirability of remote isolating valves for large hot inventories.
4. The desirability of remote electrical isolation for fin-fan motors.
5. The need to survey extensively for redundant pipework and fittings associated with line systems.
Abstract
A fire occurred involving a precipitator at a refinery Fluid Catalytic Cracker Unit (FCCU) plant.

Lessons
[None Reported]
# Abstract

A hot slurry developed when a fitter was attempting to remove the safety relief valve from the rerun tower reboiler on a catalytic cracker. The oil leak vaporised and a large vapour cloud drifted over the lubricating oil processing area. Water sprays were commissioned to disperse the vapour cloud and to protect the plant. Fitters dressed in reflecting proximity suits were able to refit the bolts and pull up the flange on the relief valve after the system had been depressured.

# Lessons

[None Reported]
**Source**: IChemE  
**Location**: California, USA  
**Injured**: 45  
**Dead**: 4

<table>
<thead>
<tr>
<th>Abstract</th>
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<tbody>
<tr>
<td>A series of explosions at an oil refinery reformer unit caused by a rupture to an 8 inch naphtha and hydrogen feed pipe. The large number of injuries was due to the close proximity of a construction crew working in the area. Two were declared dead at the scene and a further two later in hospital. The ensuing fires were quickly contained and extinguished, but caused offsite traffic within several blocks to be stopped. As a precautionary measure, a second reformer unit was shutdown pending the investigation. Fire officials cited higher than normal line pressures just before the blast. The reformer was being brought back on line after being shutdown for several weeks for repairs. Following the incident, it was expected that the plant would be returned to service within the month.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>[pipeline failure, fire - consequence, fatality, plant shutdown, refining, injury]</td>
</tr>
</tbody>
</table>

[None Reported]
A fire caused by rupture of reformer catalyst tubes.

[None Reported]
A bolt had sheared whilst being loosened on a two litre autoclave designed for alkoxylation reactions. Investigation revealed that all the remaining bolts were elongated. Examination revealed that the cause of failure was over torquing of the bolts.

Lessons

Torque wrenches set to the appropriate manufactures settings should be used.
Leak on the catalytic cracker reactor shell with ignition. The substantial fire was contained and the plant shutdown, for reactor repair. During subsequent recommissioning a seal tube inside the bypass stack seal pot collapsed as a result of external pressure in the pot. The two incidents combined were estimated as costing some £170,000 (1985) to repair.

[None Reported]
Source: LLOYDS LIST, 1985, 24 AUG.
Location: Pulua Bukom Island, SINGAPORE

Injured: 0  Dead: 0

Abstract
A fire occurred in a hydrocracker plant on a refinery.
[fire - consequence, refining, cracking]

Lessons
[None Reported]
Abstract
The tubes of a catalytic reformer ruptured causing a leak of hydrogen which caught fire.

Lessons
[None Reported]
**Abstract**

Ignition of natural gas pockets which entered the furnace of a reformer during attempts to light an auxiliary boiler burner resulted in an explosion.

**Lessons**

[None Reported]
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.

Lessons
Solutions proposed
1. Systematic cleaning of the sewer line (hydrocarbon deposits).
2. Change in the vent outlet.
Abstract
A fire occurred in a hydrogen and catalyst loading lines of heavy oil unit. The most likely cause was that a hydrogen purge pipeline failure allowing hydrogen to escape. This mixed with hot oil bringing the temperature to approximately 825 degrees F, i.e. above the auto-ignition temperature.

Lessons
[None Reported]
Abstract
An incident occurred on a 300,000 tonne per year ethylene cracker causing the plant shutdown.

Lessons
[None Reported]
Abstract
A fire occurred on an ethylene cracker causing damage to electrical and instrument cabling. Prior to the accident there was considerable voltage cycling which got worse, causing compressors to surge etc. Eventually the furnace tripped. On restoration of power, the furnace could not be restarted due to a microswitch on a damper being closed. This was not realised and it was thought that the fault was due to a programmable logic controller. While this was being sorted out, cracked gas was being wrought across to the cracker to prevent shutdown of the acetylene converter. There was a space velocity of 1/10 of the previous flow and the gas was rich in hydrogen. The temperature in the acetylene converter went off scale, the outlet line heated up causing a leak at a flange. This ignited and impinged on pipework under pressure and ruptured. The catalyst did not fuse but carbon was present downstream.

Lessons
[None Reported]
16 May 1985

Source: "LLOYDS LIST, 1985, 6 JUN.
Location: Stenungsund, SWEDEN

Injured: 0  Dead: 0

Abstract
Ethylene cracker put out of operation due to collapse of cooling tower.

Lessons
[None Reported]
Phenol and formaldehyde were added to a reactor but the agitator failed. Caustic was added and heating started, safety valve and bursting disc blew and agitator flange blown out. A gas cloud formed which ignited and removed the walls of the plant.

Lessons

[None Reported]
A power failure and extensive freezing occurred while attempting to restart one of two hydrocrackers. A fire occurred in the hydrocracker unit causing extensive physical damage to the whole unit.

Lessons

None Reported
Abstract
The jib of a contractors crane collapsed as it was being raised into position. The 300 tonne capacity crane was being fitted with a long jib to enable high lifts to be carried out at the hydrocracker complex major overhaul. The crane had already successfully carried out a high lift and was being moved to carry out a further lift on an adjacent flare stack. The jib had been removed to allow the crane to be re-positioned. On reaching the new work site the jib was reconnected and was being lifted into position when the failure occurred. Fortunately no injuries occurred and no equipment, other than the crane, was damaged.

Initial enquiries indicate that the two pins which locate the mast fall back system had been incorrectly inserted from the inside, with the result that it was possible for the jib root section to come into contact with the pins.

Lessons
[None Reported]
Abstract
During the addition of phthalic anhydride to a varnish kettle which contained a mixture of soya bean oil, glycerol and caustic at 200 degrees C, an explosion occurred at the charging hatch. The operator was blown back by the force and broke his arm as he fell to the ground. Two other operators standing nearby were not injured. The charging chute was also propelled upwards and damaged the kettle agitator motor. The content of the vessel was unaffected. The bursting disc in the kettle pressure relief line did not rupture. The steel charging chute was not bonded to the reactor because of the presence of a non-conducting gasket in between, hence the most likely cause of the explosion is the ignition of phthalic anhydride dust by a static discharge from the unbonded chute.

Since this accident, the company was required to check that all equipment used to transfer phthalic anhydride powder is bonded to earth and to amend the operating procedures and ensure that the dangers associated with phthalic anhydride are highlighted.

Lessons
[None Reported]
Abstract

A fire at a 350,000 tonne/year ethylene cracker seriously injured two workers and caused the cracker to be shut down entirely for several weeks. The cause of the fire, which started around pipes next to a furnace which had been shut down for maintenance and spread to two other furnaces, is not given. One estimate of the cost of the damage, (which was denied by the operator), was 1 billion Lira (1984), not counting loss of production costs.

Lessons

[None Reported]
Abstract
A fire occurred on the hydrocracker while three instrument mechanics were dismantling the bonnet and servo motor of an ESV valve in the high pressure reactor circuit. The plant had been shut-down on two days before the incident occurred, for repairs associated with the recycle gas compressor. The reactor circuit had then been depressurised but not gas freed. The extent of the fire was limited and it was extinguished after 45 minutes when the lines were purged with nitrogen. The three men suffered first and second degree burns but fortunately their faces were largely protected by their breathing apparatus.

Lessons
Working on a live flare header is always a hazardous operation and needs a very careful examination of each step. Detailed planning and close control is essential for this type of work.
Abstract
A fire occurred on a refinery hydrocracker plant. Source of ignition was autoignition.

Lessons
[None Reported]
Source: IChemE
Location: ERIAG

Injured: 0  Dead: 0

Abstract
Leaking drum at a refinery thermal cracker plant.
[drums, refining, cracking]

Lessons
[None Reported]
Abstract
Fire occurred on a cooling tower a refinery Fluid Catalytic Cracker Unit (FCCU) plant.

Lessons
[None Reported]
Abstract
An explosion occurred in a cracker furnace. The explosion was caused by burner valves being left open during start-up. Ignition when burners lit. Laboratory test did not show flammable mixture. Fuel gas.

Lessons
[None Reported]
2989  01 May 1984

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

Abstract
Fire on a reformer at a petrochemical methanol plant due to tube failure. Source of ignition was furnace.

[fire - consequence]

Lessons
[None Reported]
Search results from IChemE's Accident Database. Information from she@icheme.org.uk

Source: IChemE
Location: , KUWAIT
Injured: 0  Dead: 0

Abstract
Damage to a floating roof tank at a refinery hydrocracker plant when the roof sank.
[floating roof failure, damage to equipment, refining, cracking, storage]

Lessons
[None Reported]
Source : IChemE
Location : , USA
Injured : 0   Dead : 0

Abstract
Mechanical equipment failure involving a reactor on a refinery Fluid Catalytic Cracker Unit (FCCU) plant.
[reactors and reaction equipment, refining, fluid cracker]

Lessons
[None Reported]
During the recommissioning of a hydrocracker, a tube failure occurred in the hydrogen recycle heater. The resulting explosion damaged other tubes and part of the heater refractory lining. The fire service, who were already on the unit to deal with a small fire on a leaking joint, contained the fire within the furnace and minimised damage to the casing.
Apart from minor burns, no injuries were sustained.

[fire - consequence, cracking]

Lessons
[None Reported]
Source: IChemE
Location: USA
Injured: 0  Dead: 0

Abstract
Fire at a refinery reformer plant.
[fire - consequence, refining]

Lessons
[None Reported]
Abstract
A reformer furnace was lit for the third time after a shutdown and part way through the sequence there was an explosion in the firebox. Severe damage was found in the fire box. The most likely cause was a tube leak allowed combustible material pressurised in the front end of the plant to leak and collect in the firebox. A fault tree showed many possibilities for explosions.

Lessons
[None Reported]
Abstract
Damage to a reactor at a refinery Fluid Catalytic Cracker Unit (FCCU) plant caused by refractory failure.
[refining, reactors and reaction equipment, damage to equipment, fluid cracker]

Lessons
[None Reported]
An explosion occurred on a refinery Fluid Catalytic Cracker Unit (FCCU) plant burner.

[refining, fluid cracker]

[None Reported]
Abstract
The top section of both CO2 regenerator towers, on an ammonia plant, failed due to vacuum being formed inside the tower during a short plant breakdown to repair a leaking reformer tube exit pigtail. The conditions for vacuum formation were established as a result of abnormal operating conditions and actions, and maintained due to failure of the nitrogen blanket protection system.

Lessons
[None Reported]
<table>
<thead>
<tr>
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<tbody>
<tr>
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</tr>
<tr>
<td>Injured</td>
<td>0</td>
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<td>Dead</td>
<td>0</td>
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</table>

**Abstract**

Fire at a petrochemical steam cracker plant involving a compressor and lube oil which was caused by seal failure. Source of ignition was hot surface.

[fire - consequence, seal failure, cracking]

**Lessons**

[None Reported]
A fire occurred on a naphtha tank in a refinery. The tank was 50 feet high with a 100 foot circumference and contained approximately 1.56 million gallons of naphtha. It was heavily involved in fire when the fire officer arrived with four foam pumpers from the refinery. Realising that the fire was beyond the capacity of the refinery department to handle alone, the fire officer ordered a fire alarm box sounded.

[fire - consequence, refining]

Lessons

[None Reported]
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.

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.
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.

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The second part of the temperature rise to 160 degrees C was caused by the autocatalytic decomposition of the mixture.
**Abstract**

The most likely source of ignition of the 6000,000 barrel floating roof tank fire was incandescent carbon particles discharged from the top of a 250 foot high refinery flare stack situated 350 feet from the tank. The 256 foot diameter x 66 foot high tank, which contained 348,000 barrels of crude oil at the time of ignition, was arranged within a standard individual dike. It had a single mechanical seal and was equipped with a 12 inch high foam dam but no foam delivery lines or outlets. Reportedly, there were several cracks extending over 11 inches on the single plate floating roof. Inspections of the roof a few days before the fire revealed oil seepage onto the roof deck. There had been no oil transfer in the 24 hours preceding the fire.

When first noticed, the fire involved about half the tank roof area. It progressively spread to the entire surface. Cooling water streams were positioned to protect two 138 foot diameter, 142,000 barrel fixed roof vacuum gas oil and fuel oil tanks situated 200 feet away. Oils were being pumped out of the three tanks in preparation for major foam attack when, 12 hours into the fire, a violent boilover occurred in the crude tank. The ensuing fire covered 4 acres and destroyed or damaged much of the fire fighting equipment including two foam trucks. This was followed two hours later by a second less violent boilover. The major foam attack, which commenced 21 hours after ignition, continued for fourteen and a half hours before extinguishment was complete. The crude tank was destroyed, two fixed roof tanks badly damaged and 132,000 barrels of crude oil consumed.

This fire involved the use of 44 pumpers, 6 elevating platforms and 14 foam trucks from four nearby refineries and the public fire service. In addition, 66 commercial tankers and vehicles transported the 201,599 U.S gallons of 30% and 6% foam.

**Lessons**

[None Reported]
Abstract
Fire at a refinery Fluid Catalytic Cracker Unit (FCCU) plant involving a reactor. Source of ignition was electrical.

Lessons
[None Reported]
Abstract
Fire in catalytic hydrocracking unit on a refinery.
[fire - consequence, refining, hydrocracker]

Lessons
(None Reported)
06/19/1983

Source: INSTITUTE OF INSURERS
Location: Pembroke, UK

Injured: 0  Dead: 0

Abstract
50 ton of catalyst powder spilt. Spill.

Lessons
[None Reported]
Abstract
An explosion occurred on an ethylene cracking furnace causing extensive damage requiring the demolition of the furnace. At the time of the explosion the furnace was cooling back following a decoke operation. The fuel gas supply to all burners had been blanked at the end of the decoke operation. A transfer line valve on the cracked gas system was passing and this allowed gas into the furnace allowing a flammable mixture to be formed. Ignition was probably from the furnace lining. Leak [damage to equipment]

Lessons
The following recommendations were made.
1. The need for personnel to adhere to operating procedures should be emphasised in particular:
   - The fact that a furnace requires close attention during the cooling down period as much as when operating, and an initialled check list for close control should be considered for this.
   - The need to pace the rate of a shut down to a manageable rate of events.
   - The need to organise the work to achieve a clear allocation of responsibilities to individuals.
2. The cracking furnace shut down procedure should be modified so that a positive flow of steam is maintained through the furnace coil to atmosphere until after efforts to improve the reliability of the cracked gas transfer valves with regard to both operability and shut off cracked gas can be isolated from the furnace by blanking.
3. The cracking furnace shut down procedure should also be modified so that plate dampers are not fitted until after cracked gas has been isolated from the furnace by blanking.
4. Efforts to improve the reliability of the cracked gas transfer valves with regard to operability and shut off.
5. The relatively small amounts of hydrocarbon required to produce an explosive mixture in a confined space should be brought to the attention of factory personnel generally.
Source: EUROPEAN CHEMICAL NEWS, 1983, 27 JUN.
Location: Dunkerque, FRANCE

Injured: 0  Dead: 0

Abstract
Fire in control room at steam cracker.
[fire - consequence, cracking]

Lessons
[None Reported]
Abstract
An explosion occurred at igniter factory. Three employees were repacking dried, centre-core igniters with propellant when two explosions occurred. The centre-core igniter was a tubular product, made of a very porous propellant. The propellant was dried in cylindrical aluminium containers into which heated air was blown. On the morning of the explosion the drying process, which usually took some days, was terminated. Over an hour later the aluminium containers with propellant were moved to a production room for repacking. Present in the production room was a mushroom mixer. The first explosion was initiated by a propellant fire in the mixer which was followed by a deflagration of propellant in one of the aluminium containers, which stood in front of the mixer. The second explosion occurred when propellant in another aluminium container was detonated. From the investigation into the electrostatic charging of the centre-core igniters and the subsequent discharging the conclusion can be drawn that during the actual drying process the centre-core igniters were strongly charged by the air flow, and that the discharge after termination of the drying process was extremely slow. Therefore the igniters still contained a great deal of charge at the moment when repacking started. As no special measures with respect to electrostatic charging of personnel had taken place, the employees were also charged. A transfer of charge in the form of a spark could, therefore, take place. The energy released in these sparks is by no means sufficient to ignite the centre-core igniters, but is sufficient to ignite propellant dust, which was dispersed in the production room whenever the mixer was used. Therefore the most probable cause of the explosion was the electrostatic charging of the centre-core igniters followed by a transmission of the charge to one of the employees and arc discharge from this employee to a conductor. The mixer was the most probable source of spark discharge, igniting propellant remains. The resulting jet of flame ignited the propellant in front of the mixer, causing the container to explode. The propellant in the remaining container ignited later. Fatality.

Lessons
[None Reported]
Abstract
A fire occurred at a refinery Fluid Catalytic Cracker Unit (FCCU) plant.

Lessons
[None Reported]
Abstract
Rupture of a 12 inch recycle oil slurry line at 120 to 160 psi and 600 to 700 F of a FCC (Fluid Catalytic Cracking) unit resulted in immediate ignition of the slurry. The failure occurred in a pipe rack and caused the failure of a 600 psi steam line which hampered the fire fighting. The FCC reactor, regenerator, fractionator, as well as related piping, instrumentation and electrical equipment sustained severe damage.

Lessons
[None Reported]
Source: INSTITUTE OF INSURERS
Location: Baroda, INDIA
Injured: 0  Dead: 0

Abstract
Explosion in the primary reformer convection zone and in the process air piping area of an ammonia plant.

Lessons
[None Reported]
Source: IChemE
Location: PHILIPPINES
Injured: 0  Dead: 0

Abstract
Fire at a refinery Fluid Catalytic Cracker Unit (FCCU) plant.
[fire - consequence, refining, fluid cracker]

Lessons
[None Reported]
A fire and machinery breakdown on a refinery Fluid Catalytic Cracker Unit (FCCU) plant involving a compressor. The cause of this incident was blade failure.

Lessons

[None Reported]
Abstract
Explosion at ethylene plant during a non-routine start-up knocked out 2 furnaces.
Two naphtha cracking furnaces were built next to each other, using a common stack. While one furnace was in operation some burners of the other furnace had to be lit for freezing precautions. Before the main fuel gas valve could be opened, two important checks were carried out to avoid an explosive mixture in the fire box:
1. An automatic leak test via the interlock system is provided to check whether all burner valves are closed.
2. All 112 burner valves had to be checked manually to be in the closed position.
On the day of the incident, the leak test via the interlock system was in bypassed mode, several valves stood in open position and were not checked. The interlock system allowed main fuel gas valve to be opened, introducing fuel gas into the fire box. Minutes later the fuel air mixture violently ignited. Due to the pressure wave, from the explosion, emergency reliefs opened, the firebox, refractory structures and foundations were all deformed.
The cause was due to misunderstanding, miscommunication in a non-routine job, partly bypassing of interlocks and incomplete following of standard start-up procedures.

Lessons
[None Reported]
Abstract
An explosion occurred in a primary reformer of ammonia fertilizer plant.

Lessons
[None Reported]
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**Abstract**

Explosion and fire at chemical plant involving a vat of acrylonitrile.

**Lessons**

[None Reported]
Abstract
An explosion occurred on a refinery benzene plant reformer. Source of ignition was operator igniting furnace. Substances involved: fuel gas and methane.

Lessons
[None Reported]
Abstract

Explosion in a process reactor due to auto-catalytic decomposition of a mixture of Dimethyl Sulphoxide (DMSO) and p-nitrotoluene sulphonic acid. In anticipation of the return to service of the refrigeration system for a reactor following maintenance, the 2000 gallon (9090 litre) stainless steel reactor was charged with DMSO and p-nitrotoluene sulphuric acid. However, the needed repairs were found to be much more extensive than previously anticipated, and the downtime for repairs was expected to be several days. The batch was put on hold with the agitator running, cooling water on the jacket, and steam valve closed. The batch appeared to be holding a steady temperature of 60 degrees C. Operating personnel were reassigned to other tasks for the duration of the maintenance outage. The vessel was left unattended for 5 days with no routine checks.

On the day of the accident, a foreman in an adjacent office reported fumes, and they were subsequently traced to the reactor vent. When the building foreman checked the temperature recorder, he found the reactor temperature to be 160 degrees C and rising at a rate of 3 degrees C/5 minutes. The 24 hour circular chart on the temperature recorder had not been changed since the batch was charged, and the foreman noted that the pen had traced a line at 118 degrees C for 3-4 revolutions prior to the rapid rise to 160 degrees C. The manual steam valve was found to be partially open, although the controller on the downstream automatic valve was set at zero. The water supply valve was found to be only partially open and was now opened fully. The black, bubbling reaction mass began to overflow from the loose manway opening. As the temperature continued to steadily rise (the last observed vessel temperature was 190 degrees C), the foreman directed that the building be evacuated. The reactor exploded as the last person cleared the area. The reactor itself was separated into four major pieces, and damage to surrounding vessels, steelwork, and nearby buildings was substantial. Subsequent testing determined that the reaction mass would decompose violently at temperatures in excess of 200 degrees C. The most probable sequence of events determined by the investigation team was that the automatic steam valve was leaking through, slowly raising the reaction mass to boiling temperature and slowly driving off water. As the water was removed, the more concentrated acid accelerated the decomposition of the DMSO, and the degradation by-products further de-stabilised the reaction mass. With most of the water removed, self-heating of the reaction, mass began at 120 degrees C.

Lessons

[None Reported]
Abstract
Fire on a refinery Fluid Catalytic Cracker Unit (FCCU) plant involving a regenerator caused by insufficient inert gas.

[fire - consequence, refining, inert gas failure, fluid cracker]

Lessons
[None Reported]
Search results from IChemE's Accident Database. Information from she@icheme.org.uk

Source: IChemE
Location: JAPAN
Injured: 0  Dead: 0

Abstract
Explosion at a refinery reformer plant involving a reactor.
[reactors and reaction equipment, refining]

Lessons
[None Reported]
Abstract
Fracture of a glassware plant led to release of toluene and ignition causing explosion and fire. Breakage of the glass was either vibration of an agitator or pressure in a reactor forcing glassware upwards. The ignition source was probably static collected on an insulated flange.

Lessons
The following recommendations were made:
1. All plant and equipment to be installed in accordance with the designers’ and manufacturers’ instructions and then inspected and maintained to that standard.
2. Staff engaged on maintenance to receive adequate training and have their attention directed to any components which are particularly important if the plant is to be operated safely.
3. Earthing of metalwork close to valves, pipe-joints etc. on glass or other insulated pipework to prevent the accumulation of a static charge.
Abstract
Machinery breakdown on a reformer on a refinery hydrogen plant due to operator error.
[mechanical equipment failure, refining]

Lessons
[None Reported]
Abstract
Start-up was underway following a 3 week turnaround. Water batching was in progress and the initial water charge had been processed through an autoclave, through the crystalliser, and was in the filter tank. The next step was to transfer the water batch under pressure from the filter tank to the ammonia still. The operator began heating the water batch and when the temperature reached 150 degrees C, he lined up the correct valves to the ammonia still and steamed the line. He then applied the customary 110 psig steam pad to the filter tank and began transfer. All conditions were apparently normal. Approximately ten minutes into the transfer, the ammonia still ruptured, spraying hot water and steam from a vertical crack in the sidewall of the vessel. The crack extended from the bottom dish to the top head and was approximately 6 inch wide at the middle of the tank. It was found later that the pressure was 20 psig and the temperature was 118 degrees C, and that the rupture disc was found to be intact.

The cause of the rupture, which was at well below normal operating pressure, was due to corrosion of the steel tank sidewalls. This had occurred when the brick lining had become cracked and the corrosive liquid was able to seep through to the metal.

Lessons
The following recommendations included:
1. The method for evaluating the condition of brick lined vessels in pressure service should be improved and include an accurate assessment of the substrate steel thickness and strength.
2. Consideration should be given to replacing these vessels with alloy metals.
Abstract
Five maintenance personnel were killed and another eight injured following failure of a 72 inch diameter catalytic cracker riser line. The incident occurred during recommissioning following scheduled turnaround at a time when there was still a number of maintenance personnel on the plant. A complete fracture of the spent catalyst riser occurred, releasing about 400 tonnes of hot catalyst at a temperature of 1200-1300 degrees F on to a group of pipefitters working below. The spent catalyst riser comprised two sections, clamped together by a floating ring joint. The clamping arrangement included a "Van Stone" flange made up of steel plate which was butt-welded to the end of the pipe following which the weld was machined. As a result of the failure, and possibly assisted by the flexibility provided by the lower expansion joint, the curved section of the riser dropped downwards and allowed virtually the entire contents of the regenerator to empty out onto the area below. A company in the USA reported checking 22 other Van Stone flanges of all sizes from the same manufacturer in similar FCC units and found poor quality welds. It is therefore probable that the poor quality weld of 40 years ago fatigued and resulted in progressive cracking which ultimately failed. Fatality

Lessons
(None Reported)
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]
An agitator started to fail in a resin plant due to a burnt out magnetic switch. The power source was cut off and an effort was made to supply cooling water and agitation to the other autoclaves. The temperature rose and steam flowed into the odour control duct. The first explosion occurred. See 21st August, record 2387, for second explosion. Fatality.

Lessons

[None Reported]
Abstract
A fire and explosion occurred causing heavy damage and evacuations of nearby residents. The fire began inside the plant and spread to an adjacent cracking tower used to separate petroleum products. The tower exploded and toppled.
[fire - consequence, damage to equipment, collapse]

Lessons
[None Reported]
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]
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**Abstract**

Leak of fuel oil in cooling system ignited in refinery hydrocracker plant. Source of ignition was autoignition. Flange leak.

**Lessons**

[None Reported]
Abstract

One 40mm thick carbon steel reactor in a refinery cyclic catalytic reformer failed catastrophically while in standby condition under treat gas pressure. The reactor was of cold wall design with an internal insulating refractory lining. It incorporated a metal shroud to prevent hydrogen bypassing the catalyst bed through the refractory lining. There was no gas flow through the reactors. The temperature of the catalyst bed, and the reactor wall, cooled over the period of a week to atmospheric temperature. As a result of falling atmospheric temperature, the metal temperature reached 5 degrees C and one of the reactors fractured into 6 pieces. The fracture originated from the area where the shroud was welded to the shell. The fracture face contained no evidence of significant pre-existing defect or deterioration of the steel. There was no pressure surges or other process changes before failure. The internal shroud had been replaced seven months previously, and the weld joint had not been heat treated.

Data gathered in the investigation showed that the reactor steel had a low toughness at the failure temperature. However, even with this low toughness, cracks greater than 12mm would be required to initiate failure. The only pre-existing cracks that could be identified were approximately 1-3mm in depth associated with the first pass of the shroud support ring-to-shell weld. While these cracks were not of sufficient depth to initiate failure at the toughness of the base metal, they did serve to produce dynamic strainage embrittlement at the crack tip. This embrittlement was produced during the reinstallation of the shroud support ring by heat and strain of welding. The effect was to lower the already low toughness by a factor of 10. Growth of the small cracks into this embrittled zone provided the trigger for the vessel failure.

Lessons

Welding on steel that is susceptible to dynamic strainage embrittlement can produce initiating conditions for brittle fracture. Susceptible steels are carbon, carbon-molybdenum and carbon-manganese-molybdenum steels that contain nitrogen but less than 0.015 % aluminium; e.g. steel that have been air blown and not aluminium killed. Stress relief, or post weld heat treatment, will remove the effects of strain embrittlement.
Abstract

Laboratory work. A laboratory assistant was setting up an experiment in fume cupboard, which involved refluxing with petroleum ether in a 1 litre flask. A stirrer was incorporated into the top of the flask. After adding all constituents including petroleum ether to the flask, everything was ready to start the experiment. The assistant switched on the cold water for refluxing, switched on the oil bath heater (2 thermostats in oil bath), and then found that the plug for the stirrer motor was not in socket. The assistant reached over to put the plug in the socket and immediately received an electric shock. The assistant was thrown involuntarily backwards and all of the glass ware was knocked onto the floor. The flask shattered spraying the assistant and surrounding area with petroleum ether. About 2 and a half metres away, another experiment was taking place involving an electric heater. Approximately 20 seconds after the first incident, a small fire started near the second equipment due to the heat source there igniting the petroleum ether. The assistant’s coat did not catch alight. Another assistant came in and put out the fire.

Lessons

It has been concluded that a small electrical fault in the plug, probably due to wear and tear, started the chain reaction of events. The result could easily have led to a fatal injury.

It is recommended that:
1. Plugs are checked for safety regularly
2. Switches are ‘off’ when plug is removed
3. Locate electric sockets either outside of fume cupboards, or in a more accessible position in the fume cupboard
4. Be aware of other experiments being carried out nearby
5. Do not be complacent about carrying out routine work, the unexpected can happen
Shell rupture of a secondary reformer on an ammonia plant occurred. A week prior to the incident a significant increase in steam and water droplets was observed from the water jacket vent pipe. This was thought to be caused by a perforated steam collector inside the jacket and that water was being entrained by escaping steam.

A sudden blow-out occurred on the Saturday afternoon. Process gas escaped along with steam and hot water. No one was scalded by the hot water and the gas did not ignite. Following de-bricking of the refractory lining, a site weld on the process air inlet pipe was found to be faulty. This had allowed air to fill a space between two layers of refractory lining. The outer layer of light concrete refractory had disintegrated and the air ignited with process gas. The outer layer of concrete was found to be in poor mechanical condition. A bypass in the insulating concrete of the outer layer had occurred due to catalyst fusing on the lining some years earlier. This allowed combustible gases to build up behind the inner refractory layer.

**Lessons**

The following lessons were learned by the company after the incident and these were applied to future reformer operation:

1. Visual inspections of certain sections of the inner refractory are misleading and do not allow the condition of the outer layers to be determined.
2. Welds on critical plant items should only be carried out by qualified welders and the welds x-rayed afterwards.
3. Inlet air pipework should be no less than 5mm thick to improve strength & ensure good welds can be made.
Abstract
A shell rupture occurred on a secondary reformer. A week prior to the burst, a significant increase of steam and water droplets from the water jacket vent pipe had been observed, together with a slight drop in the water level on the visual gauge. This was due to the submerged part of the steam collector inside the jacket was perforated and that water was being entrained by the escaping steam.

The blowout which occurred a week later was extremely violent. There was an instantaneous drop in pressure and the escaping gas blew the hydraulic guard on the jacket and escaped through the vent.

The jacket remained intact and the gas did not ignite. Luckily, no one was scalded, as might have been the case if people had been under the guard vent of standing on the nearby primary reformer platform.

Cooling down after the plant trip provided to be a problem because of gas escaping from the leak. As soon as the plant was under nitrogen circulation, the jacket was cut open at what was judged to be the nearest point to the burst according to the noise caused by the leak.

The main crack was about 350 mm long and situated above the process air inlet nozzle at a height corresponding to the jacket-steam/water interface. The shell had clearly overheated and the cone shell had bulged over approximately 90 degrees.

The following observations from the inside were made:

Before debricking:
1. Traces of unburnt black carbon on the hot face bricks and incoloy liner.
2. The refractory lining appeared to be in a satisfactory condition, apart from hair-line cracks in the bricks and irregular spacing of the expansion joints. These points had been noted on previous inspections and were considered to be normal.

After debricking:
1. Row-by-row debricking revealed a partial absence of insulating concrete (50% alumina) above the incoloy air-inlet pipe and traces of unburnt carbon on the shell wall.
2. The cause of the trouble was immediately apparent, i.e., a site weld behind the hot face on the 200 x 3 mm incoloy air-inlet pipe had failed over about 300 degrees, allowing air to escape upwards into the light insulating concrete. The latter had disintegrated, the air had ignited.

Lessons
[None Reported]
Abstract
An explosion occurred in the batteries of an instrument 24V DC supply (40 amp) on a polyvinyl chloride plant. The unit, located behind a control panel, supplied the services and charging areas of the plant. As a result of this incident, the 24V instruments supply to the control on the reactor agitator was lost, fortunately the agitator which stopped was quickly manually re-started, thus saving the material in the reactor. The most likely cause of the explosion was the failure of the "Blocking Diode" together with the failure of at least one cell in the associated battery. This allowed the remaining three batteries to discharge through the failed unit heating it up explosively. The blocking diode failed due to an inherent fault (i.e. underrated PIV.)

Lessons
1. All sealed battery systems have their blocking diodes replaced with a PIV of at least 24V.
2. The sealed units involved did not have, in common with other site systems, remote alarms and property rated diodes. This shortcoming was corrected.
Abstract
Hydrogen sulphide (H2S) was released from a manhole of a thiophosphates neutraliser whilst the manlid was open for sampling at the end of a batch. The abnormal evolution of hydrogen sulphide occurred due to the agitator not operating during neutralisation of a batch which had been overcharged with phosphorous sulphide at the thiol acid stage. When the agitator was switched on after sampling rapid reaction occurred resulting in water of neutralisation reacting with the free phosphorous sulphide to give hydrogen sulphide.

Lessons
[None Reported]
Abstract
A gas compressor train failed catastrophically on a catalytic cracker, as a result of uncontrolled overspeed well in excess of the design limitation. The unit was in the early phases of a planned shutdown. The next step was to secure one of the two turbine-driven gas compressors to compensate for reduced gas production. Before this was done, a blower motor unexplainably tripped off the line. It could not be restarted. The reduction of air to the unit resulted in low slide valve differential pressures, triggering automatic oil diversion from the unit. The control centre instructed the operators to initiate the contingency shutdown procedure. They actuated the manual trip on the No. 1 gas compressor turbine, which should have closed the valve and stopped the turbine. As a precaution, the stop button was pushed on the electronic governor, to perform the same function as the manual trip. The stop button would have also closed the steam chest valves, if the governor had not been bypassed. The operators observed only that the valve latching mechanism had released. They were then instructed by the control centre to shut down a gas compressor and, assuming that a second compressor needed to be secured, pushed the stop button on the No. 2 gas compressor. They returned to the No. 1 gas compressor and, on beginning to close its suction valve, heard an increase in noise level. They evacuated the area and within a few seconds the machine failed in overspeed, hurling pieces of the shaft and coupling through the bearing casings and coupling guard.

Lessons
1. The trip/throttle valve internal surfaces were coated with solid deposits from the steam system, preventing the valve from slamming shut. Manually turning the unlatched valve only jammed the stem, so the valve did not close. Operating procedures were changed to require that trip/throttle valves be exercised daily rather than weekly, to ensure they were free to move.
2. Had the governor not been bypassed, the steam chest valves would have closed when the stop button was pushed. The electronic governor systems were debugged to eliminate spurious trips. Operating procedures now mandate that the governor speed control not be bypassed. The system was modified so that the steam chest valves, in addition to the trip/throttle valve, are closed when the mechanical overspeed trip mechanism is actuated.
3. Closing the compressor suction valve first unloaded the turbine, allowing uncontrolled speed increase. Operating procedures now state that the discharge valve must be shut first when securing a ‘shutdown’ compressor.
4. The second call from the control centre was made because no drop in gas flow was observed following the first call. The control centre did not know the manual trip and stop button on No. 1 compressor had been actuated. The fact that there was no decrease in gas flow following the first request was not transmitted to the operators. Re-evaluation of the overall adequacy and placement of instrument readouts was recommended.
5. Operators and control centre personnel were given refresher training on procedures using documentation revised in light of the incident.
6. The cause of the motor trip on the blower was not determined.
Vinyl chloride release when autoclave bursting disc failed due to fault on water rotameter to stirrer gland.

[bursting disc failure, instrumentation failure]

[None Reported]
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**Abstract**
Release of vinyl chloride from autoclave bursting disc due to failure of a control instrument. Instrumentation failure.

**Lessons**
[None Reported]
Abstract
This accident took place at the top manhole platform of a depropaniser spare base section at about 24 metres above ground level. During normal operation the lower part of the depropaniser column, the cracker, gradually becomes filled with rubbery polymer and eventually product quality can be affected. To avoid this, the lower part is duplicated so that one can be taken out for cleaning without interrupting production. The cleaning operation, although of a good standard, leaves small residues that need to be deactivated. This is achieved by treating with a hot solution of dilute sodium nitrite. The nitrite is received as a concentrated solution and diluted with water in the column. The water is charged by a hose introduced at the top manhole (left open after the cleaning operation) and nitrogen is blown through the strong nitrite to achieve good mixing with the water.

On the morning of the accident, all manholes except the top one had been closed, dilution of the strong nitrite with water begun and the nitrogen rousing was in commission. Because of a temporary water shortage to the site it was thought possible that the addition of water to the nitrite dilution had ceased. The supervisor decided that he would check if water was flowing. He left with an operator. The supervisor proceeded up the column. Shortly afterwards the supervisor was found with his head in the top manhole. Asphyxiation. Entry into confined space. Fatality.

Lessons
The following recommendations were made:
1. By publicity and discussions, the hazards of asphyxiating gases must be re-emphasised especially when they are in confined spaces into which personnel can put their heads.
2. Where such a situation could arise, the first consideration must be to prevent it. Thus, in the case of the depropaniser base section, a modification of procedures (and possibly of equipment) may allow the dilution operation to be carried out in such a way that it is impossible to put their heads into the nitrogen swept space at the top of the column.
3. Where a confined space containing asphyxiating gas open to the atmosphere is unavoidable, the connection aperture must be made such that people cannot put their heads into it. It is likely that most asphyxiation incidents could be avoided if this was done. There is no reason why such a device should interfere with any legitimate activities associated with the aperture, eg looking in from the outside, pouring materials etc.
Abstract
Fire at a refinery steam cracker plant involving naphtha.
[fire - consequence, refining, cracking]

Lessons
[None Reported]
Isolation of slurry pump at base of catalytic cracker by fitting a blind was being carried out. Oil sprayed out, ignited and caused a major fire. Source of fuel was the catalytic cracker column slurry. 13 lines containing hydrocarbons failed in the fire area. An 18 inch valve was found open in the suction line of pump.

[fire - consequence, cracking, slip plate insertion/removal, blind/spade/slip plate, isolation inadequate]

Lessons

[None Reported]
Abstract
A fire seriously damaged a plant. The cause was a rupture approximately 10 inches long in an oil line or pump at the base of a catalytic cracker.

Lessons
[None Reported]
Abstract
About 7 tonnes of liquid propane were released over 40 minutes from a 350 mm longitudinal crack in a 60 mm pipeline used as a startup line to the cracker and normally shut off. The pipe was connected to the bottom of the propane feed line and had collected water which had frozen in the winter period cracking the pipe. The crack was up to 5mm wide and initially a small propane leak through this crack had kept the pipe, which was insulated with poly-urethane foam, cooled down so maintaining the ice plug. On the day of the incident the weather was hot, the ice plug melted and liquid propane was released. No ignition occurred. The vapour release was dispersed with the assistance of water sprays and jets.

Lessons
The following preventive measures have been taken. The pipe connections to the propane feed line have been modified to avoid water collection. Other similar pipe connections have been checked for frost damage, and the routines for water draining have been stressed.
Abstract
Autoclave bursting disc ruptured at beginning of a vinyl chloride polymerisation due to instrument defect leading to cooling water supply failure. Instrumentation failure caused this release.

Lessons
[None Reported]
Explosion in catalytic cracking unit at refinery. A pipeline in the unit ruptured and then exploded, triggering a flash fire. Pipeline failure.

Lessons
[None Reported]
Explosion and fire caused extensive damage to catalytic cracking unit when propane and butane gas leaked from a pump which was being repaired. Resulting fireball was 600 ft in diameter. LPG. Fatality.

[fire - consequence, catalytic cracker, repair]

Lessons

[None Reported]
Autoclave bursting disc ruptured at the beginning of a vinyl chloride polymerisation due to premature failure of the disc. Bursting disc failure. Leak.

Lessons

[None Reported]
Abstract
During excavation work on, for the installation of posts for an Alkylation Unit Flare Line, an underground 3.3. KV Feeder cable to a Catalytic Reformer 2 and two pilot cables were severely damaged. The mechanical post hole digger being used struck an obstruction below ground level and a contractor commenced breaking up the obstruction with a steel bar by repetitive driving blows. Pieces of the obstructing material were found to be parts of a cable tile. There had been no immediate indication of damage to cables, and the discovery was made about twenty-four hours later, followed checking out the cause of an earth fault.

Lessons
[None Reported]
Abstract
Explosion in an unmanned laboratory. The explosion occurred on an experimental rig consisting of two small glass pressure vessels (3 Oz. vol) connected by a manifold. Metal cages surrounded the individual tubes and a wire reinforced glass screen surrounded the entire assembly. At all times, the assembly was kept in a fume cupboard.

The apparatus was being used to study the reaction of a CO/H2 mixture with methyl iodide/ methyl acetate mixtures using experimental catalysts. The reaction conditions for the experiment in question were 130 psig pressure and a temperature of 120 degrees C. the reaction mixture was left in the lab overnight and checked periodically by a supervisor. The Supervisor noticed the pressure gauge on the rig to be reading zero, but did not think this significant.

The next day staff found the tubes had shattered into small fragments. The manufacturers rated the tubes at 375 psig and tests in the laboratory by the company had found them to burst at 500 psig. The laboratory rig had a pressure relief system set at 220 psig and a maximum operating pressure of 200 psig was used.

The tubes had been used within the company for many years with no major incident.

Lessons
The following observations/recommendations were made after the incident:
1. Where there is a possibility of a fire or release of flammables, test rigs should be continuously attended.
2. If shift staff are asked to watch over experimental set-ups, they should be made thoroughly conversant with the apparatus.
Thrust bearing failure of the high pressure stage of a gas compressor in the fluid catalytic cracking unit resulted in a fire. The movement of the rotor caused seizing, seal failures and failure of the suction and discharge piping.

Lessons
1. Fire caused by failure of the high pressure stage thrust bearing - result of severe compressor fouling from sodium carbonate deposits, which induced the thrust imbalance, beyond design loading.
2. Sodium carbonate deposits were the result of either entrained sodium bearing wash water in interstage cyanide scrubber or entrained caustic in the light gasoline rotor wheel wash.
3. A properly operating vibration monitoring system could have indicated impending mechanical distress, thus allowing operating judgement to be used in planning a compressor and/or unit shutdown.
4. Seal modifications apparently caused additional interference and heat generation which increased the magnitude of the rotor failure and the size of the fire.
Abstract
A fire occurred on the gas compressor of a fluid catalytic cracker, as a result of a bearing failure. Movement of the rotor caused seizing, seal failures and failure of suction and discharge piping below the compressor deck. The release of gas and fire engulfed the compressor deck, causing severe damage to equipment.

Lessons
Conclusions:
1. Fire caused by failure of the high pressure stage thrust bearing - result of severe compressor fouling from sodium carbonate deposits, which induced the thrust imbalance, beyond design loading.
2. Sodium carbonate deposits were the result of either entrained sodium-bearing wash water in interstage cyanide scrubber or entrained caustic in the light gasoline rotor wheel wash.
3. A properly operating vibration monitoring system could have indicated impending mechanical distress, allowing shutdown to be planned.
4. Seal modifications caused additional interference and heat generation which increased the magnitude of the rotor failure and the size of the fire.
5. Hypothetical drills do pay off - proved by the efficient manner in which the unit was shut down, secured and the fire extinguished.

Recommendations:
1. Condensate will be used as interstage gas scrubber wash water, to eliminate possible source of caustic contamination.
2. Light cracked gasoline, used as high pressure stage wheel wash, will have piping and control system revised to prevent caustic contamination from treating section.
3. A new vibration monitoring system and high pressure stage seals will be installed.
Abstract
While preparing a batch for a reactor in a resins manufacturing plant, steam was applied to a catalyst in a weigh tank because of sub-zero weather. An excess of heat caused the reaction to begin in the weigh tank. Since means for cooling the weigh tank were not available, the exothermic reaction caused the boilover of the weigh tank’s contents. A vapour cloud rapidly filled the one-storey building. The explosion disabled sprinkler system. Fatality.

Lessons
[None Reported]
### 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.

### 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.
A serious fire developed on a catalytic reformer resulting in damage to equipment amounting to approximately £500,000 (1981). No one was injured in the incident. The fire was started by failure of the thrust bearing on the hydrocarbon reactor charge pump. This bearing failure caused the coupling, mechanical seal, and bearing housing to break down.

Naphtha sprayed from the damaged seal and probably ignited from the overheated bearing. The fire spread to the adjacent stripper bottoms pump and was sucked up by the overhead fin-fans causing rupture of the 6 inch stripper column feed line, the 20 inch reactor product line and several small bore steam lines in the area. The fire was contained to the area around and above the stripper bottoms and hydrocarbon charge pumps, and was extinguished in two phases. The ground level fire in the region of the two pumps was extinguished by flooding the bottom of the stripper column with water. The high level fire was extinguished by purging the reactor product condenser line with nitrogen.

A three level piperack rung over the fire area above which is located a number of fin-fan condenser units. A considerable amount of damage was done to piping, instrumentation and electrical services in this piperack. The water sprinkler system preserved the fin-fan coolers from much more damage. Tubes were denuded of their aluminium fins and subsequently sagged but no tube failures occurred. It is believed that without the sprinklers, condenser tubes would have ruptured releasing hydrocarbon to the fire area. The fireproofing applied to the support structure beneath the fin-fan preserved the integrity of the structure during the intense fire.

The stripper column had been subjected to considerable heat which buckled the insulation cladding but there was no evidence of damage to the vessel itself which was returned to service without repair.

It is believed that the failure of the hydrocarbon reactor charge pump thrust bearing initiated the fire. This bearing failure led to subsequent failure of pump seal, bearing housing and coupling. A feature of the failure was the disintegration of the bearing housing which was discovered to be of cast iron construction. The pump casing was made of cast steel.

Lessons

Cast iron bearing housings to be replaced with cast steel construction as soon as possible.
Abstract
A fire occurred in a heavy gas oil stripper in a fluid cracker. The stripper was badly bulged, with the fire erupting from a split at one of the most severely expanded areas. The fire caused only minor damage and was extinguished quickly by maximizing stripping steam.

It was suspected that the stripper had bulged and failed due to overheating from the inside. The reason for overheating was investigated. The stripping steam line was traced back to a tie-in with the plant air system, which was incorporated in the original design of the unit. A block valve and check valve segregated the two systems, and a flow indicator was installed on each of the steam lines and plant air lines. Later these flow indicators were removed, and a board-mounted HIC valve used as an indication of flow. In order to have a flow indication when steam was used, piping was installed to route the steam upstream of the HIC. Only one block valve, without a check valve, was left to segregate the air and steam systems. It was speculated that this valve was opened during the three weeks before the fire. The steam tracing systems were being commissioned so repairs could be made. The block valve in the steam line just upstream of the HIC valve could easily have been mistaken as part of the steam trap system and opened. The plant air would then have backed into the steam system. This air probably did not generate much heat while the stripper was in service. However, the day before the fire the line to the stripper bottoms became plugged and the stripper was bypassed. The conditions were then right for air injection to support high-temperature combustion. The heat weakened the vessel wall causing multiple bulges. The wall ruptured 12 hours after the stripper was placed back in service.

Lessons
The following conclusions were made:
This was an accident waiting to happen. The accident demonstrates:
1. Most incidents are attributable to a simple root cause.
2. These causes have contributed to accidents in the past.
3. Efforts must be continued and intensified to keep from repeating these experiences.

The following recommendations were made:
Corrective action included eliminating the cross-tie between plant air and steam by blinding the steam line at the check valve and disconnecting the steam line to the HIC. Provisions were made for temporary connection of a steam hose for use in place of aeration air if needed.
A 1.5 ft crack developed in the laminated reactor of a hydrocracker unit while operating at 2500 psi. The unit depressured through the crack causing heavy fire damage during a 4.5 hour period.

[fire - consequence, cracking]

Lessons

[None Reported]
Abstract
A fire occurred at a research laboratory where chemicals, soda and solvents, were being neutralised in agitator. Fatality.

Lessons
[None Reported]
Abstract
Refinery hydrocracker plant. Source of ignition was autoignition.
[fire - consequence, refining]

Lessons
[None Reported]
Abstract
Fire at a refinery hydrocracker plant.
[fire - consequence, refining, cracking]

Lessons
[None Reported]
27 June 1980

Source: IChemE
Location: , TAIWAN

Injured: 0   Dead: 0

Abstract
Fire at a refinery Fluid Catalytic Cracker Unit (FCCU) plant.
[fire - consequence, refining, fluid cracker]

Lessons
[None Reported]
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.

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.
Abstract
Fire at refinery reformer plant. Cause tube failure.

Lessons
[None Reported]
Abstract
Approximately sixteen hours prior to a fracture of a quarter inch pipe, the part that fractured was renewed due to the inability to take up a leak in the existing pipe compression fitting. During the sixteen hours that the two inch length of pipe was in service, the vibrator was used extensively with severe vibration of the catalyst fed pipework being reported on one occasion.
A leak developed at the renewed pipe section and a technician was called to take up the leak. Before he attempted to take up the leak the pipe fractured. The plant was shut down and the pipe length was renewed.
The fractured pipe was examined and it was observed that the fracture had occurred at a position on the pipe that was within one of the compression fittings.

Lessons
[None Reported]
2007  22 April 1980

Source : ICHME
Location : , THAILAND
Injured : 0    Dead : 0

Abstract
An incident occurred on a compressor at a refinery Fluid Catalytic Cracker Unit (FCCU) plant involving hydrogen. Source of ignition was hot surface.

[fire - consequence, refining, fluid cracker]

Lessons
[None Reported]
Abstract
Incident on pilot plant reactor. An apparently normal start-up reached full feed rated for thirty minutes when the exit gas meters were noticed to be slowing down. The research operator informed the assistant chemist. Within one minutes fumes were noticed coming out of the top of the reactor case and the reactor pressure began to fall. The emergency switch was operated, turning off all heat and reactor feeds. The fire alarm was sounded and the fire brigade were called. No flames were seen, however the contents of a carbon dioxide extinguisher were discharged into the area around the top of the reactor. After five minutes of the first sign of fumes, the fumes began to subside, finally ceasing after about thirty minutes. The fire brigade were not required to do anything other than stand by, and eventually refill the extinguisher. The reactor cooled back overnight and was dismantled the following day.

The following conclusions were made:
1. The incident was caused by an exotherm in the top of the catalyst bed. The exotherm was caused by high propylene and ammonia feed rates into a bed which had a high catalyst to diluent ratio.
2. The high propylene and ammonia feed rates were caused by an operating error which should have been noticed and rectified before the incident could have occurred.

Lessons
[None Reported]
Abstract
A reaction was trailing on a loop reactor due to a blockage in the catalyst feeder line. The loop operator attempted to clear the blockage by rapid opening and closing of the atmospheric vent valve on the catalyst feeder line, while maintaining flush diluent pressure on the system. The third or fourth opening of the valve resulted in the ignition of the material vented. The sudden ignition took the operator by surprise, the operator went to the control room to report the fire, leaving the valve open. Subsequently the operator returned and isolated the flush diluent supply to the catalyst feeder system and the fire was extinguished. After checks and minor repairs to instrumentation the loop was recommissioned later the same day.

It should be noted that:
1. The venting was full bore via a hand operated ball valve.
2. There were no formal procedures for clearing catalyst blockages.

The committee of enquiry, having eliminated all other sources of ignition, concluded that static generation and/or incendive sparks generated by the catalyst discharge were the likely cause of ignition.

Lessons
1. Specific procedures should be available for clearing catalyst blockages.
2. Urgent consideration should be given to devising methods of clearing catalyst blockages that do not require the full bore venting of high pressure hydrocarbons to atmosphere.
3. These valves employed for full bore venting to atmosphere should be spring loaded ball valves. Additional block valves should be provided upstream of the ball valves.
A fire occurred in a transfer/mixer unit in use for the production of synthetic resins. It spread to adjacent equipment causing fairly extensive damage. Nobody was hurt. The original fire occurred because foreign metallic material entered the mixer via damaged screens at hopper bases. This material generated friction heat and a temperature sufficient to promote a vigorous reaction between the chemicals in the mixer and a conflagration due to the presence of fine material. The particular mix of chemicals present arose due to an operational error.

Lessons
1. Prevent the ingress of foreign bodies into reaction vessels.
2. Fit fire breaks into multi-stage equipment where practical.
3. Disseminate all available information re chemical (and other) effects of incorrect operations.
4. Provide systems which make it easier to carry out procedures correctly.
Explosions and fire totally destroyed a battery of three butane spheres, four vertical iso-butane tanks and five horizontal propylene and LPG mix storage tanks. This group of tanks was located immediately east of the HF (hydrogen fluoride) alkylation unit, north of the product treater area and catalytic cracker rundown tanks, west of another group of rundown tanks and south of the lead plant and catalyst reformer. In the explosion and fire, all of these facilities adjacent to the battery of tanks were either totally or, in the case of the reformer, at least 50% destroyed. The radius of damage was approximately 400 feet. Objects from the explosions were found more than 1,200 feet from the centre of the tank farm.

The most probable cause for the disaster was overfilling an iso-butane tank. Iso-butane was being received by pipeline. The refinery concluded that a vapour cloud formed and was ignited, the fire surrounded the tanks which in turn ruptured. Several of the tanks went into orbit.

Lessons

Routine inspection and testing of equipment and instrumentation must be to a high standard and records must be meticulously kept.
Abstract
Two contractors were working on the tip of a new flare which had recently been erected. An upset on the adjacent hydrocracker complex resulted in a heavy discharge from the sulphur unit stack. The fumes were carried by the wind straight onto the top of the new flare. The contractors suffered physical reaction to the fumes and had to use the emergency escape breathing apparatus and make their descent in the safety basket held in position adjacent to their work level by a standby crane. In this case a degree of pre-thought and planned attendance avoided a more serious incident.

Lessons
The consequences of process upsets must be taken into consideration when adjacent work is in progress.
Abstract
The incident occurred during commissioning operations on the catalytic cracker unit. Eight men were treated in the refinery medical centre following the inhalation of gas. The incident occurred whilst the spade isolating the regenerator and reactor systems from the main fractionator was being removed. Both systems were under a steam blanket and work had progressed to the point where the flanges had been jacked open and the spade removed. Three of the men engaged on the job were affected by gas, the fourth apparently suffered no ill effects. Breathing apparatus were not being worn (and never had been) for this job, which had been carried out without incident over the past 28 years.
The other four men affected were those who went to the scene on hearing cries for assistance. The degree of exposure varied; two were returned to work, six were sent home, and of these, one subsequently lost three work days as a result of the incident.

Lessons
1. Breathing apparatus must be worn where there is risk of exposure to a level of nitrogen that could cause oxygen deficiency of the local surrounding atmosphere.
2. All persons and in particular supervisors must be made aware of the risks associated with nitrogen to ensure that suitable precautionary measures are taken when similar work in undertaken.
Abstract
After five days of operation of a new recovery system on a fluid catalytic cracker, an automatic shutdown trip of the new power recovery unit occurred without warning. When the shutdown occurred, the check valve in the air blower discharge line failed to prevent a reverse flow of 1,250 degrees F catalyst into the air blower. The catalyst filled the 46 inch discharge line, the air pre-heater, the blower casing and was observed blowing out the snort mute and the air intake filter building. As a result of the damage to the air blower, the power recovery unit was divorced from the fluid catalytic cracker and the plant was restated using the old steam turbine driven air blower until repairs were completed.
An investigation into the incident revealed that an instrument malfunction had caused the automatic shutdown to occur, the air blower discharge check valve was not damaged and operated properly and caused the catalyst reversal and blower damage

Lessons
[None Reported]
A bursting disc and reactor seal failed on a PTFE-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.

Lessons

[None Reported]
Abstract
A blockage occurred in the solvent removal section of a plant. The solvent removal section had to be bypassed by feeding directly from the catalyst removal section to the catalyst stripper by use of the energy line. Problems developed in the operation of the catalyst stripper and eventually throughput could only be maintained by periodic local dumping of the contents. This was accompanied by the release of significant quantities of cyclohexane and the fire station were requested to provide personnel and water spray equipment to standby.

Lessons
The following recommendations were made:
1. A separate polymer solution/water chamber arrangement to be installed for the emergency polymer solution lines entering the catalyst stripper. Improved flow control on these emergency lines is also required.
2. Consideration to be given to incident simulation to give operators some idea of the problems which could develop and to encourage supervisory staff to think ahead and consider possible operations.
Abstract
An operator was charging resol resin and cotton into a mixer grinder when there was an explosion which caused him facial injury. Spectacles prevented serious eye injury. The ignition source emanated from the grinder to ignite an explosive mixture in the mixer. There was no damage to equipment but the practice of passing cotton and resol resin through the grinder was unsatisfactory. Dust explosion.

[mixing, charging reactor, injury]

Lessons
The following recommendations were made:
1. It is essential that a reliable choke be inserted between mixer/grinder and charging hood(s).
2. Separate charging hoods for grinder and mixer would be advisable.
3. All controls should have clear indication of their position.
4. Work of contractors should be checked by a reliable engineer.
5. Resol/cotton mixture should not be ground.
6. Overhaul should always be considered when making a major modification or movement of equipment.
7. Grinding and mixing plant should be separated with a choke wherever possible to reduce the probability of an ignition source reaching an explosive mixture.
8. The extraction system should be restored to full operating standards.
9. Observation of the mixer should be maintained in order to prepare an adequate maintenance routine.
10. Whilst the vent had operated satisfactorily as far as could be ascertained the outlet should be increased if this is reasonably practicable.
11. The electrical cabling in front of the vent should be re-routed.
12. The safe operating procedure should be reviewed, re-written, understood and accepted, and followed by all operators.
13. Manufacturing procedures and records should be reviewed with a view to ensuring that management are aware of all operations within their area of responsibility.
Abstract
An operator charged P2S5 (phosphorus pentasulphide) to a thiophosphate reactor and applied steam with the intention of shutting it off prior to going for his break.

The reactor would be left gassing off, but with no steam on. However, he did not formally hand over the reactor to the relief operator and also forgot to shut the steam off.

The reactor temperature is normally raised in 6 degrees C to 8 degrees C increments with pauses to allow the H2S (hydrogen sulphide) gas generated to be removed by a steam ejector. In this case the temperature rise continued with evolution of a large volume of gas, causing pressurisation of the reactor. The increasing pressure in the reactor resulted in a leak of H2S (hydrogen sulphide) gas, probably from the agitator gland and it was necessary to evacuate the plant.

Lessons
1. A much more formal handover system is required.
2. Operator providing "meal relief" must be adequately trained.
3. Consideration should be given to automatically override the steam supply in the event of overpressurisation.
Abstract
The ignition of a small leak on a methane reformer initiated catalyst tube flange leaks which impinged on the transfer pipeline. Trip action was initiated but before the unit could be depressured the pipeline burst open over a metre in length causing a short but intense fire. Metallurgical.

Lessons
[None Reported]
An explosion and fire occurred at a petrochemical steam cracker plant involving a furnace and methane.

[fire - consequence, cracking, operator error]

Lessons
[None Reported]
Abstract
Whilst manually emptying oxalic acid from a poly-ethylene lined, polypropylene woven sack into a batch reactor via the vessel manway/charge port, ignition occurred and a small fire erupted from the reactor. The operator received burns to his arms, chest and face.
Investigation into the incident revealed that most likely cause of ignition was the discharge of static electricity to the vessel. The charge being generated by the emptying of oxalic acid from the composite plastic sack. Vessel atmosphere at time of operation would have contained inflammable liquids above their flash point.

Lessons
1. A new charging system was installed by the company, in which oxalic acid was not charged directly into the reactor but instead was charged via an earthed screw conveyor.
Abstract
A fire occurred at a refinery hydrocracker plant involving a gauge glass and hydrogen gas oil.

Lessons
[None Reported]
Abstract
Failure of a dead ended section of pipeline in a fluid catalytic cracking unit allowed the release of propane and butane. The vapour cloud had covered an area of about 1.5 acres to a depth of 5 to 6 ft when it ignited. Water sprays were ineffective in dispersing the vapours. An unused control room filled with vapours and exploded. Flying bricks and debris severed small pipelines in the area releasing further hydrocarbons. Pipeline failure.

Lessons
[None Reported]
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.

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.
A fire occurred at a refinery Fluid Catalytic Cracker Unit (FCCU) plant involving a compressor and gasoline which was caused by mechanical equipment failure.

[fire - consequence, refining, fluid cracker]

Lessons

[None Reported]
Source: IChemE
Location: USA
Injured: 0  Dead: 0

Abstract
A large oil refinery storage tank (75 m dia by 15 m high) containing catalytic cracker feed (plus some light ends) was struck by lightning during a severe storm. This resulted in a fire at the tank roof seal (the tank being of the floating roof type). The fire took about four hours to extinguish using both cooling water on the shell of the tank and foam injection nozzles. The fire caused appreciable damage to the tank. Because of the design of the tank seals, it was impossible to extinguish the flames completely until foam was applied from a hose at the top of the tank.

Lessons
The following recommendations were made:
1. Design changes should be made to tank seals to improve access to foam.
2. Greater supplies of foam should be available.
3. Traffic control and portable lighting at the scene of the incident should be improved.
A fire occurred at a refinery Fluid Catalytic Cracker Unit (FCCU) plant.

[fire - consequence, refining, fluid cracker, cracking]

[None Reported]
Abstract
Pressure explosion while mixing vat containing 75% phenol and 25% formaldehyde was being diluted with water. Fatality.

Lessons
[None Reported]
22 January 1978

Source: GUARDIAN, 1978, 23 JAN.
Location: Chatteris; Cambridgeshire, UK

Injured: 0  Dead: 0

Abstract
Vat of paraffin wax overheated and was in danger of exploding.
Area evacuated. Near miss.
[overheating, evacuation]

Lessons
[None Reported]
An incident occurred during the shutdown of an ammonia plant. The incident occurred after repairs to a reformer were carried out. A technician entered the reformer to take pictures of a weld, many hours later the technician was found dead inside the reformer.

During the welding job the atmosphere inside was regularly tested for oxygen.

The incident occurred due to a failure to comply with existing regulations for the entry into confined spaces.

[fatality, human causes]

Lessons
[None Reported]
Abstract
Two pipeworkers inhaled escaping gas whilst they were attempting to install blind to isolate the fractionator feed reactor effluent exchangers on a hydrocracker.

Causes:
1. Permit procedures not strictly adhered to.
2. Should have made use of fresh air equipment.
3. Poor communications between all personnel involved.

[gas / vapour release, maintenance, people]

Lessons
Preventative measures:
1. Tighten up permit procedure.
2. Improve shift charge communication procedures and re-emphasise importance of good communication.
3. Make high pressure breathing air more readily available for use on site.
4. Initiate the installation of isolation valves to separate reactor and fractionation sections.
Abstract
A fire occurred at a refinery hydrocracker plant.

[fire - consequence, refining, cracking]

Lessons
[None Reported]
Abstract
Water contamination of the naphtha feed to an ethylene plant caused a plant shutdown. When the contaminated naphtha entered the cracking furnaces, an automatic shutdown sequence tripped out two furnaces, which shut down without damage. However, six further furnaces were kept in operation under manual control, and serious damage resulted.

Water had been deliberately introduced into one of the two naphtha feed tanks to clean it out prior to inspection. The contents of this tank were then being pumped to the other tank which was feeding the furnaces. The tanks were of the floating-roof/floatation suction type, and since naphtha formed the upper liquid layer, it was assumed that water would not carry over into the furnace feed. Because of the excessive quantity of water introduced, this assumption was false.

The ethylene plant personnel were unaware of the operations taking place on the tank farm, and this hindered correct diagnosis of the ensuing furnace problems.

Lessons
1. When tanks are taken out of service, the possibility of contamination of feedstocks should be eliminated by positive isolation.
2. Communication between different sections of the plant (e.g., tank farm and furnaces) should be improved.
3. Provision of water alarms and automatic draining devices in the naphtha feed system should be examined.
4. Additional trips for furnace protection should be considered.
On the 21st November 1977, a catalytic reformer was shutdown for the statutory inspection of steam coils in the furnaces. The adjacent No.2 Hydrofiner was also under maintenance shutdown. It was decided to install a cross connection between the unifiner section stripper bottom/feed exchanger and the hydrofiner. To make this tie-in the bottoms line of the stripper had to be isolated and gas freed. In attempting to do this it was found that the bottom valve of the stripper would not shut and it was therefore necessary to empty the stripper itself.

The stripper at that time had an inventory of 8m³ of naphtha at a temperature of about 120 degrees C and was floating on the refinery's gas main at a pressure of 2.5 bar. Attempts were first made to empty the tower by means of a "drain situated after the bottom/feed exchanger. The drained product, quenched with water was directed into the sewer system. As the emptying of the tower did not progress at a satisfactory rate, it was then decided by the operator to accelerate it by opening the main 2 inch drain sited between the tower and the exchangers. He did not endeavour to empty the tower to blow down (because the blow down pit pump was defective). On opening this 2 inch drain valve the operator discovered that the drain was blocked, and he therefore obtained the assistance of a shift fitter to dismantle the spool piece between the drain valve and the sewer. Initially no flow was obtained, so the operator tried opening/closing the valve a few times and hammering on the drain pipe before the valve. Suddenly with a half open valve, there was a release of dirt followed by a large quantity of gas and liquid. The operator could not close the valve, so he ran to the control room to fetch an air mask. As he left the control room there was an explosion followed by the outbreak of a serious fire around the stripper. The first explosion was followed by two secondary explosions and fires at various locations on the catalytic reformer.

Some of the secondary fires may be attributed to glowing aluminium particles which were seen flying about after the explosion. The aluminium came from cladding on the stripping tower which had been installed some years previously (aluminium with 0.97% magnesium). It is probable that some of the flanges on the platforming section heat exchangers were leaking slightly (after the shutdown) and these leaks were ignited by the aluminium particles causing the secondary fires and explosions.

The incident is regarded as occurring due to the consequence of the operator's mistake. The operator had the possibility of despatching the drainings to the blow down drum even though the drum's disposal pump was not available, and certainly he should never have drained a hot flammable product into the sewer system.

The source of ignition was not definitely established although a number of possibilities were investigated as follows:

1. Static electricity was regarded as a good possibility with the high velocity and splashing of the drained product.
2. Flash-back from operating furnaces on the No.1 Catalytic Reformer (about 40m away) was felt to be unlikely from observations by witnesses and subsequent fire damage limits.
3. Autoignition of the naphtha at 120 degrees C was felt to have been unlikely since tests gave an auto-ignition temperature of 235 degrees C.
4. Ignition from nearby hot flanges of the high pressure steam system (225 degrees C) was however considered as very possible and the most probable source.
5. There was no evidence of pyrophoric products in the system.

[shutdown, inspection, catalytic reformer, operator error, explosion, fire - consequence]

Lessons

All operators have been retrained in groups by their respective shift controllers on the correct safe procedures for draining flammable products. The cladding covering the lagging of the stripper column has been replaced with aluminised steel.
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.

Lessons
[None Reported]
An accidental short circuit created while the furnace instrumentation was being relocated to a new control building caused an explosion in a new preheat furnace for a FCC (fluid catalytic cracking) unit. The furnace and an adjoining one were severely damaged. The short circuit lasted for 5 minutes and shut down all the fuel gas and pilot gas to the two furnaces. When power was restored the gas supplies were restarted as the valves reopened and the gas ignited on hot brickwork.

Lessons

[None Reported]
Abstract
A catalytic cracker compressor tripped out and a large volume of gas/liquid was discharged to a flare. This flare had no condensate knock-out facilities and a very large flare was produced initially. With a fairly strong wind blowing, the flames and smoke were projected over the tank farm to the immediate north.

Immediately following this incident a tank rim seal fire was reported on an adjacent tank, in which a blend of 2.5 million gallons of petrol was being made. The tank was almost full, with the tank mixers still in operation.

A passing tank dipper heard a small bang from the tank and then noticed flames appearing above the rim of the tank. He immediately summoned the fire service who quickly extinguished the fire with foam. As no foam dam was present on the tank a liberal application of foam compound was required to extinguish the fire.

The cause of the fire was either:
1. A small quantity of burning liquid landing on the tank roof and igniting the vapours at the rim.
2. Vapours from the tank being ignited from the flame or heat of the flare giving rise to a flash back effect.

The quick discovery of this fire allowed firemen to go on the tank roof and tackle it before it got out of control.

Lessons
The incident has reinforced the need for two requirements:
1. Knock-out facilities and disposal facilities for large slugs of hydrocarbon condensate being discharged to the flare.
2. Foam dams on all floating roofs containing Class 1 products.
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.

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.
<table>
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**Abstract**

A vat which had contained explosives was salvaged and sold. The new owners made a quick inspection and then allowed burning. Explosion occurred within one hour. Fatality.

**Lessons**

[None Reported]
Source : IChemE
Location : 
Injured : 0  Dead : 0

Abstract
Fire at refinery reformer plant. Source of ignition was furnace. Cause: tube failure.

Lessons
[None Reported]
Thirty tonnes of HDPE, high density polyethylene, were being transferred from a double cone mixer to a 100 cum (cubic metres), 50 tonnes storage bin or silo. 10 minutes later there was an explosion which destroyed 2 silos and a vent bag filter. Parts of the silos were blown several hundred yards and into an adjacent factory. Ignition thought to be in bag filter and possibly caused by static. Dust explosion.

Lessons

[None Reported]
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**Abstract**

Aluminium powder and oxidising agents ignited while being blended in enclosed bakery type mixer. This dry mixing was subsequently banned ending production of metallized plastics. Fatality.

**Lessons**

[None Reported]
Abstract
Fire at a refinery reformer plant. Source of ignition was autoignition. Equipment involved: heat exchanger.

Lessons
[None Reported]
Abstract
Fire at refinery reformer plant. Source of ignition was furnace.

Lessons
[None Reported]
Two fitters wearing breathing apparatus were attempting to replace a valve in the relief system from a catalytic reformer unit, to the refinery flare main. The system was open to the refinery flare main and a pressure surge in the main caused hydrogen sulphide containing gasses to be released from the open end of the flare side flange of the valve.

One fitter became unwell and subsequently collapsed and later died despite attempts at resuscitation. There was personal risk to those attending the scene until the flange was bolted up. The gas release did not ignite.

Lessons
1. Any work which involves opening a flare line should be considered in detail beforehand and to be accompanied by a written work permit stipulating the conditions and the precautions required.
2. One hazard in opening a flare system lies in the admission of air to it from a flammable mixture. Ignition may occur from the oxidation of pyrophoric scale which is invariably present in some parts of a refinery flare main.
3. Usual devices such as flame arresters and water seals, cannot be considered as totally reliable in preventing internal flash-back from the flare tip should a significant quantity of air be introduced upstream of them during the work.
4. Another more likely danger in opening a flare system is from the escape of flammable and/or toxic gas to atmosphere at the work point with a consequent fire and health hazard.
Abstract
Explosion of a polypropylene glycols batch reactor, reacting glycerol with ethylene oxide. Circulation had not been established and trip setting was changed allowing ethylene oxide to enter the reactor. Circulation was started leading to an uncontrolled exothermic reaction.

Lessons
[None Reported]
Abstract
After charging a production autoclave, the operator forgot to uncouple the water hose and to close the inlet valve on the autoclave. When the autoclave was heated up, the water hose was pressurised, at a pressure of approximately 9 bar it burst.
Through the open charging nozzle, some 3000 litres of reaction mass and 500 kg of monomethylamine were released.
The fire brigade managed to absorb most of the methylamine emanating from the building by maintaining water curtains by means of powerful water monitors.

Lessons
[None Reported]
Abstract
An operator charging o-nitroaniline from drums into an autoclave was found to have a blue discoloration of the lips. The operator was wearing all prescribed protective gear, gloves, sleeves, apron and gas mask.
A medical examination revealed that the operator suffered from deficiency of a certain ferment which in turn causes hypersensitivity against aromatic amines. [poisoning, processing]

Lessons
This illustrates that even when prescribed protective measures are followed, one should always look out for critical symptoms.
Abstract
The dry gas from the product stabiliser on a pentane isomerisation unit contained HCl (hydrochloric acid), which was used to activate the catalyst. To prevent corrosion downstream the gas was passed through a caustic scrubber. However, the mixing was not instantaneous or completely effective. This led to serious corrosion in the bottom of the scrubber and its trays.

Lessons
1. When neutralising an acid all the equipment in contact with it has to be corrosion resistant up to the point that neutralisation is complete.
2. To reduce the amount of expensive corrosion resistant alloy used, rapid mixing is desirable. In this case a static mixer with the caustic and gas flowing directly to the inlet was installed. 3. The mixing zone was only 30cms long.
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.

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.
Abstract

Lessons
[None Reported]
### Abstract

One hundred litres of reaction mixture were released out of a high pressure autoclave. The incident was caused by a deviation from the operating instruction. Due to premature charging of ethylene, the pressure rose too high during the heating up period. By immediate maximum cooling the situation could have been controlled. However, the hand operated blowdown valve was opened hastily and due to a mechanical defect, could no more be closed completely when pressure had fallen to an acceptable level.

[high pressure, mechanical equipment failure]

### Lessons

[None Reported]
Abstract
The following incident occurred on a catalytic reformer.
During shutdown and draining operations on the desulphuriser unit, operators discovered that the mechanical seal of the catalytic reformer debutaniser reboiler recirculating pump was leaking badly with a cloud of vapour starting to drift towards the unit heaters. The alternative pump was commissioned, and a steam lance was positioned against the leaking pump. The latter pump was stopped and the operators started to valve isolate it from the column. When the pump's 10 inch suction valve was closed, its spindle and handwheel suddenly fell out, hitting and knocking over one of the operators. As the operator was wearing a safety helmet the glancing blow he received to the head, did not cause him any injury. Although the spindle and handwheel of the valve were no longer in position, there was no external leakage from the closed valve.
There have been a number of incidents in refineries over the years where valve handwheels, or chain assemblies on chain operated valves have become detached. The loss of the valve spindle complete with handwheel is very rare. This would imply excessive wear at the collar on the end of the spindle sufficient for it to finally pass through the bushes, glands, valve cover, etc.

Lessons
[None Reported]
Abstract
Approximately fourteen hours after a catalytic reformer had been brought on stream following a major overhaul and catalyst rejuvenation, a fire occurred at a group of thermocouples on the inlet piping to the reformer reactor. During the overhaul, detailed inspections of furnaces and general equipment and piping took place requiring a considerable number of ring type joints in the reformer recycle system to be broken and remade. During the start-up period, drying of furnace refractory was carried out coincident with completion of work on other items of equipment in the high pressure recycle system and the latter stages of catalyst rejuvenation. Consequently the pressure testing of the high pressure recycle system was limited to a 50 psi nitrogen pressure test instead of the customary working pressure cold hydrogen pressure test. At the final stages of rejuvenation, reactor inlet temperatures were raised to 950 degrees F while circulating hydrogen gas at 100 psi. Following completion of rejuvenation, the recycle system was depressured and the necessary blanks swung to on-stream position. The flanges broken during blank swinging were subjected to a further 50 psi nitrogen pressure test and proven tight.

At time of fire the unit had been in reasonably steady operation at 12,000 BPSD with reactor inlets at 900 degrees F and plant pressure of 380 psi for several hours. Then difficulty was experienced in maintaining suction on the reformer charge pump. An attempt was made to change over to the standby pump in the belief that the suction strainer may have been blocked. Before the pumps could be changed, the running pump lost suction, and at that time a fire was discovered adjacent to the reheat furnace on the inlet piping to the reactor. Following the fire the recycle system was purged with nitrogen until all flammable gas was removed. An inspection showed that four thermowells with ring type joints located in the split stream outlets of the reheat furnace to the reactor were all leaking excessively at their ring joints; the four thermowells are located close together. The ring type joints had four bolt flanges, and the flange bolts were loose when inspected, however the joints were in good condition. The joints were remade and proved tight under hydrogen pressure. A 200 psi hydrogen pressure test of the entire recycle system was carried out. A number of flanges were found to be leaking. In several instances, jointing compound was found on the rings and grooves of the ring type joint flanges. The reformer charge pump suction strainer was inspected for blockage but was found to be clean. The initial failure of the reformer charge pump was most likely caused by hot recycle gas passing to the suction of the charge pump. Although the two isolating valves in the chloride injection piping to the other reactor were shut they were passing sufficiently to give problems. The fire at the four thermocouples on the reactor inlet piping was considered as being a result of a minor thermal shock caused by loss of the reformer charge. Due to the close location to one another of the four thermocouple flanges it is likely that the leak and subsequent fire from one flange resulted in the other three leaking from exposure to excessive heat. The reason for the thermocouple leaking from such minor temperature variation is not clear but attributable factors include.

1. That jointing compound was found on several ring type joints It was not certain that this compound had been used on the flanges of the thermocouples, but if it had been, a cold pressure test would possibly not have found a leak.
2. The normal working pressure cold hydrogen test had not been carried out, the 50 psi nitrogen pressure test may not have been sufficient to show any leakage.

Lessons
The following recommendations were made:
1. A working pressure test with hydrogen-rich gas on high pressure systems in hydrogen service to be done after flanges have been broken and re-made.
2. The use of jointing compounds in ring type joints to be discontinued. Engineering workers to be given further instructions in the correct procedures in remaking such joints.
3. The chloride injection system requires some minor redesign and change in procedures to avoid the necessity for draining back through non-return valves and to reduce the possibility of hydrogen or recycle gas reaching the reformer charge pump suction.
On a Saturday afternoon there was an emission of a plume of aerosol from the vent of an unattended reactor at an Italian chemical works. The emission, which lasted some twenty minutes, discharged a complex mixture of several tonnes of chemicals. These included the sodium salts of trichlorophenol, sodium hydroxide, sodium glyoxides and sodium oxalate. The propelling gas was probably hydrogen. There was also present in the plume approximately 0.25 kg of highly toxic 2,3,7,8-tetrachlorodibenzo-p-dioxin, commonly called dioxin or TCDD. The immediate effect was for over 400 local inhabitants to require treatment for chemical burns, the deaths of local small animals, and damage to vegetation. Twenty days later chloracne, a characteristic of dioxin poisoning, developed in those who had received chemical burns, and several weeks later further numerous chloracne symptoms were reported. Over 17 km² was contaminated, with 1 km² being most severely affected.

2,4,5-trichlorophenol was produced at this plant by reacting 1,2,4,5-tetrachlorobenzene with sodium hydroxide in the presence of ethylene glycol. The reaction operated below 180 degrees C using steam heating at 12 bar, in preference to oil as the heating medium.

On the day of the incident at around 5 am the process was shut-down half way through the vacuum distillation of the solvent when the batch temperature was 158 degrees C. The vessel was left unattended and at 12:37 a bursting disc ruptured releasing the plume of chemicals. A foreman entered the building and applied cooling water to the coils which eventually caused the plume to cease. The maximum temperature achieved was 450-500 degrees C which clearly established that an exotherm had occurred. This would have evolved a permanent gas, hydrogen, which would have rapidly pressurised the system and ruptured the bursting disc. The bursting disc was rated at 3.5 bar, but was installed not to relieve excess pressure during reaction, but to prevent dangerous overpressure when using compressed air for transferring the contents of the reactor to another vessel.

Lessons

Some conclusions/recommendations made include:

The reactor used steam at 12 bar, and had neither automatic controls nor alarms. It was believed that as the vessel of the reactor was heated by 12 bar steam, the temperature of the reactor walls could not exceed 180-183 degrees C, and therefore prevent an exotherm occurring. However, it was later reported that it was common for the steam to be superheated to 300 degrees C. The vessel had an agitator, which was shut off during the shut-down. It was believed that even with the vessel walls at 300 degrees C, the reactor contents would not be subjected to a significant temperature rise. However, as organic liquids are poor conductors of heat and as the reactor contents were stagnant, a theory for the onset of the exotherm has been put forward and generally accepted. It involved the vessel walls conducting heat to a thin top layer, which could have then reached temperatures of 220-230 degrees C, sufficient to set up the exotherm. This reaction would then evolve a permanent gas, hydrogen, which would have rapidly pressurised the system, and ruptured the bursting disc. The agitator should not have been shut-down, and instead left running so that excess heat would have been absorbed into the bulk of the material.

There was no system for trapping or scrubbing any material emitted if the bursting disc failed. This is obviously an unsatisfactory situation when toxic chemicals are used, or are likely to be present in any reaction (process or runaway).

The steam used was at 12 bar, but superheated to 300 degrees C. If the reactor had been provided with a guaranteed source of saturated steam at an appropriate and automatically controlled pressure, the vessel could have been safely left at 158 degrees C.

The reactor was periodically inspected though no hydraulic test was carried out as the Company management claimed that the vessel was only operated at atmospheric conditions. Further the bursting disc had not been inspected.

The reactor was housed in a building originally used to manufacture another product and therefore the reactor is unlikely to have been custom built for the process. Hazops, which were in their infancy at the time, would have highlighted the dangers and should be used, particularly when converting plant to other processes.
Abstract
A fire occurred on a cracking furnace on an ethylene plant. Two neighbouring furnaces were shut down as a precaution. The Works Fire Brigade brought the fire under control. Substantial damage was done to the furnace.
The primary cause of the initial fire was the 'urning back' of two burners due to a high ethylene content of the fuel gas. This caused extensive heating external to the furnace. The service steam system on the plant had been contaminated by quench oil at some time previously - this had blocked some steam outlet points which had been left open. The burner fire had, in turn, led to the unfreezing of these blocked steam points and the release of a steam/oil spray which led to a more general fire.

Lessons
The investigating team recommended that:
1. A number of hardware and procedural changes should be made to minimise the recurrence of contamination of the steam system by oil.
2. Technical studies should be carried out to determine the maximum safe ethylene concentration in the fuel gas.
3. The provision of 'dry risers' in the furnace area should be investigated.
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.

Lessons
[None Reported]
Abstract
Fire at pipework on a steam cracker plant. Substance involved: naphtha.
[fire - consequence, cracking]

Lessons
[None Reported]
A fire occurred on a steam cracker at a refinery. Source of ignition was furnace. Substance involved: naphtha.

[refining, fire - consequence, cracking]

[Lessons]

[None Reported]
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**Abstract**
An explosion and fire occurred on a reformer at a fertiliser plant. Source of ignition was autoignition or electric motor. Substance involved: hydrogen. Cause was operator error.

**Lessons**
[None Reported]
Search results from IChemE's Accident Database. Information from she@icheme.org.uk

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. 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-dichloroanilinohydroxylamine (DCPHA). The most likely trigger for the reaction was a 10 degrees C increase in the reactor temperature set point.

Lessons
[None Reported]
Abstract
During start-up of a naphtha cracker there was a release of mainly propylene which ignited and the resultant explosion caused extensive damage to equipment and an adjacent tank farm. Metallurgical inspection of fractures concluded that the cause could be attributed to cold brittleness of a weld of a pipe to a relief valve. Many injuries were caused by flying glass. Fatality.

Lessons
1. Hazard and operability studies to be carried out to find potential weak spots, taking into consideration deviations in process conditions, especially process abnormalities as are often encountered in start-up situations.
2. P and I diagrams must be up to date.
3. Updating of operating guides, instruction, and retraining needs considerable care.
4. The Plant Manager should approve changes in his plant. He must be advised by a multi-disciplinary acceptance committee on every change including non-identical replacements.

Source:

Location: Beek, NETHERLANDS

Injured: 107  Dead: 14
Injured: 11  Dead: 1

Abstract
Explosion damages ethylene cracker. Fatality.

Lessons
[None Reported]
Abstract
An explosion occurred in the mixing plant of a propellant, explosives, manufacturer. Fatality.

Lessons
[None Reported]
Abstract
A tee in the primary to secondary reformer transfer line ruptured suddenly and violently causing an immediate shutdown of the ammonia plant. No precise cause for the failure was found. The general problem is discussed. Unidentified cause.

Lessons
[None Reported]
Abstract
A fire and explosion occurred at a catalytic reformer unionfiner complex. The fire centred between the reactors and fired heaters of the reformer and resulted in extensive damage to the unit.
The explosion rocked the nearby refinery control centre and broke windows half a mile away. There were no injuries. After the shock of the explosion, the operating crew isolated all hydrocarbon and utilities lines at the unit battery limit. The columns and vessels could not be pumped out due to total loss of power. A 750 gpm stationary monitor located north of the unit was directed on the piperow to cool down and prevent further failures.
The fire caused major damage to four reformer heaters, piping, wiring, instrumentation and structures in the area.
After investigations into the cause of the incident it was found that metallurgical failure probably caused by hydrogen attack was to blame. Metallurgical analysis revealed that high temperature hydrogen attack occurred in various forms throughout the steel lines.

Lessons
[None Reported]
Abstract
Rupture of pressure vessel caused explosion on shift conversion unit of ammonia plant. The incident started when the injection cooler on the shift unit ruptured.

The main conclusion as to the cause of this incident was corrosion, in that a clear pattern of corrosive attack occurred on the inside surface of the vessel related to the distribution of water through the vessel. This thinned the walls of the vessel, eventually causing a ductile fracture. Although the fracture was through a vertical weld, it was considered that this was coincidental but that the weld corroded preferentially.

Lessons
[None Reported]
Corrosion on a 80 mm pipeline from a vinyl chloride monomer (VCM) hydrogen chloride separator released vinyl chloride monomer and cloud ignited in cracking furnace after 10 to 20 seconds.

Lessons
[None Reported]
Abstract
An explosion followed by a ground fire occurred in a cat cracker pre-heater as a result of spirit carryover from a phenolic soda washery. A pilot gas line located 20ft. above the fire ruptured after exposure to flame. No personnel were injured but the pre-heater and nearby pipework suffered damage. Operational difficulties had been experienced in the washery during the two days prior to the fire and it had recently been recommissioned. The trouble was subsequently found to be due to blockages in the pipework caused by the precipitation of solids while operating with a phenolic soda strength in the region of 14%. The carryover was attributed to a build-up of spirit in the soda regenerator due to these blockages. Shortly before the incident the washery had once again been taken out of service and the soda and wash systems shut down. However the foul gas line to the pre-heater was left in service and the air to the regenerating column kept in commission.

Lessons
This incident could have been avoided if:
1. The personnel on duty had been fully aware of the potential dangers associated with the carryover problems experienced by previous shifts, thus emphasising the necessity for good handovers in changes of shift
2. The soda regenerator off-gas line had been isolated from the pre-heater when the soda system was shut down.
A serious incident occurred at a refinery at which a 56m tetraethyl lead weigh tank exploded. Although no one was hurt, the blending plant building and weigh tank were destroyed.

The cause of the explosion is not yet definitely established but the possibility of a chemical reaction in the tank cannot be ignored; self heating of leaded sludge exposed to air has been known.

During blending operations all liquid was removed from the tank which was then refilled with 5,000 lbs from a tank car. Blending continued until the tank had been emptied of all the residual irrecoverable material. The blending system was shut down and all valves reportedly closed, with the partially unloaded tank car left connected to the unloading line. Twelve hours later the weigh tank exploded.

It is thought that ignition occurred because of pyrophoric impurities in the sludge developing hot spots which eventually ignited a vapour-air mixture in the tank, air having entered through the loading connections.

If this was so, then the vapour explosion would have created additional heat, accelerating thermal decomposition of the lead resulting in a violent explosion and destruction of the tank. The physical condition of the tank is said to have been good with only minor internal corrosion evident.

Lessons

The following recommendations were made:

1. Do not allow the lead alkyl compound level to go right down and expose any sludge (and possibly also eliminating the glycerine). Maintenance of adequate stocks in tanks also reduces the possibility of explosion in the case of a fire outside the tank.
2. Maintain the glycerine layer. This not only reduces the slow oxidation of compound and formation of sludge, but helps to isolate the sludge from the air if the level of compound is extremely low. The layer should be checked and topped up at least annually.
3. Follow the plant operating instructions exactly. For example, do not leave air bubbling through compound in a tank at the end of a transfer.
4. Tank wagons and other bulk containers should be completely emptied at one transfer operation. They should not be left connected to the unloading line after the transfer is complete.
5. Ensure that all tanks are provided with an adequate cooling water system. Measures must be taken to prevent freezing of the cooling water during cold weather and the systems should be tested at regular intervals.
An ethylene cracker was being brought on steam for the first time. Some hours after the furnaces had first received feed and were producing cracked gas, one of a series of low pressure heat exchangers in the gas separation plant became over-pressurised and fractured. In turn this split open a high pressure heat exchanger and large amounts of flammable vapour escaped. Ignition occurred after 34 seconds and the serious fire that occurred burned for 12 hours. The aluminium heat exchangers, 30m above ground on an open steel structure, were destroyed and ancillary equipment was seriously damaged.

Abstract

Lessons

[None Reported]
A trickle phase (liquid) pretreater consisting of feed-effluent exchanger and a liquid phase reactor was installed in 1956 to provide moderate desulphurisation. By 1959 it was necessary to increase its severity. A preheater charger heater was then installed and used intermittently for start-ups or when sulphur contents of the charge increased due to the type of crude being processed. Ultimately it was operated continuously. At approximately 2.40am an explosion and fire occurred at the older motor reformer caused by a rupture and explosion in the pretreater charge heater outlet transfer line. No personnel were injured but the area suffered significant damage. A thorough investigation revealed the cause to be overheating because of the coincidental appearance of the following three design problems.

1. The newer motor reformer had been shut down for compressor repair and was in start-up phase at the time of the explosion. A common charge system at the two reformers allowed charge to be robbed from the old booster pump as charge was increased to the newer one during start-up. The resulting low suction pressure at the booster pump caused the automatic pump shutdown system to be activated and flow was lost to the charge heater. A panel alarm bulb was previously burned out and the operator was unaware of the problem.

2. The DDC alarm system typewriters could not print the alarm message as conditions were occurring. Consequently low flow and temperature alarms were delayed by 6-8 minutes giving the operator no time to prevent a disaster.

3. The older pretreater fired heater (more than 25 years old) was protected from flame-out and explosive re-ignition by a bypass line with a limiting orifice around the main gas control valve although this provided a pilot-type fire in the furnace in the event the main gas valve were closed, it also admitted sufficient fuel gas to raise the tube temperatures above 1500 degrees F if the naphtha flow were stopped. The outlet temperature did exceed this and when the operator restarted the booster charge pump the hot gas exiting from the heater exceeding safe operating temperature of the transfer line which ruptured.

Lessons
The motor reformer fire was caused by instrument malfunctions and inadequacies piping design oversight and use of a small old heater which was not equipped with a modern pilot burner system. None of these design flaws could have individually caused an explosion or fire. Piping and instrumentation design changes have been made to prevent recurrence and the old style bypass around the fuel gas control valve have been replaced with a separate pilot burner installation.
Abstract
Two unrelated fires, one in reformer unit one in desulphuriser. Probable cause: rupture in fuel tubes.

[fire - consequence, separation equipment, processing]

Lessons
[None Reported]
Abstract

A tube split in the stabiliser reboiler furnace in the distillation section of a hydrocracker plant. The ensuing fire was extinguished in about 45 minutes with the use of 8,000 litres of foam. No personnel were injured but the superstructure of the reboiler and framework supporting the flues and common stack were damaged together with some of the refractory in the flue gas ducts to the common stack.

The first fire appliance was at the scene of the fire within 2-3 minutes of the outbreak and within 15 minutes the following equipment was in action:

1. Two water cannons supplied from the high pressure fire main system.
2. One foam lance fed from a 4 m³ capacity foam tanker equipped with a pump.
3. External support summoned from a nearby chemical complex, arrived with a 10,000 litre foam tender, but this was not required.

The incident occurred during a change in shift personnel at the fire station and the strength of professional and auxiliary firemen was doubled.

The tube failure occurred in the cross-over section between the radiation and convection sections and the fire spread to the flue gas ducts and common stack of the group of units. An emergency shut down of the hydrocracker and hydrogen production plants was carried out, but with no isolating valve on the transfer line from the reboiler to the stabiliser column, the latter had to be decompressed from 20 to 10 bars before steam, at 15 bars, could be injected into the furnace tubes.

The flue-gas suction fans of the hydrogen unit furnace, which has a common flue gas duct with the stabiliser furnace and is situated downstream with its burners until, remained in operation during the incident and supplied the combustion products with air. This had the effect of localising a large part of the fire in the flue duct thus limiting the spread of gas and explosion risks.

Subsequent investigation showed that the tube had failed after only 2.50 hours operation as a result of severe corrosion. This high corrosion rate is attributed to the action of residual gaseous HS in the stabiliser column, following poor fractionation, associate with high furnace tube skin temperatures. Thirty-one furnace tubes (27 convection and 4 radiation) were affected and renewed. The transfer line to the stabiliser column was also renewed together with two outlet bends on nos. 1 and 2 passes of the nearby fractionator feed heater.

The efficiency of the stabiliser was improved by a number of modifications.

Lessons

[None Reported]
Abstract
Rupture in a reformer vessel and jacket on an ammonia plant caused by crack in refractory lining.

Lessons
[None Reported]
Abstract
Hydrogen, carbon monoxide and carbon dioxide leaked from a crude oil cracker after the pipe ruptured on the carbon dioxide absorption tower in the carbon monoxide purification process.

The cause of the rupture was due to water in the feed crude oil, which changed the composition of the mixed gas to cause an excessive reaction and an unusual rise in pressure.

No injuries occurred.

Lessons
[None Reported]
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 and 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.

Lessons
Flange leaks are not unusual where hydrogen is circulated during start-up. It is common practice to fit known leak prone flanges with steam 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 occurring 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.
A tapered plug was being removed from one end of a tube bundle (U-tubes) by tapping with a hammer when the plug was ejected from the tube with sufficient force to penetrate a 14 gauge steel sheet screen and continue travelling a further 20 feet. The tube bundle operated in the desulphuriser effluent condenser on a catalytic reformer, with desulphuriser reactor effluent through the tubes and salt water on the shell side.

The tube bundle had been washed and pressure jetted externally in the special area allocated for this duty. Upon examination of the bundle, it was recommended that seventeen tubes which had been plugged in February 1971 following signs of external wastage of the tubes, should be removed to allow further inspection of the tubes deeper into the tube nest.

To do this, it was necessary to remove the plugs with the result described above. The remaining plugs were ejected in the same manner but under controlled safe conditions.

Analysis of the liquid ejected from the tube showed it to be water with 1300 ppm of sodium chloride. There were no traces of organic material.

**Lessons**

Tubes which have not failed and are plugged off should be deliberately punctured beforehand.
748  15 March 1973

Source: MIDDLE EAST ECONOMIC DIGEST, 1973, 23 MAR.
Location: BAHRAIN

Injured: 0  Dead: 0

Abstract
Fire on catalytic cracker extinguished in 30 minutes. Little damage.

[fire - consequence, cracking]

Lessons
[None Reported]
Abstract
Fire and explosion during commissioning of new ethylene cracker.

Lessons
[None Reported]
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.

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.
Abstract
A fire occurred on the phthalic anhydride plant, due to the failure of the shaft of a heat transfer salt pump. Similar shaft failures had occurred on two previous occasions. A spare shaft which was fitted following the first failure was repaired and returned to service when this in turn failed in October 1972.
When an unexplained hot spot temperature in excess of 600 degrees C was noted by the operator, he, contrary to regulations, tried to reduce the temperature by fully opening the control valve to allow maximum flow of salt through the salt cooler. He also shut off the salt furnace. The operating instructions state that the plant should be manually tripped if temperatures in excess of 585 degrees C were noted. The temperature continued to rise until it reached 700 degrees C, the maximum indication on the chart. At this point, the o-xylene and air feed to the reactor was cut off by a high pressure trip.
Normal shut down drill was then followed and the reactor was purged with nitrogen. Since the catalyst could be damaged by prolonged bed temperatures in excess of 60 degrees C, the air compressor was restarted in an attempt to reduce the catalyst bed temperature which had continued to remain high. After air had been purging for about an hour, smoke and flame appeared at the vent and finally the reactor outlet pipe melted, releasing burning salt. The fire was promptly tackled by the works brigade and was finally extinguished at 01.00 hours on 5th January.
Two suffered minor injury and extensive damage was caused requiring a virtual rebuild of the reactor.
The subsequent investigation revealed that the shaft of the heat transfer pump had again fractured. The control room had no indication since the plant trip operated only when the pump motor stopped. In this case, although the pump was inoperative, the motor continued to run.

Lessons
1. Add additional instrumentation to provide warning of low salt flow through the reactor.
2. Provide facilities to an alarm and automatic feed-stock trip on high spot temperatures.
3. Provide facilities to prevent a complete draining of salt back to the pump in the event of pump failure.
A serious fire occurred on a Hydrocracking Unit when a backflow of feed through a shut down pump caused it to rotate at high speed in the reverse direction. The reverse rotation and acceleration of the pump impeller caused the connecting shaft between the motor and pump to fail, followed by rupture of the packing gland and gland/seal oil piping. The motor disintegrated, igniting the oil leak from the gland/seal oil system.

The fire took about 3 hours to extinguish, causing damage to the base of a fractionator column, pumps and motors, and extensive damage to electrical wiring and instruments. The drains in the immediate vicinity of the fire became blocked with insulation debris from the fractionator column, and this caused flooding. Water with an oil layer on top reached an adjacent process area where ignition occurred and caused further damage. Portable air driven pumps had to be used to limit flooding. A further feature of the fire damage was that the fractionator column, pipeline etc. insulation was of aluminum sheeting, which burnt off exposing large areas of bare metal. The impact of water jets also knocked off the cladding in some areas. Radiant heat from the fire also destroyed a 400 wire communication cable run, disrupting communications and some control systems.

The pump which failed had a suction pressure of over 12.4 bar (180 psig) and a discharge pressure of over 138 bar (2,200 psig) at a temperature of over 260 degrees C (500 degrees F), and was fitted with dual piston type check valves on the discharge side, and also a manually operated minimum flow-valve. An additional automatic minimum flow valve situated in the pump discharge line was not in use due to long term control problems associated with the fractionator column.

When closing the manual minimum flow valve it had been found by experience that the low rate of flow caused a high discharge pressure in the pump and the pump gland packing would blow. Therefore a change in operating procedure had been practised from 1969 to 1972, the procedure was to shut the pump down before closing the discharge valve and to rely on the dual check valves to prevent reverse flow until the discharge valve could be closed.

Investigation after the fire showed that both check valves had failed to close as required due to internal corrosion causing sticking of the discs in their guides.

Lessons
1. Reinstate the automatic minimum flow valve facilities to allow the gear operated discharge valve on the pump to be closed before shutdown of the pump.
2. Instigate a regular programme of inspection of check valves.
3. Replace the fractionator tower aluminium insulation with stainless steel.
Abstract
A fire occurred involving a refinery plant reformer. Substances involved, hydrogen and naphtha.

Lessons
[None Reported]
Abstract
Following an operational upset on the catalytic cracker on 29th July, 1972, flow through the south pass tubes of the unit's feed preheater furnace was interrupted for about 10 minutes while the heater was still being fired. The heater tubes were subjected to `creep shock' which resulted in leakage at the expanded ends of 11 of the tubes. The leaking vapours ignited and a minor fire occurred in the east end header box of the south radiant wall tubes. The fire was readily extinguished by a fire steam hose and the vapours blanketed by the fixed snuffing steam. There were no injuries to personnel and damage to the heater was minimal.

Prompt emergency action was taken by the operating staff in opening steam to the header boxes and shutting down the furnaces. The refinery fire service was on site within 2 mins. of receiving the alarm and the fire in the header box was extinguished without difficulty using a fire steam lance and controlled thereafter by the snuffing steam to the header boxes.

The initiating cause of the incident was the loss of the gas compressor but the tube overheating and subsequent escape of oil with a fire was due to the faulty furnace temperature controller.

[fire - consequence, refining, instrumentation failure, cracking, temperature meter/control]

Lessons
The heater outlet thermocouples were located ca 30 ft. downstream of the heater and sufficiently remote so as not to be influenced by conducted heat from the furnace. This `dead-leg' location was responsible for no temperature increase being recorded during the no-flow condition.
Abstract
At 1750 hours on 15th July, 1972, and again at 0605 hours on 26th July small fires occurred at the inlet nozzle flange of the catalytic reformer effluent heat exchanger. Both fires were extinguished with dry chemical and the flange bolts tightened.

Lessons
The occurrence of flange fires in plants on hydrogen service was investigated and a questionnaire was circulated within the company to establish whether this hazard continued to be a problem or whether it has decreased to acceptable levels.
Abstract
Explosion in pressure vessel. Spark ignited clothing in presence of oxygen. Fatality.

Lessons
[None Reported]
Abstract
An explosion occurred during maintenance operation on an empty mixer of the titanium dioxide plant. The blast occurred as repair teams were heating bolts to remove them from a piece of equipment. The explosion threw a heavy metal plate ontop of a group of workers. The force of the blast shattered windows in other parts of the plant.

Lessons
[None Reported]
An explosion and fire occurred in the dust extraction system of a banbury mixer in a PVC compounding department. Damage was slight and was centred upon a reverse jet cleaning dust collection unit situated in an enclosure. Subsequent examination showed that the filter bags within the dust collection unit had been destroyed and the fire had caused heat effects on the supporting metal frames, the metal case and the hopper below, including distortion of the main access door. The indications from the damage as a whole were that first, a fire had occurred in the dust collection unit. After this had developed to some extent, most probably resulting in perforation of the filter bag material, a dust cloud suddenly arose, possibly due to the operation of the reverse jet blowing mechanism, and ignition of the cloud by the fire led to explosion pressure effects both upstream and downstream of the unit. It is quite likely that the cause of the fire that finally gave rise to the explosion in the dust collection unit has its origin at some earlier time. Sometime prior to the incident, the dust collection unit had been cleaned and fitted with new filter bags. It emerged that the replacement bags were of terylene felt, whereas those previous in use during the nine years life of the unit - during which no similar incident had been experienced - had always been wool felt, so far as is known. It seems unlikely however that, after 16 days of uneventful use of the new material, this change could be responsible for the primary cause of fire. It is possible however that the rather greater susceptibility of terylene to failure by heat may have meant that a small fire that would not normally penetrate wool before falling into the collecting bin to be smothered, in this instance perforated the terylene and so led to a dust cloud and explosion.

The charge in the banbury mixer, from which the extraction system drew fume and dust, was polystyrene-based, as had been the case for the last five years. Subsequent examination showed that the batch mix, which was of a particular formation that had been run for the last five days was quite normal. The overwhelming probability is that burning material of some kind was drawn into the dust collection unit some time before the explosion occurred. It is unlikely that anything large enough to create the fire could be drawn in through the main opening to the banbury mixer, through which the linear air speed is relatively low. For the same reason, it is unlikely that the source was drawn from the mixer itself. On the other hand, the 7 inch air extraction duct, in which the air speed was much higher, had three 2 and a half inch branch openings and an adventitious hole at the point of connection, via a rubber hose, to the case of the mixer. The branches are said to have been closed, as a rule, by plastic cups. It is not difficult to visualise an ignition source as large as a cigarette end, or a tobacco dottle, being introduced into these openings, either accidentally or perhaps absentmindedly. It is understood that the mixer operator, although a smoker, says that he was not smoking at the time of the explosion. Smoking was not forbidden by the rules of the factory. It is unlikely that the fire was caused by any spontaneous or electrostatic effect in the dust collection unit itself. A subsequent small fire, discovered in the dust collecting bin under the filter unit some 24 hours after the explosion, is likely to have been the consequence of failure to extinguish completely the first fire. It illustrates the smouldering propensity of the material concerned.

The following conclusions and recommendations were made.

The best situation for any unit collecting flammable dust is in the open air, although with a unit as small as the one concerned in this case, the explosion potential when situated in a clean building of some size is not large. In the outdoor situation however, an explosion relief panel can be provided on top of the unit, which is the safest and most convenient place for it. Such a panel must be strongly hinged, or chained to the unit so that it can not become a dangerous missile, but at the same time can lift easily. This relief having been provided, connections to the dust collecting unit can be made relatively strong and the inspection panels must be firmly be secured. The dust collecting unit with its associated fan and final air outlet duct can be given overhead weather projection provided that this does not impede the operation of the relief. The air extraction duct must be sized to give an air velocity sufficient to minimise dust deposition, and bends, tee-pieces and obstructions to be reduced to a minimum. There must be no points of entry to the extraction duct other than the main extraction point, where the air speed is adequate to collect fine powder and fume, but no larger objects. A sound joint must be made to the mixer case, designed to be disconnected and re-connected at intervals for purposes of cleaning. It is good practice not to permit smoking and the use of naked lights in areas where combustible materials, whether powders or otherwise, are handled, since these practices can give rise to fire or explosion in several ways.
During the recycle gas purging of a reactor on an ultraformer unit, a large release of gas emanated from the cover of the discharge valve on the spare (standby) debutaniser reflux pump. The vapour was ignited by an unknown source and the central area of the unit was engulfed in flames. One fireman died, from an apparent heart attack while setting up hoses, and another sustained a back injury. Damage to equipment was extensive and included damage to electrical cabling, instruments, pipelines, several pumps, valves, reinforced concrete supports, etc.

The fire was brought under control in about five hours and finally extinguished some two hours later. The fire was fought under extremely adverse conditions:

1. Sub-freezing temperatures caused ice to form over equipment and ground areas the large amount of water being directed against the fire which overloaded the drainage facilities and flooded the area to several inches
2. Numerous failures of steam line valves resulted in the escape of clouds of steam which obscured vision, and in some areas the noise from escaping steam was almost deafening

Investigation of the original source of the leak on the spare reflux pump discharge valve cover revealed that the metallic gasket had been blown out of its seat and broken into two segments; the breaks being approximately 180 degrees apart. The cover to body joint on the check valve is a male and female configuration which fully contains the gasket. With such a design it would be virtually impossible to blow the gasket out unless the flange had been loosened in some manner. Since water is continuously injected into the debutaniser system for corrosion control, either into the reflux pump discharge line or debutaniser overheads, it is surmised that water had collected in the discharge valve, froze, and exerted a tremendous force on the cover bolting which caused the bolts to stretch. Before the incident, ambient temperatures had remained below -18 degrees C for some thirty-six hours and had risen to about -9 degrees C at the time of the fire. With the temperature of the area around the pump being somewhat higher than ambient because of the close proximity of a number of hot exchangers, this rise in temperature resulted in the line thawing out and the liquid stream penetrating the loose cover, blowing out the gasket.

Normally, the standby pump is held with the discharge valve shut and the suction valve and discharge bypass valve open; and this was the state of valving at the time of the incident.

Note: The decision to leave the discharge valve open was specific to this particular case, due to the low ambient temperatures experienced and the ability of water to enter the system. Normal practice with shut down pumps is to leave the discharge, bypass, warm up, and flushing oil valves shut to avoid overpressuring the pump body.

Lessons
To prevent the accumulation of water in idle cold pumps, in future the discharge valve should additionally be cracked open.
Source: EUROPEAN CHEMICAL NEWS, 1972, 11 FEB.
Location: Mazingarbe, FRANCE
Injured: 0  Dead: 0

Abstract
Explosion in synthesis gas unit of ammonia methanol plant. Reactor tube failure.
[reactors and reaction equipment, processing]

Lessons
[None Reported]
<table>
<thead>
<tr>
<th>Source</th>
<th>EUROPEAN CHEMICAL NEWS, 1972, 26 MAY.</th>
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Abstract

Fire on ethylene cracker.

[fire - consequence, cracking]

Lessons

[None Reported]
**Source**: CHEMICAL AGE, 1972, 2 JUN.
**Location**: Sarnia, CANADA
**Injured**: 0  **Dead**: 0

<table>
<thead>
<tr>
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<tr>
<td>Tube fracture in furnace in catalytic cracking unit resulted in fire.</td>
</tr>
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<table>
<thead>
<tr>
<th>Lessons</th>
</tr>
</thead>
<tbody>
<tr>
<td>[None Reported]</td>
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</table>
Source: CHEMICAL AGE, 1971, 10 DEC.
Location: Terneuzen, WEST GERMANY
Injured: 0  Dead: 0

Abstract
Fire in naphtha cracker furnace.
[fire - consequence, cracking]

Lessons
[None Reported]
Abstract
At 01.00 hours on the 3rd August, 1971 an internal fire occurred in a pressure-reducing section of the catalytic cracker unit regenerator effluent gas system. There were no injuries to operating personnel but damage of approximately £20,000 (1971) was caused to the area of the plant affected by the fire. In addition, the unit was offstream for a fortnight with consequent loss of products.

The incident began when a faulty control valve on the catalyst circulation system failed to operate and initiated a sequence of events which ultimately allowed oil-laden catalyst into the regenerator vessel.

Spontaneous evaporation and burning of this oil caused a pressure rise which in turn created a large increase in flow through the regenerator cyclones. Oil-laden catalyst was entrained in this flow and carried forward to the pressure reducing chamber downstream of the regenerator.

When excess oxygen reappeared in the regenerator tail gas, the oil-soaked catalyst in the chamber self-ignited and burned, destroying parts of the refractory to an extent that the outer steel casing was seen glowing. This was about two hours after the upset conditions began.

The faulty controller in this case was the regenerator slide valve which adjusts the flow of catalyst to the reactor vessel.

Lessons
1. Installing an automatic shut-off of feed to the riser when the differential pressure across the regenerator slide valve falls below 0.1 bar might be considered.
2. The ability to put critical instrumentation on to manual control or, failing that, on to hand control is something which should be part of an operator's training. It may be necessary not only in emergencies but also during normal start-ups when instruments can be outside their operating range.
3. Where such valves are located remote from the control room, then the value of good in-plant communications, i.e. walkie/talkie sets, tannoy talk-back systems, becomes apparent.
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.

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.
Abstract
The AZDN (azodi-isobutyronitrile, AIBN) plant was extensively damaged by a fire which started above the neutralisation vessel on the ground floor and spread to AZDN in kegs on the first floor awaiting retreat. The neutralisation vessel agitator had been 'tripping' during the previous shift. Investigations revealed that set screws in the shaft coupling had become unscrewed, allowing the agitator to drop 6cm onto the vessel floor; however the design of the keyway ensured that it kept turning. Precession of the shaft in contact with the vessel floor put a heavy sideways load on the gland housing causing overheating and a fire to start in the graphite impregnated gland packing. This spread via lube oil and product on the vessel roof.

Lessons
Gland seals on AZDN containing vessels were changed to an internal bucket water seal type, to avoid close clearances, and to ensure that AZDN was kept out of moving parts. The storage of AZDN on plant was reviewed. A water deluge system was installed on the rebuilt plant.
Source: LOCAL NEWSPAPER
Location: South Killingholme, UK
Injured: 0  Dead: 0

Abstract
Fire on thermal cracker.
[fire - consequence, cracking]

Lessons
[None Reported]
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.

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

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.
<table>
<thead>
<tr>
<th>Source</th>
<th>ATTEBERY J.R &amp; LTHOPSON L.E, PRIMARY REFORMER TRANSFER HEADER FAILURE, AMMONIA PLANT SAFETY VOL 14, 1972, 37-38.</th>
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<td>Location</td>
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</table>

**Abstract**

This incident occurred in an anhydrous ammonia plant where a primary reformer transfer header failed. Metallurgical examination after the failure revealed that the pressure wall failed from a short time creep rupture under conditions of rapidly increasing temperature.

**Lessons**

[None Reported]
Abstract
A short circuit developed in the wiring of a fire eye system on one of two 600 psig boilers serving a refinery. This triggered a rapid sequence of events that resulted in a one week shutdown of much of the refinery. Fortunately no one was injured and equipment damage was negligible.

When the hydrocracker make-up compressor started slowing down, the control system at the reformer released the excess hydrogen to the flare. However, no increase flame was observed at the flare and the crude unit pressure went over 50 psig. The trouble was quickly diagnosed as a blockage in the flare system. The hydrocracker units were shutdown. Quick action by operating personnel prevented potentially catastrophic failures to the flare system and other operating equipment.

No major leak occurred and within two hours, it was concluded that the molecular seal was plugged. Witnesses at the time of the upset observed debris flying out of the flare. A search revealed five or six ice boulders, each weighing 50 to 60 pounds at the base of the flare. Also the 3 inch centre steam pipe and nozzle was found in the area.

Lessons
[None Reported]
Abstract

During routine stock checks of gaseous nitrogen cylinders on a catalytic reformer a member of operations staff noticed that one nitrogen cylinder smelled strongly of what appeared to be acetone. It was later established that the cylinder was contaminated with several gallons of methyl ethyl ketone (MEK). Investigations showed that the cylinder was used previously on a solvent dewaxing unit to provide a nitrogen blanket on certain vessels during overhauls. The nitrogen cylinder with a reducing valve had been connected to the solvent storage system for an extended period which was unnecessarily prolonged. Whilst connected, MEK had diffused into and contaminated the nitrogen cylinder which obviously occurred at low nitrogen pressure, which was assisted by varying ambient temperatures.

As a precautionary measure, suppliers of gaseous nitrogen have been requested to invert all cylinders (to remove any liquid present) before commencing any filling operations. However, the use of positive measures to prevent entry of liquid, gas or any contaminant into nitrogen cylinders remains the responsibility of the users.

Lessons

1. Reducing valves must be used on all possible occasions.
2. Vacuum conditions and low pressure in cylinders must be avoided. 50 p.s.i.g. nitrogen in a cylinder is considered a minimum safe operating pressure.
3. Cylinders must be connected to a system for the required period only. On completion of a purging or blanketing operation, disconnect the nitrogen cylinder.
4. Check that the pressure of the nitrogen cylinder is sufficiently higher than the pressure in the system before connecting up any cylinder.
5. Ensure the oxygen level of any nitrogen source is within the required limits before use of nitrogen in any purging operation.
Abstract

Whilst carrying out maintenance work on the radiation cone assembly of a desulphuriser heater on a catalytic reformer, a bolt fractured as it was being removed. The 1" bolt of 25% chromium/12% nickel alloy steel had fractured at the first thread adjacent to the plain shank in a brittle manner with apparently little force being exerted by the fitter. When this work was being carried out several maintenance personnel were working on and below the radiation cone, which was freely suspended by these bolts and able to swing. Under these conditions there was a definite risk of bolt or flange failure as all the cone components are made from alloy steel.

This note draws attention to the danger to which men working on and beneath the cone may be exposed. The testing of the bolt which failed showed that the ultimate tensile strength had fallen from at least 70,000 p.s.i to 56,700 p.s.i., the yield point which should have been over 35,000 p.s.i. could not be detected and the percentage elongation had fallen from at least 10% to 1%. These figures show the reduction in ductility and the decreasing strength which had occurred after thirteen years in service. Metallurgical examination of the bolt revealed that the originally sound material had suffered very slight oxygen penetration at the surface and the etched structures showed severe embrittlement.

From the appearance of the micro-structures it was estimated that in this case the cone components, all of which are made from this material, had been operating at around 70 degrees C.

This phenomenon is well known and has been observed in furnace tube supports and flue gas baffles.

Lessons

1. Be aware that when carrying out maintenance work in the type of heaters, either above or below the radiation cone, reasonable care should be taken to ensure the cone and the support bolting are not used to carry any additional loads and in particular are not subject to any sort of impact loading whatsoever.

2. Personnel must not be allowed access to the cone unless temporary additional supports have been provided for the cone assembly.
Abstract
Asphyxiation Incident on an Ammonia Plant. A contract labourer was asphyxiated as a result of working in an oxygen deficient atmosphere whilst wearing a dust mask. Prompt action by operating staff in rescue and resuscitation saved this man's life. Catalyst was being dumped from the Desulphurising Reactor which was under a nitrogen purge to prevent self ignition.
During this operation workers working outside the vessel wore dust masks. Most of the catalyst had been removed and workers were now required (one at a time) to enter the vessel and clean out the remaining catalyst.
An 'Entry Permit' was issued to allow workers to enter the reactor, which clearly stated that the vessel was:
1. Under a nitrogen purge.
2. Deficient in oxygen.
3. That breathing apparatus must be worn.
Two workers who had worked inside the vessel wore breathing apparatus, but the asphyxiated person entered wearing a dust mask and, after a period of 7 - 10 minutes he collapsed.
Statements made by personnel concerned are contradictory and show that there was some confusion as to what instructions were issued to the men at the time. Facts emerging from the investigation showed that there were:
1. A series of supervisory failures.
2. Conditions were not explained to the person in charge of the job, and that the men carrying out the work were not informed that the vessel was under a nitrogen purge and the atmosphere deficient in oxygen.
3. There was a lack of training of personnel in the use of breathing apparatus.
Previously the workers had worked inside a similar vessel near the one that the incident occurred in. This vessel was gas free and its oxygen content was acceptable and the workers worked inside wearing dust masks.

Lessons
The following recommendations were put forward by the investigating committee:
1. Suitable signs to be placed at the entrance to open vessels having an oxygen deficient/toxic atmosphere.
2. All personnel required to wear breathing apparatus are properly trained.
3. Supervisors should be given specific guidelines on their areas of responsibility for supervision.
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<tr>
<td>Location</td>
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**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.

**Lessons**
[None Reported]
A 7 inch thick reactor of a wide range hydrocracking unit being operated by computer at 2500 psi failed explosively due to localised heating. The blast caused widespread damage over a 300 yard radius including an adjoining catalytic cracker and crude pipe still where the roof of the control building collapsed. Other units were safely shut down from a blast resistant control building which sustained minor damage.

Lessons

[None Reported]
Failure of reformer outlet header occurred in an ammonia plant. It was found that the header had ruptured under extended creep conditions.

Lessons
[None Reported]
Abstract
Hurricane and rain storm hit refinery. The main structure of a 19 year old thermofor catalytic cracking unit was toppled. 30 tanks were damaged and power disrupted.

Lessons
[None Reported]
Abstract
An explosion occurred in a fluid cracker. Fatality.

Lessons
[None Reported]
Abstract
An operator was injured after having entered a vessel where the agitator was not isolated and which suddenly restarted. In this incident a plant operator entered a polystyrene reactor to obtain a sample of resin build-up on the reactor wall. The Shift Foreman was working with the plant Development Chemist at the time of the incident. The Chemist had not successfully communicated to the Foreman his intention that he, the Chemist, should enter the tank and not the foreman himself. A second Operator from another plant provided the Foreman with assistance. All the connections to the vessel were blanked and the electrical supply to the reactor switched off at the control room stop button. No electrical isolations were performed and no entry permit was completed or signed.

The Foreman entered the tank via a ladder, while the Chemist was in the control room. Shortly after entering the vessel, the agitator started up and the Foreman received a broken leg and lacerations having come into contact with the agitator. The agitator was stopped in the control room a few seconds after it had started by the Plant Operator upon the shouted request of the relief plant operator watching the Foreman in the reactor.

The cause for the agitator restarting suddenly was believed to be a fault in the automatic switch-over mechanism of the control room transformers.

Lessons
The following observations/recommendations were made after the incident:
1. Reinforcement of the need for an authorised person to always sign a permit to enter and not only the person entering.
2. Stop-buttons on agitators should be locked off as a safeguard before entering any vessel that contains an agitator.
A split tube occurred on a main boiler in a refinery causing shutdown of the catalytic cracker. The back pressure controller controlling a butterfly valve in the flue gas stack from the catalytic cracker began to malfunction. This resulted in a pressure surge back through the unit, all the way to the air blower. A catalyst circulation hold-up was experienced, but circulation was soon re-established after the differential across the unit was correct. About fifteen minutes later the air blower began to go through extremely heavy surges. During one of these surges an explosion occurred which blew out a large section of the blower case and opened a crack almost completely around the circumference of the case. The force of the explosion shattered the glass window of the building housing the blower, as well as those in the central control room located some 75 feet away. The blower building is of cement block construction and some of the mortar joints were even cracked by the blast. Fortunately, no-one was injured and all personnel reacted properly to the emergency condition.

[control failure, damage to equipment, process control & instrumentation]

Lessons
[None Reported]
A large intense fire and explosion occurred at a catalytic reforming unit in a refinery. The fire centred on the effluent circuit of the hydrofiner which prepares feed for the reformer and resulted in extensive damage. Inspection of the rupture exchanger inlet piping showed that prior to the fire there was severe metal loss from the pipe wall directly opposite the inlet connection. Within this area a section of the wall, approximately 8 inch. long had been reduced from the original 0.375 - to 0.015 inch. which is the rupture thickness calculated for the operating pressure and temperature. There is no doubt that the pipe failed at this point. It is worth noting that a rupture rather than a pinhole leak developed, which is unusual as a mechanism of pipe wall failure, unless general thinning occurs.

Lessons

The following recommendations were made:

1. Chlorides present in feedstock to hydrofiner units to be identified, and the possibility of corrosion mechanisms checked out so that appropriate corrective measures can be provided.
2. Tackling a very large fire in a light hydrocarbon process unit requires the classical approach of emergency process shutdown, isolation of sources of fuel release and the application of large quantities of cooling water to project equipment and structures against further failures until the flammable inventory has been removed or exhausted. This incident demonstrated the need for additional emphasis on protective features. These include the more extensive application of remote valves for emergency isolation and depressuring, wider applications of fireproofing to vessels and structural steel and the use of water spray systems in areas of particular equipment congestion.
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 than heat generation, in other words a "runaway reaction".

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.
On the evening of 17 April an ethanol plant was being operated at low throughputs as ethylene feedstock was in short supply. The two reaction trains were being fed by one feed compressor and gas circulation to both trains was handled by the recycle compressor. A sharp fall in fuel gas pressure occurred at 19:00 and dropped further at 20:00. The pressure then began to rise, this caused temperature swings within the furnace, with this swing stopping twenty minutes before the incident. The temperature controller failed and the furnace outlet temperature rose rapidly (520-800 degrees F). The large temperature increase on the feed to the reactor caused the train pressure to rise just prior to the failure. The very high reactor inlet temperature to the first reactor caused large quantities of carbon to be made some of which was found later in the HP separator. The carbon build up on the catalyst carrier increased the resistance to flow and one minute before failure a sharp reduction of the recycle gas flow rate to the furnace was observed. Calculations indicated that the temperature of the gas leaving the furnace rose to 1110 degrees F before the reduction of recycle gas flow and 1380 degrees F when failure occurred. At a pressure of 1020 psig in the line and a temperature of 1380 degrees F the yield stress of the 20 cm mild steel line was exceed and the line failed. The resultant fire was preceded by a loud roar.

The fire lasted for 90 minutes before it burned out.

Recommendations included:

1. New high temperature alarms, giving audible warning, should be fitted to the outlet of the furnaces and ethanol plants.
2. New temperature controllers, with proven improved process reliability over the current, are required for service on ethanol plants.
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.

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.
<table>
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| 14 January 1969 | **Abstract**  
Mechanical failure of a batch alcohol reactor containing about 2000 gallons of kerosene and triethyl aluminium under high pressure caused a flash fire and localised blast damage including destruction of the process control room. The reactor head landed in a pipe rack 80 ft distant but did not rupture the lines.  

[mechanical equipment failure, damage to equipment, fire - consequence, batch reaction, batch reactor]  

**Lessons**  
[None Reported] |
Overheating during mixing caused vapour to escape via the opening to the agitator shaft. The gas cloud was ignited by the motor started causing an explosion, which caused serious damage to the building.

[Abstract]

Lessons

[Lessons]
<table>
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**Abstract**

An indoor vapour cloud explosion occurred when hot xylene used for washing equipment leaked from an unatched filter cover and flashed into vapour. The ignition source was a fired autoclave in an adjacent building with communication through an open door in a fire wall.

**Lessons**

[None Reported]
Abstract
Fuel for jet engine starter cartridges was being compounded in a 10 gallon stainless steel mixer of special design and close tolerances. Near the completion of the mixing, the mixer was shut off, the mixture inspected and the mixer started remotely. The restarting caused a violent explosion.

Lessons
[None Reported]
Abstract
Lightning hit a substation and polystyrene resin set in five reactor systems when the agitator motors stopped. Four units were started successfully but attempting to restart the fifth one damaged the agitator gear drive and internal cooling cols.

Lessons
[None Reported]
A 1200 lb containing 700 lbs ethylene oxide exploded causing considerable damage but no injuries. The explosion occurred on a plant making choline carbonate. The cylinder was connected to an autoclave and the ethylene oxide was pressured in with nitrogen to react with tma solution and carbon dioxide. Liquid phase polymerisation of eo occurred as a result of backflow of catalyst from the reaction vessel.

Lessons
[None Reported]
Contamination led to the explosion of a reformer at a refinery. Substance involved naphtha.

Lessons
[None Reported]
Abstract
A batch of 300 kg of AZDN (azodi-isobutyronitrile, AIBN) was being made by the batch oxidation of the intermediate hydrazodi-isobutyronitrile (HZDN) with sodium hypochlorite liquor (bleach). An accumulation of bleach, compounded by late application of cooling, caused the batch to exceed 50 degrees C and to froth badly. The operator decided to stop the agitator to reduce the frothing. An hour later, despite falling temperature indications in the liquid bulk, the lid blew off the 500 gall vessel.
[overpressure, container, processing, low temperature]

Lessons
The mistake was to stop the agitator. Calculations suggested an SADT for the floating 'disk' of AZDN of c. 50 degrees C. The vessel burst as a result of the large volumes of gas generated as the AZDN decomposed, despite lower temperatures in the liquid bulk beneath. The process was later changed to oxidation by continuous chlorination, in which the reaction is conducted at end-of-reaction conditions with little or no accumulation of either HZDN or oxidant.
Abstract
Repairs were being carried out on autoclaves No's 1 and 3 in a chemical production unit. A rigger went to the unit to open the autoclaves and checked before opening No 1. Then, unknown to operating unit personnel, he opened the top manhole on No 3, at the third level. He then went down to the second level to remove a manhole cover there. Instead of opening No 3, he accidentally opened No 4., which contained vinyl chloride at 70 psig. Polymer had formed around the inside of the manhole, so that when the bolts were removed there was no immediate evidence of pressure, although almost immediately the pressure blew off the cover and released the vinyl chloride. This was ignited by a static electricity spark or friction spark when the manlidhit a nearby steel railing. The rigger and two nearby labourers were blown from the second level to the ground and were killed.

Lessons
[None Reported]
During maintenance work on autoclaves in a chemical production unit, a rigger opened the wrong manhole cover. The autoclave contained 7 tonnes of vinyl chloride under 500 Nm⁻² nitrogen pressure. Polymer had formed around the inside of the manhole, so when the rigger removed the bolts there were no immediate signs of pressure inside the vessel. Almost immediately after all the bolts had been removed, however, the pressure blew off the cover and released the vinyl chloride. The escaping material ignited from a static electricity spark or a mechanical spark when the manhole cover hit a steel railing.

**Lessons**

[None Reported]
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.

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.
During maintenance work on autoclaves in a chemical production unit, a rigger opened the wrong manhole cover. The autoclave contained 7 tones of vinyl chloride under 500 Nm² nitrogen pressure. Polymer had formed around the inside of the manhole, so when the rigger removed the bolts there were no immediate signs of pressure inside the vessel.

[human causes]

Lessons
[None Reported]
Abstract
An explosion occurred in the precipitator of a fluid catalytic cracking unit. The unit consisted of two separate reactors with a common regenerator. The regenerator was equipped with ten single stage cyclones, a waste heat boiler and the precipitator. The air for regeneration was supplied by two motor driven blowers operating in parallel.

At the time of the incident the unit was being returned to operation, after having been essentially shut down in the morning due to a total electrical power supply failure. Gas oil circulation had begun, and spent catalyst was being added to the regenerator from the storage hopper to build the level to normal. The air heater had been lit to start increasing regenerator temperature which had fallen to about 500 degrees F. The reactors were bottled up. The explosion was caused by oil vapour that was ignited by a spark in the precipitator. The oil leaked into one of the reactors during gas oil circulation after the electric power was restored, and leaked through the reactor spent catalyst slide valve into the air stream to the regenerator. There was insufficient heat in the regenerator lean phase to burn this oil, but enough heat to vaporize it. The explosion ruptured the shell of the precipitator and caused severe damage to the internals. There was fire erupting from the ruptured vessel. One air blower was vented to the atmosphere and steam was opened to the regenerator risers. The fire was quickly snuffed out. The unit was out of service for a total of 53 days as a result of the accident.

Lessons
The following conclusions were made:

- The operators were putting the unit back on stream following a power failure. While this was not a direct cause of the explosion, the total failure of power and the length of time that the unit was without power were major contributory factors.
- There were two separate feeders to the unit from an outdoor electrical substation, assuring power for the unit as long as either of two buses was in service at the substation. The first power interruption, at 10.23 a.m., was caused by the failure of a micarta bus support. This was probably due in part to the very foggy and humid weather that day. Failure of the second electrical feeder occurred at 10.49 a.m., and was most likely due to a loose connection caused by a faulty bolt head. The fact that the power failure to the unit was total and continued for 2 hours and 41 minutes was significant, in that the operators had no experience of returning the unit to operation after this long a period without the blowers in operation, and it allowed the temperature in the regenerator to drop to the point where burning would not take place.
- The following recommendations were made:
  - Replace all the bus supports at the electrical substation with a less hydroscopic material constructed from polyester and spun glass.
  - Investigate the possibility of adding heaters to crossover bus housing to minimize the effect of humidity.
  - Establish a procedure for regular routine inspection and maintenance of electrical substations.
  - Prepare a detailed check-list of important critical items concerning the start-up and shutdown of the unit on both a regular and emergency basis, to be carefully reviewed with the operators.
  - Issue instructions and sketches to all operators aimed at preventing oil from getting into reactors at any time that catalyst is not circulating. These instructions are to provide specifically that the reactors must be blocked off from the circulating gas oil system with a double valve and bleed arrangement.
An explosion and fire occurred in a reactor of a catalytic reformer handling naphtha. The operating crew reacted immediately to depressurise the recovery system to the flare through remotely operated relief valves and to shut off all inlet and outlet oil and gas streams. The shift fire crew responded to the emergency. The fire burned vigorously for 10 to 15 minutes after which it diminished rapidly. 30 minutes after the explosion the fire was almost burned out. Immediately prior to the accident all conditions were normal. Just before the explosion the operating crew heard a hissing noise. Almost simultaneously the reactor pressure was observed to go down and the explosion occurred. The top head of the reactor was blown about 275 feet, and other pieces of debris were hurled up to 750 feet from the reformer. Fortunately damage was primarily confined to electric transmission supports and lines.

The manhead nozzle of the reactor was found to have an 18 inch crack at the top edge of the nozzle weld that penetrated through the nozzle. Cracks at this nozzle had previously been chipped out and backwelded. One belief is that this area failed first (supported by the hissing sound prior to the explosion) and that the opening served as a source of air for entry into the reactor that resulted in the internal detonation with the ripping off of the top head. Since 15 September 1964 the reactor was known to be operating with several hot spots on its shell (approximately 800 degrees F). The temperature of the hot spot areas was immediately reduced by the installation of steam rings and it was agreed that operation could be continued with the skin temperature kept at 700 degrees F.

Lessons

The following conclusions were made:

The tentative conclusion that the manway nozzle neck cracked first, and that the opening served as entry for air prior to explosion, was advanced. A more plausible theory must be advanced. First, it appears improbable that air could have entered the vessel through the crack in the manway nozzle in sufficient quantity in the time between indicated decrease in pressure and the audible reports to have contributed to an explosion. Second, it may not be relevant whether the crack in the nozzle occurred before, after or simultaneously with the rupture of the vessel head in the tangent (or 'knuckle') area. Third, attention must be called to the appearance of the vessel head fracture face. The cross-section of the fracture appeared to consist of an appreciable thickness of coarse-grained metal on the interior side, followed by fine-grained metal on the exterior. The metal in the area of fracture had not been exposed to inspection since the vessel was installed in 1954. Further, the fracture occurred outside of and adjacent to the welded-in steel support ring to which the stainless steel shroud was attached. Thus, visual indications are that hydrogen attack may have decreased the effective thickness of the metal. This theory must be disproved or made plausible by complete metallurgical examination and evaluation of the metal at both fracture faces, the shroud support ring, the manway nozzle, and the entire remaining shell of the vessel.

This theory could lead to the following conclusions: that an initial crack occurred to result in the 'hissing' sound; that a more or less complete circumferential failure of the vessel head in the knuckle occurred, accompanied by sudden depressurising and mixing of the vapours with air to cause the final explosion.

The top head appeared distorted in the same axis with the crack in the manway nozzle neck.

Less incidental indications included circumferential cracks on the inner surface of the manway nozzle-to-head weld. Visual examination did not indicate that these cracks had progressed to complete penetration.

The following recommendations were made:

1. Make metallurgical examinations as detailed above, immediately.
2. Completely denude interiors of the reactors and make all possible inspection to establish their present condition, preparatory to reaching a decision regarding their possible replacement.
3. Ascertain if the reactors can be insulated to operate satisfactorily without the present type shroud, or can be modified to operate as radial flow reactors.
An incident occurred in a benzoyl peroxide paste building at an organic peroxide plant when decomposition of benzoyl peroxide and dimethyl phalate paste where added together and mixed in a mixer bowl. Fortunately no fire occurred.

The decomposition occurred due to heat generated by friction between the scraper blade and the metal bowl. Inside the mixing bowl friction marks were found some of which matched the scraper blade.

An operator received slight burns in the incident.

Lessons

[None Reported]
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.

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.
Abstract
An explosion occurred in a mixing installation of a fertiliser plant. A combination of urea-ammonium nitrate solutions were in use.

Lessons
[None Reported]
Abstract
The ammonia unit was in normal operation when a type 304 stainless steel primary reformer 12 inch outlet piping suddenly ruptured along its longitudinal weld seam. The fire was extinguished quickly.

[fire - consequence, pipe, material of construction failure, processing]

Lessons
[None Reported]
A pipe exploded at a catalytic cracker unit during start-up after a 2 month turn around period. The ensuing fire was quickly extinguished but the unit was heavily damaged by shock waves.

[fire - consequence, damage to equipment, cracking]

Lessons

[None Reported]
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.

Lessons
[None Reported]
Abstract
On a naphtha catalytic reformer with radial 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.

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.
Abstract
Cleaning out experimental nylon polymer from an autoclave with hot 62% nitric acid caused an explosion. Fatality.

Lessons
[None Reported]
Abstract
Explosion ruptured phthalic anhydride converter shell and expelled heat transfer salt up to 100 ft. In this fixed bed process, the naphthalene-air mixture was passed up through the packed tubes from a feed plenum at the bottom of the reactor. The heat transfer salt was pumped from the top of the reactor to the bottom through numerous baffles generally countercurrent to the naphthalene-air flow. After investigation it was concluded that an undetected leak had occurred in the tubes near the bottom of the reactor. The naphthalene-air leaking into the nitrate bath interfered with the salt flow, the gases being trapped due to the design of the unit. The reactor tubes became so hot that the salt and chrome steel tubes began to react.

Lessons
The following changes to the plant were made;
The redesigned reactor had the salt flow changed so that it now proceeds upward with special provision to vent any gases from leaking tubes. The heat transfer salt is now analysed weekly for chromium to detect any corrosion abnormalities.
Abstract
An explosion involving thermal decomposition of an acetylenic compound during a pressure hydrogenation reaction occurred in a large rocker autoclave containing pentenol and hydrogen at 1000 psig.

Lessons
The following lessons were learnt:
Heating 1-pentol isomers above 100 degrees C during vacuum distillation should be avoided to prevent the polymerisation of these compounds. The presence of small quantities of sulphuric acid and potassium hydroxide reduce the temperature of instability.
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.

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 thorough.
Abstract
A large fractionator operating at just above atmospheric pressure was used to split a heavy naphtha cut. The column was tall and the condensers were well above the overhead receiver. When the unit was commissioned this fractionator gave all the symptoms of tray flooding despite being operated at well below design throughput. The pressure reading on the overhead receiver was normal but on installing a pressure gauge on the reboiler return, the pressure was 0.35 bar A. The column was hurriedly shut down because it was not designed for vacuum service. The explanation was that the 3” vent hole at the top of the drop pipe in the overhead receiver was not there. In its absence the pipe from the overhead condenser acted as a barometric leg. There was no permanent gas present and so the vacuum could be pulled without need for an ejector. It was only good fortune that the column did not implode and collapse.

Lessons
1. An independent final check to be made on new plant preferably by a process engineer, before it is boxed up and commissioned.
2. Any even slightly unexpected response on a new plant requires immediate and careful analysis.
Abstract
During nitric acid oxidation, p-xylene under pressure in a 500 gallon autoclave exploded.

Lessons
[None Reported]
Abstract
A bromination reaction was being carried out at a temperature of 125-130 degrees C and a pressure of 0.5-1.0 bar in a 2.5 m3 glass-lined steel batch reactor. Perforation of the heating jacket occurred, and Mobiltherm heat transfer fluid flowed into the reaction mass. This caused a temperature rise which could only be brought under control by transferring the batch to another vessel containing ice.
The incident occurred only one day before the quarterly check of the enamel lining was due.

Lessons
An investigation showed that the reactor had previously been used under particularly severe conditions - for agitating a very viscous melt of aluminium chloride/sodium chloride at a temperature of 220 degrees C.
Two tantalum plugs in the lower part of the vessel were missing. At one point where the defective enamel had been covered by a tantalum plug one year previously, there was a hole in the wall of the vessel about 1 cm diameter, caused by corrosion.
It was noted that:
1. When a highly viscous mass has to be stirred, or when solid material is charged first and the solvent added later, high shear forces are created which may loosen a tantalum plug.
2. High temperatures may cause Teflon gaskets to soften or creep, which again can lead to a plug becoming loose.
Abstract
The agitator on a nitrobenzene hydrogenator failed and it was decided to remove it for maintenance. The aniline burden together with catalyst was discharged from the reactor and the reactor was then cleaned by filing with boiling water. This was repeated a further five times and then the reactor was filled with cold water. This again was repeated five times.

A fitter and his foreman, both wearing air fed suits commenced the maintenance work after being instructed not to remove the hoods of their suits. They removed the manhole cover from the reactor and the agitator drive and gearbox.

At this stage, they decided that the hoods were a bit uncomfortable and removed them. Both suffered aniline poisoning, one being hospitalised for a week (oxygen and methylene blue treatment), the other recovered in about eight hours. The source of aniline was never found.

The breathing air compressor was located in a safe place and no contamination of the breathing air distribution system could be detected. The ambient air temperature at the time of the incident was 12 degrees C, and the aniline vapour pressure was low.

Lessons
[None Reported]
Abstract
An explosion occurred during a bromination reaction to manufacture a herbicide. The bromination was being carried out in dichloroethane with elementary bromine and the addition of sodium hypochlorite. The compound to be brominated had been prepared in a previous methylation reaction. The glass fittings of the batch reactor and windows nearby were shattered, and one employee was injured by glass fragments.

Lessons
It is known that, in the course of methylation reactions with dimethyl sulphate in the presence of aqueous alkali, methanol is formed by hydrolysis:

\[(\text{CH}_3\text{SO}_4) + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{CH}_3\text{SO}_4\text{H}\]

\[\text{CH}_3\text{SO}_4\text{H} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{SO}_4\]

This methanol can in turn react with more dimethyl sulphate to form dimethyl ether:

\[(\text{CH}_3\text{SO}_4) + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_3 + \text{CH}_3\text{SO}_4\text{H}\]

It is thought that dimethyl ether from the methylation stage was carried forward into the bromination step and was the cause of the explosion.
Abstract
Pure hydrogen, for gas chromatographic use, was prepared by passing commercial hydrogen through a catalyst contained in a stainless steel body. Leakage and ignition of hydrogen occurred through a stress corrosion crack in the weld of the stainless steel body. Subsequent analysis of the commercial hydrogen showed that chlorides were present, despite the supplier's specification that they were "not detectable". The company concerned now analyses the supplied hydrogen and has installed a chloride removal system before the catalysis section.

Lessons
Impurities can markedly affect the choice of material for a particular duty. Continuous testing should be carried out to ensure that process changes etc. do not make the initial material choice invalid.
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.

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.
An incident occurred in a pilot plant where picoline sulphate was being prepared by the slow addition of picoline to a 100 litre glass flask containing 60 litres of sulphuric acid. The flask was set in a cooling bath and the addition rate was controlled by the acid temperature.

The agitator was a glass swivel-paddle type that could be held in line with the shaft for fitting into the flask, but which swung at right angles to the shaft when rotated.

The operation had been carried out several times without incident but on this occasion the paddle stayed in line with the shaft thus providing no agitation and consequently no reaction. The charge of picoline was made but remained in a layer on top of the acid. The temperature remained very steady. The situation was appreciated soon after the addition was complete and it was presumed that the agitator had broken. The drive was stopped for the acid to be separated through the bottom outlet. However, the agitator swung into action as the drive slowed down and the entire contents rapidly discharged through a 6" nozzle in the flask.

The flask remained intact but less than 100 ml remained in it after the eruption. Explosion. No one was hurt but the acid mist created a highly corrosive atmosphere contaminating everything in the area.

Lessons

[None Reported]
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.

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.
A contractor was asked to perform some cutting and grinding work in a small (3m³) vessel under permit control. The two contractor mechanics were familiar with plant confined space entry procedures. The vessel had been well cleaned and normal lockout and blanking steps had been taken. Gas tests were carried out and showed an oxygen level of 21.5%. One of the mechanics was designated as an attendant and a portable blower was set up to ventilate the space. The cutting part of the job was completed without incident. When the mechanic in the vessel started grinding he found that the blower made conditions difficult: The high volume of air in the small space was blowing grindings and dust around excessively. The blower was shut off and the two mechanics left the job for about 45 minutes.

On their return the grinding operation was resumed without the blower on. After about three minutes the mechanic in the vessel became lightheaded and immediately climbed out. The mechanics reported to plant personnel. A recheck on oxygen level showed that it had decreased to 15.5%.

After investigation the vessel lockout and blanking operation revealed that a subtle source of nitrogen had not been recognised. The vessel had an agitator with a double mechanical seal. This was faulty and the barrier liquid had leaked through the vessel side seal. With the liquid reservoir empty the nitrogen blanket on the reservoir had an open path into the vessel.

The prime cause was the failure to recognise an insidious source of inert gas and carry out adequate preparation for entry. There was also a lack of recognition of the importance of forced ventilation.

Lessons
The following recommendations were made:
1. Vessels may often have unexpected sources of fluid entry via agitator seals or instrument connections. It is important that permit issuers are trained to recognise and eliminate these hazards. A pre-prepared checklist for each vessel can also be used.
2. Although preventative measures are the key to safe confined space entry, protective actions, such as fresh air blowing, can further reduce the risk and help compensate for the unexpected. The wearing of personal oxygen monitors is also recommended.
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 pyrolysed. The kettle was flooded with water.

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.
Abstract
A special epoxy resin was manufactured by an addition reaction between a heterocyclic secondary/secondary/secondary triamine and epichlorhydrin. During distillation of the raw resin to remove excess epichlorhydrin, an explosive decomposition took place, rupturing the top part of the vessel. Fortunately the operator was warned by a rapid rise in temperature and blockage of the agitator, and was able to escape in time.

Lessons
After dehydrochlorination, the raw resin showed an abnormally high content of hydrolyzable chlorine, indicating that dehydrochlorination was not complete. In spite of this, distillation was attempted. The presence of unstable components during distillation caused spontaneous decomposition.
An explosion occurred in a cracking furnace of a large ethylene plant causing extensive damage to the furnace and gas ducting. The firebox was split open with debris from the furnace lining thrown around the immediate area. There were no casualties resulting from the incident.

The transfer line valve on the cracked gas system was passing and hydrocarbons passed back into the furnace via a decoke valve which had not been closed. A flammable mixture built up in the firebox and was ignited probably by hot refractory lining in the furnace.

After investigation it was found:

1. The explosion took place while the furnace was `cooling' following a de-coke. Further, high levels of process activity took place immediately before the incident, as the plant was being prepared for a major shut-down.
2. The ethane had been taken out of commission, the furnace exit temperature had cooled to 370 degrees C, and the quench flow had been isolated with the fuel gas supply to the terrace burners blanked in preparation for turning the furnace effluent to atmosphere. The operators then found that they were unable to move the cracked gas transfer valve. Subsequent modification was needed.
3. After the explosion, the atmospheric valve was found to be closed and the de-coke valve which should have been closed when the furnace outlet temperature had fallen to 370 degrees C was found to be open into the firebox.

Lessons

The following recommendations were made:

1. The furnace required close attention during a cooling down period and the use of a check list requiring an initial for the completion of each step was proposed.
2. The cracking furnace procedure should be modified to maintain a positive flow of steam through the coil to atmosphere until the cracked gas can be isolated by blanking.
3. The shutdown procedure should also be modified so that the plate dampers are not fitted until the cracked gas has been isolated from the furnace by blanking.
4. Efforts should be made to improve the reliability of cracked gas transfer valves with regard to operability and tight shut-off.
5. The relatively small amounts of hydrocarbon to produce an explosion in a confined space should be brought to the attention of operators and other staff.
6. A non-routine operation requires more attention than normal operation, and the use of check lists can be useful when a series of critical steps need to be undertaken.
7. On processes subject to fouling and deposition of solids, it cannot always be certain that a closed valve gives a tight shut-off and further means of protection may be necessary for potentially hazardous conditions.
8. Furnaces even after several hours cooling can often still provide a source of ignition and flammable atmospheres should be avoided.
9. Relatively small quantities of flammable substances contained within a confined system can produce damaging overpressures if ignition occurs.
Abstract
During cleaning a pressurised reactor in a resin plant, it overpressured, ruptured its pressure relief device and discharged a solvent mixture consisting primarily of xylene and esters. The solvent formed a vapour cloud which settled into the facility and ignited within seconds. Two workers were killed in the resulting explosion and more than eighty others were injured, including some nearby residents.

In addition, the explosion destroyed five buildings and damaged 161 other structures in the area.

Installed in 1960 and replaced in 1985, the resin reactor operated entirely under manual controls.
The primary control panel was located several feet from the top of the reactor at the mezzanine level. However, the steam valve controlling application of heat to the lower zone of the reactor was on the ground floor at the bottom of the reactor.
The primary control panel contained chart recorders and gauges for both temperature and pressure, but no alarms for overpressure or high temperature nor emergency interlocks to shut down the heat or relieve the pressure if either exceeded desired levels. Thus the reactor required constant monitoring during operation.
The only protective device associated with the reactor was a rupture disc rated at 40 psi. The discharge line from the rupture disc penetrated the roof of the building, terminating with a 90 degree bend towards the centre of the facility. A concrete chute had been added to the end of the discharge line to act as a deflecting apparatus.
The ignition source for the explosion could not be conclusively determined due to the extensive damage and inaccessibility of some equipment. However, there were several possibilities within the general area covered by the vapour cloud. These included an inert gas generator, and several electrical switches in areas not classified as hazardous locations. OSHA investigators considered that a gas-fired oil heater was the most likely source of ignition. Fatality.

Lessons
The following recommendations were made:
1. Install visual and audible alarms to alert for high temperature, unacceptably high pressures or dangerous emissions, and shutdown devices to stop product flow into pressurised reactors.
2. To train operators, using written procedures, to handle both normal operations and potential problems, and to ensure that operators are at the control panel when a reactor is in operation.
3. Vent reactors to a knockout drum and/or catchtank or other safe location, eliminating ignition sources in locations near to the termination of vent lines.
4. To implement an inspection programme for rupture discs.
5. The feed rate to the reactor should be appropriately controlled with the provision of interlocks between the reactor feed lines and reactor parameters.
Search results from IChemE's Accident Database. Information from she@icheme.org.uk

Source: CONTROLLING ELECTROSTATIC HAZARDS, ICHME, SAFETY TRAINING PACKAGE, 016, 4.33.

Location: ,

Injured: 0  Dead: 0

Abstract
An explosion and fire occurred during the filling with acetic anhydride or a 160 000 litre aluminium mixing tank, which mixes acetic anhydride and glacial acetic acid (A mix). The tank lid was seen to lift off completely and yellow flames were shooting out of the top.
No one was injured by either the explosion or fire, but the tank and its contents, acetic hydride, were completely destroyed. After investigation it was concluded that the explosion was caused by either heat generation from the side entry stirrer or by static discharge generated by the fall of the liquid from the fill pipe.

[fire - consequence, material transfer, lack of earthing, mixer]

Lessons
To eliminate static charge:
1. The filling system was changed to bottom filling for all A mix tanks.
2. The filling methods for all tanks containing hazardous material was audited.
3. All A mix tanks should be electrically bonded to earth.
Abstract
While a catalytic reformer unit was undergoing regeneration, hydrogen escaped and ignited from a crack in the fusion zone of the weld where a 10 inch furnace outlet joined the weldolet on the 16 inch header.
Examination of the failure zone indicated that the fracture was probably due to creep from local stresses set up, possibly as a result of inadequate support of the pipework.
Investigations also revealed that the weldolet was a casting of 1% chromium and 0.5% molybdenum instead of forged steel of 1.25% chromium and 0.5% molybdenum specified for the duty.

Lessons
[None Reported]
A rupture in a 6 inch, high pressure, flash-gas pipe caused damage and production loss. The rupture occurred downstream of an air fin-fan exchanger on the vacuum gas oil desulphuriser/hydrocracker of a medium sized oil refinery. The rupture of the 6 inch line was attributed to erosion, corrosion, by high velocity (50-70 f.p.s) sour water, containing ammonium hydrosulphide (NH4HS). Due to the high pH (8-9) of the NH4HS sour water, the normally protective iron sulphide film (scale) is relatively soft and thus, easily eroded by high velocity sour water streams.

The escaping gas, mainly hydrogen, exploded (ignition possibly by static electricity) disrupting 23 pipes of various diameters carrying hydrocarbons, steam and water. The hydrocarbons caught fire from the ignited hydrogen, enveloping all the piping in the area. Electrical power lines were cut in the explosion and destroyed in the immediate fire. As a result of the failure of steam and power lines to the hydrogen generators the process was thrown out of balance and came to a sudden stop. Imbalance in pressure caused hydrocarbons to overrun the catalyst in all the reactors.

The ruptured pipe which contained ammonium hydrosulphide in condensed water had a drop of nineteen feet in a total run of thirty feet and during this run there were no fewer than eight elbows in the pipe. It would appear that the erosion/corrosion was due to a combination of the following:

i. The turbulence set up in the multi-elbowed pipe by the flow.
ii. The high pH (8-9) of the NH4HS flow softening the sulphide scale deposited by the inhibitor.

Lessons

The following recommendations were made to overcome this type of problem:
1. Increase the size of the pipe to 12 inch nominal bore and hence reduce the velocity.
2. Remove the trim condenser which is not essential to the process and thereby simplify the pipe-work and minimising the number of bends or elbows.
3. Continue with inhibitor injection.
4. Closely monitor the pipe sections and exchangers for further corrosion/erosion.
A senior relief supervisor was found in a kneeling position with his hips and legs protruding from a manhole on a vessel containing nitrogen. He showed no sign of life and efforts to resuscitate him were unsuccessful.

A depropaniser column on the ethylene cracker had been emptied and was being nitrite washed in a nitrogen atmosphere. This process involved the addition of concentrated nitrite solution followed by water with nitrogen being blown through the mixture.

At about 11.00 pm, the supervisor went to the top of the depropaniser to check if the water was being added in sufficient quantities, following previous difficulties with the water supply. He was aware of the nitrogen atmosphere. Though equipped with a radio, he failed to respond to messages subsequently relayed to him. Fatality.

[asphyxiation, maintenance, safety procedures inadequate, cracking]

Lessons

[None Reported]
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.

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.
Abstract

During start-up of a catalytic reformer and desulphuriser units the outlet header on the desulphuriser heater ruptured. The resultant fire was extinguished in approximately 48 minutes and damage is estimated at £600,000 (1979). The rupture was caused by overheating due to the cessation of flow through the heater tubes. This loss of flow was caused by a sudden increase in pressure in the gas separator. The steam turbine driven feed pump had been manually throttled back so that it was unable to develop the "head" necessary to overcome the sudden increase in back-pressure. After a thorough investigation it was concluded that the most likely cause of this increase in pressure was unintentional feeding-in of hydrogen into the gas separator on the desulphuriser unit at the time the hydrogen supply was being recommissioned to pressurise the catalytic reformer. After the catalyst in the desulphuriser reactor had been presulphided with DMDS (dimethyl disulphide) using the standard procedure, the reactor was shut down and blocked-in, and the recycle gas compressor was shut down.

The desulphuriser unit was then flushed through with light naphtha to slop using the steam drives turbine pump throttled back to 2,000 RPM which gave a flow of 45m3/hr at a total head of 15 bar. The fuel gas supply to the heater was being manually controlled to give a nominal outlet temperature of 250°C for a 45m3/hr feed rate.

All pilot burners and six out of the twenty main burners (three each side to provide equal distribution of heat transfer) were in operation. The pressure in the system was maintained at 7 bar by the intermittent manual operation of a valve in the hydrogen supply manifold. The manifold in turn was supplied from a battery of hydrogen cylinders mounted on a lorry trailer. The pressure in the cylinders as supplied was 200 bar. When the outgoing product was free of DMDS, it was directed to the reformer stabiliser in order to establish a level in the column for reheater furnace circulation. The reformer section had already been commissioned with hydrogen, and it is believed that the valve on the hydrogen manifold to the desulphuriser unit was open in error at the time when it was decided to increase the pressure in the reformer section.

The operating staff had just noticed that the pressure in the gas separator of the desulphuriser had risen to 29-30 bar and were taking action to release to the fuel gas system when the rupture occurred. Fortunately the operating staff were able to shut the hydrogen valves, shut off the fuel gas supply to the heaters, open the steam purge to the fire box and stop the feed by closing the steam valve to the turbine driven pump. None of these operations would have been possible a few minutes later due to rapid escalation of the fire.

There were a number of contributory factors:

1. The hydrogen cylinders were sited 80 metres from the compressor house where the manifold valves were operated; the hydrogen system was not equipped with a pressure reducing station.
2. The outlet temperature from the heater had to be controlled manually because the measuring element is isolated when the desulphuriser reactor is bypassed.
3. The steam supply to the turbine driven pump was throttled back manually to give a speed of 2,000 RPM equivalent to a flow of 45m3/hr at a 15 bar head. The pump is capable of 45m3/hr with a total available head of 57 bar at a speed of 3,600 RPM.
4. The feed controller was manually set to give 45m3/hr flow but there was no other control room instrument or alarm to warn the operators of low flow to the heater.
5. After the reactor was blocked in, it was only possible to monitor the furnace outlet temperatures by the multipoint instrument.

Lessons

The following recommendations were made;

1. Steam turbine driven pumps feeding a furnace should not be operated with the steam supply throttled back. The differential head generated by a centrifugal pump is proportional to the square of the rotation, and hence operation below the governed speed will significantly reduce the head available at the pump discharge.
2. The feed controller should be switched to `automatic' as soon as the pump has been started up. Consideration should be given to regulating the steam supply to the turbine drive through the set point of the feed controller under `auto' control, not through a pressure controller as at present.
3. The temperature from each outlet pass of the furnace should be recorded separately on the same instrument equipped with a high temperature alarm and trip function to shut down the fuel gas supply.
4. The temperature controller should be provided with two separate measuring elements with switch-over facility for start ups. One measuring element should remain as it is at present, but the additional element should be installed in the header after the furnace but before the bypass around the reactor.
5. The instrument should be equipped with a high temperature alarm.
6. The local flow indicators in each feed pass to the heater should be moved into the control room to facilitate easier monitoring of the flow through each pass. Each flow indicator should be equipped with an alarm which should also initiate shutdown of the fuel gas supply in the event of low flow.
7. A relief valve should be fitted on the outlet side of the heater tubes.
8. Hydrogen should not be taken directly into the plant from the cylinders. It should first pass through a pressure reducing station so that a set pressure can be guaranteed to ensure that equipment cannot be subjected to pressure exceeding safe working levels.

The incident occurred on night shift and was associated with a considerable amount of operational activity on the two plants in question. During initial commissioning and re-streaming of plant it is often necessary to disarm or bypass safety trips and to be alert to faulty instrument readings such as levels, pressures etc. Good communications and attention by personnel outside and inside the control room is therefore of particular importance at these times and the aim of plant designers and refinery plant management should be to achieve a balance such that men and instruments are adequate for start-ups and shut-downs as well as for all routine operations.
Abstract
Due to a combination of unusual circumstances prior to and during an unscheduled shutdown of a Fluid Catalytic Cracker Unit (FCCU), a flammable mixture of air and residual tail gas reached a flare system where an explosion occurred in the knockout drum. The force of explosion deformed the knockout drum and blew a 2 inch nozzle and valve off the end of the vessel. The source of ignition was probably pyrophoric scale. The FCCU was shut down because it was believed that a blockage had occurred in the standpipe upstream of the slide valve. Afterwards it was found that the slide valve stem had become detached from the slide gate (due to erosion) when it was in the closed position.

In normal operation the FCCU sends gas to the fuel gas main with much less than 1% volume air, the air originating from the air ‘bleeds’ to the instrument tappings on the reactor. Start-ups and shutdowns present the greatest potential hazard from air because these ‘bleeds’ are in use when the gas flow from the plant is low. A further risk has been the requirement to route air to the aeration nozzles on the standpipe and lateral, upstream and downstream of the slide valve, at specific times during start-up and shutdown but this is only done when the unit is isolated from the flare.

It is essential to use a dry gas, not steam, for aeration when the temperature of the reactor and circulation system is below the condensation temperature of steam: problems have occurred before at previous shutdowns with catalyst blockages in the lateral owing to the condensation of steam. HP steam is used for aeration at all other times.

Shutdown activities had proceeded according to instructions but during catalyst unloading from the regenerator a decision was taken to change aeration on the standpipe and lateral from steam to air. (It was considered that a catalyst blockage already existed, being the reason for the shutdown, and further use of HP steam at the reducing temperatures would make the situation worse).

It is also probable that air was passing the closed plug valve from the regenerator to the reactor at the time of the explosion. There had been a fault with the slide valve control system during this period and a decision to improve catalyst unloading by increasing the regenerator pressure may have been sufficient to cause a backflow of air. Another contributory factor to the incident was the amount of special attention that was required on other problems that cropped up during the shutdown.

An investigation determined that it was possible that burning had also occurred in the reactor shortly after shutdown but before (fortunately) the air was routed to the aeration nozzles on the lateral. There was a sharp increase in reactor temperatures for approximately half an hour, about one hour after the feed was taken out, and this has been postulated as the combustion of tail gas due to air that had accumulated in the reactor dome from the instrument air bleeds. A coke layer between 6 and 8 inches thick was found fairly evenly distributed around the top of the reactor above the cyclone inlet level.

Lessons
The following recommendations were made;
1. Steam supply headers serving aeration nozzles on the regenerated catalyst standpipe above the slide valve and the lateral below the slide valve have been modified so that each system can be supplied separately either with air or steam.
2. Operating procedures have been or will be revised to place greater emphasis on the precautions associated with air aeration during start-ups and shutdowns and the need to ensure that reactor/ regenerator differential pressures are maintained.
3. A temporary nitrogen supply is now available for use instead of air during start-ups and shutdowns on reactor instrument tappings. A permanent nitrogen system will be installed so that selected reactor instrument tappings will be supplied with nitrogen and not air in normal operation.
4. Deviations from operating procedures will be more fully considered before any changes are effected.
5. The incident will be discussed with all the FCCU operating personnel so that lessons to be learned are clearly understood.
6. 2 mm restriction orifices have been installed on the slide valve and operating instructional now clearly state that the restricted flow to the stem purge should be the only purge in continuous operation. Purges to the valve guides will only be used for a few minutes with an operator in attendance if the valve sticks during operation. Unrestricted purges via the 20 mm bypass lines should only be used if purging via the orifices proves ineffective but the bypass lines must be shut after a few minutes use.
To prevent one solvent contaminating another, a common rundown line to storage from a catalytic reformer needed to be flushed with water at product change-overs. The rundown line was not equipped with permanent flushing facilities so a canvas fire hose was used with water from a nearby fire main, as a temporary measure.

The receiving tank, sited approximately 3/4 Km away, was already filled to a level of 12.8m with liquid when water was supplied to the hose. The end blew off the temporary connection and since there was no isolation valve at this point on the line, the solvent poured out. Approximately 1,000 gallons escaped from the pipe before someone could reach and shut off the isolation valve at the base of the tank. Although the solvent flowed near a furnace it did not ignite, due to favourable wind conditions and an effective foam coverage applied by the refinery’s fire brigade.

[spill, near miss, material transfer]  
Lessons
[None Reported]
Abstract
During the pre-commissioning of a refrigeration plant, nine gate valves of the same type and manufacturer were found to be leaking. Consequently, a technician from the manufacturer was instructed to repair the leaking valves with the assistance of a fitter from the company accepting the plant. The construction engineer instructed the technician to repair the six valves on the pipelines which had been depressurised first as the remaining three were on systems still at a test pressure of 12 bar. The top-works of the first gate valve were successfully removed but instead of commencing work on a second adjacent valve on the depressurised lines they turned their attention to a gate valve, which was also in the vicinity but still under pressure. On loosening the retaining screws and forcing open the upper part of the valve, it blew off striking the technician and fitter and threw them from a 2.5 metre high working platform. Both suffered fatal injuries. Fatality.

Lessons
[None Reported]
Abstract
A propane cylinder split open and caught fire when a section of column rolled and a piece of pipework attached to it struck the cylinder.
The incident occurred during demolition of a redundant catalytic reformer.

[damage to equipment]

Lessons
Demolition work should be carried out in a safe and controlled manner through proper systems of work, e.g. work permits, in accordance with recognised codes of practice. Major demolition work is often very complicated and requires detailed pre-planning, specifically including safety aspects, and close supervision.
Abstract
A fire occurred on a hydrocracker unit at a refinery causing extensive damage to equipment.
[fire - consequence, refining]

Lessons
[None Reported]
A hydrocracker reactor was being emptied whilst under a nitrogen blanket by contractors specialising in inert gas entry. Two of the contractors employees were working inside the reactor with their breathing air supplies being continuously monitored from outside. The breathing air flow to one of the persons inside the reactor was seen to increase significantly which was followed shortly afterwards by a similar increase in the second person's air supply. The men were immediately recovered from inside the reactor without suffering any adverse effect and an investigation revealed that the two breathing air hoses had come into contact with a hot steam line. This line had been cold at the start of the work, but somehow the steam had been turned back on and the reinforced rubber breathing air hoses (tested to 130 bars) were damaged by the heat and started to leak.

Lessons
[None Reported]
Abstract
The hydrocracker complex came very close to total shutdown when the battery supplying the plant emergency system failed. Undetected overcharging caused by a faulty charger boiled many of the battery cells dry resulting in individual cell short circuits, overcurrent, severe overheating and dangerously low voltage.

The first indication of any problem was smoke emanating from the battery room situated in the main control building. The battery charging system was not fitted with an overcharging or low electrolyte alarm. Fortunately the refinery's electrical maintenance department had a spare battery available from a redundant plant and were able to install this in time to prevent a plant shutdown. An electrician sustained a minor caustic chemical burn during the incident.

Lessons
[None Reported]
Abstract
A fluid catalytic cracking unit was shutdown for a short period due to a power failure. Because the shutdown was short the operator did not close the manual block valves on an oil feed line to the reactor. The control valve and motor operated valve were closed but leaked oil into the catalytic. When catalytic circulation was restarted the oil soaked catalytic burned with air in the 1.6 metre catalytic riser pipe, the high temperature caused the pipe to rupture.

Lessons
1. Operating procedures were modified to emphasise that the manual feed line block valves were to be closed for any shutdown which went on for more than a few minutes.
2. Maintenance procedures were modified to ensure that the feed line control and motor operated valves were serviced at planned shutdowns to ensure tight shut off.
3. Skin thermocouples were installed on the 1.6 metre riser to alarm on high temperature.
Abstract
A fluid catalytic cracking unit reactor suffered internal stiffening where the external stripper vessel was attached to it. During shutdown it was found that the
welds that attached the stiffeners had cracked and the reactor shell was distorted in that area. It determined that this was due to different thermal expansion.
The stiffeners would heat up and cool down more quickly than the shell during start up and shutdown. A 60cm ring of the shell was replaced and the
stiffeners redesigned.

Lessons
1. In designing high temperature equipment to minimise thermal expansion stressed start up and shutdown condition must be allowed for.
2. Careful inspection during shutdowns can detect faults before they lead to a disastrous failure.
Two catalytic cracking unit reactors were each fed by two passes of a four pass feed preheater furnace. A valve crossover line was fitted between the feed line to the two reactors, to permit all four passes to feed one reactor. A leak occurred in the cross over line and when the insulation was removed it ignited. The crossover line was severely corroded after one and a half years service though there was little corrosion elsewhere. This was because the dead cured crossover line was operating at around 370 degrees C where sulphur corrosion was at a maximum.

**Lessons**

1. Dead ends of all types are particularly prone to corrosion and should be high on the list for inspection to detect.
2. This was a new unit and the first inspection should be especially thorough to detect problems such as that above and the use of substandard materials or designs.
Abstract
In a moving bed catalytic cracking unit catalyst was fed to the reactor through a vertical seal pipe full of catalyst and purged with steam which maintained the pressure in the reactor and prevented loss of hydrocarbon vapours at atmosphere. Should the catalyst seal fail there was a plug valve which closed to prevent leakage. There were several small fires over the years then a large one due to failure of the plug valve to close properly. It was then replaced by a slide valve which cured the problem.

Lessons
When a piece of equipment fails repetitively in the same manner a check should be made to see if there is a design problem, rather than just making a repair or replacing like with like. To wait until a serious incident occurs before changing the design is not normally the most cost effective solution.
Hot air for start-up of a catalytic cracking unit was supplied by an air blower feeding through a gas fired in line air heater. Faulty and/or inadequate instrumentation permitted heavy surging of the air blower which blew out the flame in the air heater. The fuel gas was on temperature control so the control valve now opened wide. The gas ignited possibly from hot refractory and the explosion cracked the blower case.

**Lessons**

1. Heaters of this types should be fitted with a fire eye to shut off the fuel gas in case of flame failure.
2. Large, high pressure air blowers require adequate surge protection independent of the normal plant control system.
A 12 s bar differential hydrocracker charge pump was shutdown before closing the discharge valve. The dual non return valve leaked, the pump overspeeded reverse flow, the coupling and packing gland were destroyed resulting in major fire. The original auto minimum flow valve audits manual replacement had not provided smooth start up and shutdown with the pump discharge valve closed so their use had been is continued. There had also been a problem with unstable fractionator level control which was thought to be related.

| hydrocarbons, hydrogen, shutdown, cracking, non-return valve, hydrocracker, damage to equipment, fire - consequence, valve failure, design inadequate, safety procedures inadequate |

**Lessons**

1. Non return valves in critical services such as this should be inspected and repaired to as new condition at each planned shutdown.
2. Safety features such as the minimum flow by pass in his case, should not be discharged because of initial difficulties. After the fire it proved possible to modify the system to make it effective.
3. After the fire, to make the unit safe in case of a pump trip out, a system was installed which automatically caused the reactor charge control on trip out.
Abstract
A fluid catalytic cracking unit was being restarted after a 2.5 hour shut down due to an electrical fault. During the shutdown oil had leaked into the reactor and some of the oil soaked catalyst then leaked through the side valve into the regenerator. The catalyst there had fallen to a temperature which would vaporise but not ignite the oil. When air was fed to the regenerator a flammable mixture was formed and this was ignited by a spark in the electrostatic precipitator.

gas oil, start-up, cracking, precipitator, catalytic cracker, explosion, power supply failure, spark, design fault, safety procedures inadequate

Lessons
1. A double block and bleed valve system was fitted on the gas oil feed lines.
2. The operators were provided with more detailed procedures for these circumstances.
Abstract
An operator was splashed in the face whilst caustic potash flake and caustic soda were being charged to a pan. The incident occurred when he noticed he'd forgotten to start the agitator. As soon as he started the agitator the batch erupted and splashed him in the face.

Conclusions:
1. The operator switched on the pan agitator when most of the charging had been completed instead of prior to the charging operation.
2. The operator was not wearing the specified personal protective equipment.

Lessons
[None Reported]
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<td><strong>Source:</strong> STEPHENS T.J.R LIVINGSTON C.B, EXPLOSION OF A CHLORINE DISTILLATE RECEIVER, LOSS PREVENTION VOL 7, AICHE, 1973, 104-107</td>
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**Abstract**
The pressure vessel in a chlorine separation system exploded after the corrosion of the steel process equipment allowed chlorine and hydrogen to mix and rupture violently into 5 pieces. The rupture disc on the tank was broken, and there was evidence that the back-up pressure relief valve had opened. The tank had failed by a rapid brittle fracture at a pressure of 1500 psi

**Lessons**
[None Reported]
A fire occurred in a dissolver during recycling of waste acetate bales by charging to a mixer. The bales re-dissolve in acetone. Immediately after a bale had been charged there was a discharge of vapour from the charge chute and a fire occurred in the mixer itself. The fire was successfully extinguished before much damage had been done by closing the lid on the charging port so that the inert gas purge to the vessel suffocated the fire.

The incident occurred due to the oxygen content of the atmosphere in the mixer not being checked immediately before the bale was added. An earlier check showed that it was probably about 10% below the level at which acetone will burn. The bale was unusually large and was added quickly. It is believed that sufficient air was entrained during the charging operation to raise the oxygen levels above the critical limit.

The source of ignition is thought to have been static electricity generated by the movement of the bale down the charge chute. Standard procedures called for through wetting of the bale to minimise the danger, but problems with water spillage on the floor had resulted in operators being sparing in their use of water. In addition, the remains of polypropylene liner under the bale may have acted as an insulator.

The addition of solid materials to solvent mixers through open charging chutes is potentially hazardous, since the combination of flammable gas mixtures and static discharge is likely to occur. Wherever possible, charging through some kind of air lock e.g. a screw conveyor for powders, should be used and all equipment must be earthed.

Lessons
[None Reported]
Abstract
During the pressure filtration of a diazo compound solution, large quantities of nitrous gases emanated from the vent line of the nitrite solution tank. In a pilot batch, nitrite solution for a diazotation reaction had been dosed through a dip pipe. When the addition of nitrite was complete, the electromagnetic dosage valve closed correctly, but two manual valves in the same line remained open. When the reactor was pressurised for subsequent filtration, the electromagnetic valve was forced open by the applied pressure. The strongly acid diazo solution was blown into the nitrite tank and caused decomposition of the nitrite solution and formation of nitrous gases. Luckily the incident caused only material damage.

Lessons
When dosage of a reactant is made through a dip pipe, back flow from the reactor must be reliably prevented. Some possible methods include:
1. Two valves in series, interlocked mechanically with an intermediate drain valve.
2. Use of a ball valve (with electromagnetic operation) as the automatic dosage valve. This would not have been forced open when the reactor was pressurised.
3. Automatic locking of the dosage valve when the reactor is under pressure or when the vent line is closed.
4. Strict written operating procedures - e.g. to interrupt the dosage line physically by taking out a spool piece or uncoupling a hose.
Abstract
Following the addition of nitration acid to a batch reactor, a batch had to be blown to a kettle two floors higher up, using 2-bar compressed air. The acid had been added via a dip pie, and inadvertently two manual valves and a pneumatic valve in the acid line were left open. As a result, a major part of the batch was blown back into the nitration acid charge vessel and from there through the vent system into other charge vessels. The extent of the contamination of the nitration acid system was not realised for a few days. 12 days later, whilst cleaning was in progress, two nitration acid charge vessels exploded due to spontaneous decomposition of compounds with a higher degree of nitration.

Lessons
The following safeguards were suggested:
1. Automatic locking of the acid addition valve when the reactor is under pressure
2. Reactor vent line permanently open (no valves) and transfer of batch by pump
3. Sequential interlocks in computer controlled equipment
Abstract
Melted product leaked from the seal of the agitator shaft of a reactor. The melt penetrated into the rock-wool lagging, where it ignited. A plugged pipeline had been blown out with nitrogen and steam. The resulting overpressure in the reactor forced the melt to leak out. The hot product reacted with air. This exothermic reaction was furthered by the fine distribution of the product on/in the lagging material. Under the prevailing quasi-adiabatic conditions, a temperature above the ignition temperature (470 degrees C) was reached. Thus the lagging soaked with product was set on fire by autoignition.

Lessons
A collection collar was mounted below the stuffing box to prevent product penetrating into the lagging leak testing was instituted.
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.

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.
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.

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.
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Abstract
Two 2-tonne capacity mixing tanks were used in a continuous process as an intermediate 'storage' facility for an aqueous mixture containing 14% industrial ether alcohol. As the temperature of the mixture was approximately 55 degrees C, the vaporisation of 'alcohol' was significant so each vessel had extraction ducts that combined into a common duct fitted with an internal exhaust fan. In the duct above the fan was a flow switch connected in such a manner that the fan had to operate and air pass along the ducting before the 'alcohol' could be added. The ventilation system on the mixing vessel was originally designed to prevent vapour escape into the working environment. However, with the fan operating at its design flow rate and neglecting the effects of the pressure drop in the system, the concentration of alcohol present in the duct was likely to be approximately 50% of the lower explosive limit.

The plant was operating normally when an explosion in one of the two vessels buckled the lid, sheared approximately twenty 10mm steel bolts, and caused misalignment of the stirrer drive. No one was injured.

Cause of the incident:
1. The three support brackets, which held the fan motor in place, had completely corroded away thus allowing the motor to fall until supported by the electrical connection.
2. The conduit carrying the power cable to the motor was severely corroded but about one quarter of its circumference was bright, indicating a recent fracture.
3. The yellow-phase conductor insulation had been cut at the fracture point of the conduit and the corresponding thermal overload element was burnt out. The motor would continue to run under these conditions.
4. One of the three fan blades was found covered with material, in such a position and with an oxidised fracture that indicated failure sometime prior to this incident.
5. The fan hub and the two remaining blades were not on the motor spindle but there was no evidence to suggest when they had come off the shaft.
6. The airflow switch was jammed in a position, which indicated correct airflow, and the vane itself was missing from the sensing alarm.

It was concluded that a flammable 'alcohol'/air mixture had accumulated in the vessel and duct and this was most probably ignited by an electrical spark when the conduit failed.

Actions taken to prevent a recurrence:
1. Clearly there are implications for the design of the ventilation system but:
2. The quality of inspection and maintenance of the equipment should be improved.
3. Any equipment on which the safety of the plant depends, e.g., motor, fan and flow control switch, merits routine preventative maintenance.
4. Breakdown maintenance alone is only acceptable where there are no safety implications.
5. The process operator may also be able to check periodically whether the equipment continues to operate, e.g., by attempting to start the process without the extraction fan operating.
Abstract
High-pressure alarms sounded on an autoclave, two operators started to take remedial action. Before gas in the vessel could be released to a gasholder, a bursting disc ruptured and at the same time a welded joint on the vent pipe opened causing vinyl chloride gas and slurry to escape into the plant. Personnel in the vicinity took refuge in the control room until the plant atmosphere cleared. An estimated 100 kg of polymer and 20 kg of gas entered the plant. Examination of the weld joint revealed the use of unsuitable material in the form of odd pieces of pipe of varying wall thickness and an extremely bad standard of workmanship in the weld.

Lessons
[None Reported]
On a fluid catalytic cracking unit a leak was noted at a one inch connection on a 350 °C slurry oil line. While trying to inspect the leak by removing insulation a screwed nipple and valve blow off. A fire and shutdown followed. The screwed connection had been installed for hydrostatic testing during a plant modification. It should have been replaced by a back welded plug after the test.

Lessons
1. Failure of screwed joints in severe services is not uncommon.
2. Inspection of plant on completion of modification needs to be as thorough a for new plant.
3. This is not the only case where removal of insulation for inspection has caused a leak to worsen drastically. If the potential risk is high as in the present case the equipment concerned should be depressured before doing so.
Abstract
A dust explosion occurred when charging a 5.2 m³ batch mixer with 200 kg of very fine aluminium flake, sulphur and some other ingredients. The total charge was 1200 kg. After the explosion there was a serious fire, which completely destroyed the building. The mixing vessel consisted of a cylindrical vessel with a conical base. Powder was charged through a side branch at the base. Mixing took place by a vertical screw in a rubber lined earthen steel tube which raised the powder from the base to the top of the vessel and discharged it so that it fell to the base. The ignition energy of the aluminium was only 1 mJoule and the pressure generated in a test apparatus was considerable. The investigation indicated that ignition took place in the screw lifting tube ignited by brush discharge and this ignited the bulk of the material. The vessel was purged with nitrogen and there was an oxygen meter positioned at the top of the vessel. Both the nitrogen flow and the oxygen meter position were found to be inadequate.

Lessons
The low ignition energy of fine aluminium flake and the importance of the nitrogen flow and oxygen meter position.
Abstract
A fire occurred in a mixer containing acetone, flake and filter aid under an inert atmosphere. The incident occurred when a bale of waste was added dry over about 5-10 minutes this resulted in a fire in the mouth of the mixer. It is thought that the cause was due to static.

Lessons
1. The operator was possibly insulated from metal plate dust on the floor.
2. Air added in with the waste may have overcome the inerting.
3. The large number of operator movements may have built up the charge.
4. Flue gas (with oxygen content 8-11%) used for inerting.
5. Components of the waste may be isolated and charged even if the operator was grounded.
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.

Lessons
[None Reported]
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.

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.
Abstract
On a fluid coking unit under construction a 13m dia x 33m high vessel failed while under a hydrostatic test of 4 bar at the bottom head. This was within design. The failure was due to brittle fracture. The temperature was about 10 degrees C below the above code figure of 15.6 degrees C. The knuckle radius of the bottom head was at the minimum allowable due to process considerations. It was at the skirt attachment that the head failed.

Lessons
[None Reported]
Abstract
A treating mixture of clay, cupric oxide and kerosene was mixed in an open topped drum before slurry was pumped to a naphtha treating unit. Due to leaking non-return valves and an open block valve in the slurry injection line, naphtha flowed backwards into the drum and overflowed the spill ignited from an unknown source.

Lessons
1. Open topped vessels should not be used to contain flammable liquids.
2. Closed top vessels in such services should have an overflow piped to a safe location.
3. Non return valves should not be relied on to prevent reverse flow. Slurry service is particularly prone to cause leakage.
4. The drum suction valve and/or the injection pump valves should be kept closed except when the pump is running.
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.

Abstract

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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.
Abstract
Modification to a hydrocracker compressor resulted in seal oil flow increasing by more than 1000% sour gas was carried into the seal system and caused a build up of iron sulphide. Due to an addition of antifoam much of the iron sulphide went into suspension and this plugged both seal oil filters. The compressor shutdowns actuated, but one relay failed to shutdown the fresh feed pump. The cold feed backed into the recycle gas heater through a faulty non return valve and thermal shock opened a flange joint.

Lessons
1. Modifications to proven designs should not be approved without a full review of the possible consequences.
2. In this case there had been indications of problems before the incident occurred. The dose of an antifoam was then five times the normally effective dosage, in response to seal oil foaming problems.
3. The shutdown relay had corroded because it was not adequately protected from a temporary water pray system.
4. Non return valves can not be relied on to prevent reverse flow as previous experience on this plant and many others have demonstrated.
During a hydrocracker start-up, when hydrogen pressure rose above 70 bar, two shell to shell nozzle flanges on the charge/effluent heat exchangers started to leak heavily. These had not been unbolted in the shutdown. With the pressure at 70 bar maintenance workers started to tighten the flange bolts, as was the normal practice. However on this occasion the hydrogen ignited almost immediately. The unit was depressed to put out the fire.

Lessons
1. The cause of ignition was probably a spark from the bolt tightening operation. However high pressure hydrogen leaks have been known to ignite with no external cause evident.
2. To reduce the risk of dangerous leaks like this, flange bolting procedures were improved by use of hydraulic torque wrenches and a strict order for tightening the bolts.
3. If serious leaks still occurred the pressure was reduced to minimise the leak before tightening the bolts.
Abstract
Due to problems with the turbine drive a recycle gas compressor on a hydrocracker was running at 60% of design speed. Most of the gas was flowing back to the compressor suction to prevent it from surging. The remaining flow to the third recycle gas heater was below the set point of the shutdown which therefore cut off the full gas flow to the burners. An operator opened the shutdown valve bypass to relight the burners. However he set the fuel gas flow too high and a tube ruptured through overheating.

Lessons
1. Operators to be warned against trying to keep a unit online at all costs.
2. Safety shutdown should not be taken out of service or bypassed unless following pre-set procedures which are known to be safe.
3. In the present case tying to keep the unit on stream when the problem on the turbine driver was unresolved proved unwise.
Abstract
A 3 inch connection and line was attached to the suction of a hydrocracker hydrogen compressor. This was to supply air for occasional catalyst regeneration. However with the unit in normal operation this dead end contained sour condensate as there was no blank or valve to isolate it from the compressor suction line. The bottom of the 3 inch line corroded through. Fortunately, the leak did not ignite and the unit was safely shutdown.

Lessons
[None Reported]
Abstract
On a delayed coker coke drum a hairline circumferential crack, 0.4 metres long, developed. It was successfully welded and stress relieved. The vessel was then hydrostatically tested and failed catastrophically at below the allowable test pressure. The failure was remote from the repair. Charpy v notch impact testing showed the drum steel plate was in the brittle range at the temperature of the hydrostatic test.

Lessons
1. A minimum metal temperature of 40 degrees C was set for coke drum hydrostatic tests.
2. All heavy wall vessels and suitable pressure equipment should be evaluated to ensure that they are not hydrotested when the metal is in the brittle range.
Abstract
After 11 years operation on a coker, the welds between the coke drum and its skirt failed and the vessel dropped 0.3 metres. The piping bent but did not rupture. Coking is a batch operation and the drum had undergone 2200 cycles from 40 to 480 degrees C. The failure was shown to be fatigue due to stresses from differential thermal expansion. This is a well known problem on cokers. The supports on a second drum were found to be near failure. Some skirt welds had cracked and been repaired before.

Lessons
1. Over the years the design of the coke drum to skirt attachment has been improved to reduce but not eliminate this problem.
2. For any given design it is necessary to start with frequent inspections. Only when the fatigue life is well established should the inspection frequently be reduced to suit.
Abstract
On a fluid catalytic cracking unit both fractionator overhead transfer pumps failed. Despite cutting back then cutting out the feed to the unit the level in the overhead receiver continued to rise. After 20 minutes the wet gas compressor operation because erratic and after 30 the internals failed due to liquid carry over. The coupling an seals then failed and the turbine driver overspeed and disintegrated. In investigation revealed that the operator had ignored the high level alarm. The high level shutdown had failed due to rapid lube oil deterioration making the hydraulic cylinder on the turbine steam valve stick open.

Lessons
1. Safety equipment needs routine checking to ensure it remains serviceable.
2. Lube oil should be checked for deterioration if this is rapid the cause should be sought and corrected.
3. Operators must be aware of the serious consequences of liquid carry over to a compressor. There was ample time for a manual compressor shutdown in this case.
A petroleum refinery was experiencing a series of leaks on its hydrocracking unit. The leaks were due to failure of the root welds connecting small diameter nozzles to large diameter pipes. The nozzles most likely to fail were those which carried valves which accentuated any vibration of the main pipework. There were a large number of these suspects nozzles and all had been designed to a lower schedule than the pipe to which they were attached. The appropriate schedule specified various methods for reinforcing the root and supporting the nozzle.

Lessons

[None Reported]
Abstract
In a vinyl chloride monomer plant the temperature of the outlet stream from the EDC cracker was reduced by injection below the liquid level in a quench tower. Water supply to the top mounted condenser was controlled by the level in the bottom of the quencher. The level controller was locally mounted and operation of the cooling water control valve therefore was not possible from the control room. On one occasion the level transmitter failed due to clogging. The cooling water control valve got fixed in a position delivering too little water so that the liquid phase in the bottom of the quencher disappeared. Consequently the hot gases passed through unquenched. The high temperature, approximately 500 degrees C, caused the gasket material in the flange below the condenser to soften and the gasket blew out. The escaping gas immediately ignited. The operator in the control room observed the sudden temperature rise in the quencher bottom, but the leak occurred before it was possible to get the cooling water valve opened.
The cracker was immediately shut down, the flow of flammable material ceased and the fire went out. The fire caused some damage to electrical cables and instrument lines, and the plant was out of operation for one week. No one was injured.

Lessons
After this accident the following changes were made:
1. The temperature recorder was equipped with an alarm.
2. The level controller was mounted on the control panel in the control room.
Abstract
An incident occurred when an operator opened a door to a filter on a catalyst before blowing off the pressure. Unfortunately he was standing in front of it and was crushed between the door and part of the structure and was instantly killed. Fatality.

[operator error, maintenance]

Lessons
The following recommendations were made:

1. Whenever someone has to open up equipment which has been under pressure, using quick release devices:
   · Interlocks should be fitted so that the vessel cannot be opened until the source of pressure is isolated and the vent valve opened (one way of doing this would be to arrange for the handles of ball valves on the steam and vent lines to protect over the door handle when the steam valve is open and the vent valve closed).
   · The design of the door or cover should be such that it can be opened about .25 inch (6 mm) while still capable of carrying the full pressure and a separate operation should be required to release the door fully. If the cover is released while the vessel is under pressure, this is immediately apparent and the pressure can be allowed to blow off through the gap or the door can be released.

2. The pressure gauge and vent valve should be located near to the door so that they are clearly visible to the operator when he is about to open the door. They were located on the floor above.

3. The handle on the door should be modified so that it can be operated without the operator having to stand in front of the door.
A mixer/grinder had been relocated and rebuilt, the only modification during the rebuild had been the positioning and length of the mixer discharge. After various checks and essential work being carried out the plant was declared ready for production and a dry run of 30 minutes duration was carried out. The material to be produced was made from ground, bleached cotton linters (cotton fibres of length 0.36 mm and apparent density 0.23 g/ml) and resol (a low melting point resin). The manufacturing instructions called for the cotton linters to be charged into the mixer and the resol to be charged first into the grinder which sits atop of the same mixer and discharges directly into it at a restricted rate. Both materials were charged from a common loading hood and an air operated flap valve was used to direct the material either straight into the mixer - the linters - or into the grinder - the resol. The mixture created was used in the production of a moulding material.

One batch had been completed satisfactorily. Due to operator error or plant malfunction the resol for the second batch was loaded directly into the mixer and the resultant mix of crushed resol and linters was removed for reworking. Batch 3 was produced by the operators who added two kegs of material from batch 2 through the grinder to the mix without incident. Batch 4 was then commenced, the linters being charged directly to the mixer and the resol added via the grinder. One keg of reworked material had been charged through the grinder and the operator was commencing to add the second keg of rework when an explosion occurred. The explosion vented to atmosphere via the explosion relief panels, but also flashed up the charging hood and the operator sustained superficial burns to his face and ears. The emergency procedures were implemented and worked according to plan.

Lessons

The following recommendations were made:
1. A reliable choke be inserted between the mixer/grinder and charging hood.
2. Separate charging hoods for grinder and mixer should be considered.
3. Controls should have a clear indication of their position.
4. Grinding and mixing plant should be separated by a choke wherever possible to reduce the probability of an ignition source reaching an explosive mixture.
5. The explosion vent should be increased in size.

The following changes of procedure were also made:
1. Resol/cotton mixture should not be ground.
2. The operating procedure should be reviewed, rewritten, understood, accepted and followed by all operators.
3. When movement of equipment or major modification has occurred then an overhaul should be carried out.
4. An adequate maintenance procedure should be drawn up for the equipment.
5. Manufacturing procedures and records should be reviewed with a view to ensuring that management are aware of all operations within their area of responsibility.
A bursting disc on a naphtha cracking furnace failed due to increased back pressure caused by the tripping out of service of the downstream cracked gas compressor. The disc released cracked gas and quench oil to atmosphere, the quench oil igniting at ground level, and the subsequent fire spread up the furnace structure, igniting the escaping from the bursting disc vent. The fires were extinguished and resultant damage was found to be minor, enabling the plant to be recommissioned within twenty four hours.

The cracked gas compressor had tripped due to a high level in one of the interstage drums. The machine tripping increased the pressure at the first stage suction drum which relieved to flare via the pressure indicating control valve which was set at 1.1 barg (16 psig). Shortly after the machine tripped the bursting disc failed. It was some minutes before it was realised that the bursting disc had blown and only then was the naphtha, fuel gas and quench oil feed to the furnace shut off from the control room. This delay, along with the fact that the quench oil shut off valve was subsequently found to be passing, resulted in a considerable quantity of hydrocarbons, especially quench oil, escaping to atmosphere. The quench oil accumulated at ground level and was subsequently ignited by a furnace that had just pressurised.

An investigation revealed that both the primary and secondary bursting disc had failed. The primary disc was found to have been fitted in the reverse direction.

Lessons

The following recommendations were made:

1. A high temperature alarm should be provided on the bursting disc vent, downstream of the discs to give indication of disc failure in the control room.
2. The quench oil control valves should be modified so that tight shut off can be achieved from the control room.
3. The possibility of remote operation of the cracked gas and quench oil block valves from the control room should be explored.
4. The bursting disc flanges and disc carrier assemblies should be modified to ensure location of the bursting discs in the correct fitting position and to give better protection to the disc membrane.
5. An established procedure for change of primary and inspection of secondary discs at each major furnace shut down should be written up and should be enforced.
6. The 0.64 cm (¼") weep hole on the vent is a source of hazard and should be valved off and a suitable means found to prevent build up of rainwater.
7. A pressure gauge should be installed between the primary and secondary discs to give indication of primary disc failure.
8. An operating procedure should be written for handling the failure of bursting discs on a furnace.

Other points raised for consideration were:

1. A reassessment of bursting disc pressures should be made and consideration given to the advantages of re-siting the secondary disc sufficient distance away from the primary so as not to be damaged on failure of the primary.
2. Raising the height of discharge vent.
3. Whether alternative methods of furnace protection could be provided instead of discs.
Abstract
A 90 degree, 100 mm pipe bend ruptured and discharged 6 - 10 tonnes of vinyl chloride monomer (VCM)/Ethylene Dichloride (EDC). The bend was part of a reflux system of a quench, downstream of the EDC crackers, operating at 140 degrees C and a pressure of 33 bar. The resulting vapour cloud was ignited by the cracker burners less than a minute later and caused a flash fire/explosion, producing less than 0.1 bar overpressure. An extensive fire resulted in the area of the ruptured bend. The heat caused the rupture of other pipelines, adding more flammable material to the fire. A total of 90 tonnes of EDC/VCM was consumed in the fire.
In addition, the heat started a chemical reaction between chlorine and the steel in a pipeline causing the discharge of approximately 5 tonnes of chlorine which was mostly sucked into the fire and dispersed. The fire was confined more or less to the quench section thanks to the quick action by the plant fire brigade and the trained shift personnel. Large amounts of water was used which saved all process equipment like pumps, drums and heat exchangers. The all-concrete structures proved their value by not collapsing, but extensive repair work was necessary. The explosion and fire caused no injuries. One man was operating a valve when the bend below the valve ruptured. He just made it to the control building 50 m away before the cloud ignited.
The cause. Downstream of the EDC-crackers the process gas was quenched by direct contact with a recycle of partly condensed quench vessel overheads. The quench unit also serves to arrest coke particles. Due to wear and a resulting loss of efficiency of the spray nozzle system there had been more than normal carry over of coke particles in the overhead. Accumulating in the reflux system the coke caused erosion of the piping. Loss of wall thickness had been detected prior to the accident. Parts of the piping had been replaced and the remaining pipe system was scheduled to be replaced.

Lessons
1. Process systems where a risk exists for abrasive particle contamination should be designed with erosion in mind (low linear velocities, smooth piping).
2. Systems of this kind should be monitored for particles.
3. Inspection programmes for wall thickness must be specific as to when and where to measure.
4. Criteria for minimum acceptable wall thickness must be unambiguously stated.
Abstract
A fire occurred in an ethanol esterification batch reactor whilst an operator was emptying the last contents of a bag of oxalic acid into the reactor. The reactor had been filled to about two-thirds full with recovered ethanol containing about 10% of cyclohexane and was at a temperature of 15-20 degrees C. The stirrer and dust extraction equipment were in operation. Crystalline oxalic acid was being added through a hood into the manhole from 50 kg plastic bags. About 40 bags had been added when an ignition occurred at the manhole opening just as the operator was shaking out an emptied bag. The operator sustained burns to the exposed parts of the body.

The investigation showed:
1. The resistance to earth of an operator wearing the shoes worn during the incident was 2+ 1 x 10^7 ohms. This is within the range 10^4-10^9 ohms specified for anti-static footwear.
2. The resistance to earth of an operator wearing a new pair of standard issue shoes was 3+ l x 10^9 ohms.
3. Tests carried out on an operator wearing PVC gloves, earthed footwear and vigorously shaking a woven polypropylene sack with an inner polyethylene liner (the type used) showed the bag was electrostatically charged. Discharges with a maximum charge transfer of -60 x 10^9 Coulombs were detected between the inner polyethylene liner and the spherical probe.
4. The oxalic acid used was noted to be of two types. One form of the acid comprised moist agglomerates of crystalline material, and other a much drier, free flowing crystalline material. At the time of the incident, a bag of the second type was being added.
5. Emptying a full bag of moist acid into an insulated drum produced lower charge levels than emptying a full bag of dry acid. Discharges with maximum charge transfer of +40 x 10^9 Coulombs and -10 x 10^9 Coulombs could be measured from the bag and wet acid powder respectively when using a probe and electrometer. When emptying a full bag of dry powder into an insulated drum charge transfers of +200 x l0^9 Coulombs and -120 x 10^9 Coulombs were measured respectively.
6. With the extraction system in operation the lower flammable limit boundary was 300 mm below the manhole lid. With the extraction system off, the boundary was 300 mm above the manhole lid. The extraction system was impaired by a partial collapse of the ducting. The flash point of ethanol is 12 degrees C and of cyclohexane -17 degrees C.

It was concluded that the most likely source of ignition was static discharge from the plastic bag. Modifications were put in hand to provide an earthed screw conveyor for the oxalic acid and alterations to the extractor systems.

Lessons
[None Reported]
Abstract
During a shutdown of an ammonia plant a nozzle on the reformer had to be repaired, for which welding on the inside of the reformer was necessary. During the welding job the atmosphere inside was regularly tested for oxygen. Four hours after the welding job was finished a technician entered the reformer to take pictures of the weld and many hours later he was found dead inside the reformer.

The following conclusions were made:
The oxygen content inside the reformer appeared not to have been checked before the technician entered it. Oxygen measurements after the incident showed a lowered oxygen content inside the reformer as a very likely cause of the fatality.

Lessons
This accident occurred because of a clear failure to comply with the existing regulations. Every resumption of a job being carried out by non-operational personnel after any significant interruption should be reported to the operational staff of that area. Such reporting is required to ascertain whether the job can be carried out under the terms of the existing Safety Certificate or whether a new Certificate has to be made out. In any event, working in a confined space has to be made conditional on regular testing of the atmosphere inside that space for safe composition.

Apart from deciding whether the atmosphere has to be tested for oxygen and/or for absence of toxic gas, it is important that a sound judgement is made on the frequency of testing. This frequency is completely dependent on conditions in and around the confined space.

There should have been a trained operator outside the reformer, equipped with breathing apparatus.
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]
Abstract
An incident occurred during the preparation of a batch of phenoxy acid weed killer.
All the materials, glycol, chlorocresol and sodium methoxide had been completely charged but it was observed that the temperature had not risen as normal and the liquid in the reactor was not boiling. The liquid surface was in fact strangely calm when it was realised that the agitator was not working. The plant manager who observed this with considerable haste and without anticipating the consequences quickly pushed the agitator motor start button. This could be done while looking into the vessel, which at this stage was about half full. The mixture responded with a rumble which immediately turned into a roar as it rose bodily towards the top of the reactor. It then filled the whole of the vapour system, cyclone separator, condenser, distillate receiver and vacuum knockout pot. The reactor and building shook. The plant was liberally supplied with observation sight glasses, every one of which filled with reactants. Several gaskets in the vapour line failed and as a consequence phenolic vapours spread through the building which had to be evacuated. Within a few minutes the noise subsided, as did the level in the reactor. The system was drained, most of the material saved, the plant cleaned, made tight, pressure tested and production restarted. A few days later it was found that a few tubes had become loose. These were removed and new tubes fitted. Several thousand batches were made for many years thereafter without further incident.

Written operating instructions called for the agitator to be stopped during the draining of the reactor and to be started again at the beginning of the next batch.

Lessons
Consequently the operating procedure was changed to:
1. Leave the agitator running at all times.
2. Carry out a special visual check that the agitator was running before the second reactant addition was started.
Abstract
A fire started in the cold end section of a steam cracker. The fire could not be contained and eventually destroyed most of the cracker.
Due to false temperature signal, the back end acetylene converters downstream of the de-ethaniser tripped. The trip activated valves which isolate the converters and dump the hydrocarbon content to flare. The gas feed to the converters is normally re-routed to the flare so that the process up to the de-ethaniser runs as normal.
This cracker did not have such a dumping system so that the safety valves of the de-ethaniser started to blow. There are three pressure relief valve installations at this tower. Two are installed at the reboiler vapour return lines of both reboilers and the other at the overhead line of the tower itself. All the safety valves have the same capacity. On the day of the incident the spare reboiler was not in service. The feed line to the reboiler was closed by a block valve and the vapour return valve of the reboiler was left open. The other reboiler was lined up as normal. The operators detected the false trip signal and tried to put everything back to normal condition. Since the safety valves were blowing they did not have enough pressure to move gas through the converters and they decided to close the block valve downstream of the safety valve located in the overhead line. When they walked out of the control room they heard a loud shattering noise and when reaching the de-ethaniser area they noticed a vapour cloud. They stopped their original plan to close the safety relief valves and tried to close the vapour return block valve from the spare reboiler. They evacuated the area since the cloud became too large and eventually ignited.
The investigation team found that as a result of the chattering, one of the safety relief valve broke off from the main vapour return line of the reboiler. The flames impinged on the 600 mm diameter vapour return line from the adjacent splitter reboiler and this line eventually ruptured. The total inventory of the de-ethaniser and the splitter was lost and the incident got out of control. Most of the vessels in the cold ends BLEVE’d (Boiling Liquid Expanding Vapour Explosion) but it is not clear whether these vessels are storage vessels or process vessels.

Lessons
The focus of the investigation was on the chattering phenomenon of spring loaded safety valves and their consequences. The following characteristics have been identified as causing chattering and vibration of relief valves.
1. Grossly oversized safety valves.
2. Excessive back-pressure in the safety valve outlet system.
3. Excessive pressure drop in the inlet piping of the safety valve.
The above features must be considered when performing a process design.
A polymerisation batch reactor was being controlled by a Programmable Logic Controller (PLC). Although it was provided with a back-up unit the power supply was interrupted for a short time. The PLC reset to the initial set which caused the bottom valve and vent valve on the reactor to open and resulted in product loss. Another programme was operated inadvertently also. Prompt operation by the operators prevented any loss or risk to people. The batch was terminated manually.

In an investigation several factors were taken into consideration:
1. There were a number of irregularities in the alarm system to indicate that the back-up unit was in operation. The system was not well understood by the operators.
2. The operators had not been sufficiently well trained in how to react to failure in the power supply. It would have been possible to by-pass the PLC and finish the batch manually.
3. The reset position on the PLC was not fail safe.
4. PLC’s are often used for sequencing operation on batch reactors. Reverting to the initial state in the middle of a batch is usually not a fail safe position. The plant had recognised this to some extent by providing a back-up unit, but had not given sufficient attention to design and operation of the back-up unit to ensure an adequate overall reliability.

Lessons
[None Reported]
Lock-out procedure ignored. An operator entered a 600 gallon mixer wearing a harness and life line. He asked his helper to check whether the power was off. The helper, instead of visually checking the disconnect switch, pushed the starter switch on and off. This started the agitator and knocked the operator off his feet. He was dragged around until his body became partially wedged under a paddle. It is not certain whether the motor overload shut off the power or the helper finally pulled the switch.

The use of the established lock-out procedures would have prevented this accident.

Lessons

The important lesson of this injury is that engineers, supervisors and other professional people may subject themselves to severe injury by not taking all the precautions necessary, especially those relating to locking-out equipment, keeping guards in place and keeping out of dangerous areas.
Abstract
Fatality through failure to lock-out. An operator sustained a fractured skull and neck injuries when the agitator motor on a kettle started while he was in the kettle manually removing product accumulations. This was a routine operation performed normally one or more times per shift. How the motor was energised has not been determined.

The operator, contrary to established procedure for cleaning this kettle, had not disconnected the switch, nor tagged and locked it out. In addition, the motor cable was not disconnected from the electrical supply. Fatality.
[cleaning, isolation inadequate]

Lessons
The procedure for cleaning the kettle has now been changed to require not only the man who plans to enter the kettle but also the standby man to lock and tag the controls, individually, in the off position before the kettle is entered.
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.

Lessons
[None Reported]
During cleaning of a reaction vessel for internal maintenance. It was filled with water and heated up to boiling point with the agitator running. The operator was instructed to cut off the steam to the reactor, let it cool off for 20 minutes then blow air through the dip pipe and drain the reactor. However, he opened the air valve much earlier. To reach the air valve, he leaned over the open manhole. The operator sustained burns over 90% of his body and died several days later. Fatality.

[cleaning procedure incorrect]

Lessons

The reactor cleaning procedure was changed.
Abstract
Corroded manhole cover bolts on a pressure vessel which contained nitrogen at 50 bar were to be replaced. The vessel should have been de-pressurised but this would have meant shutting down a large process plant. It was therefore decided to replace the bolts one-by-one with the vessel under pressure. Two fitters completed the manhole at the bottom of the vessel and then one of the fitters went to start the top one.

The fitter on the top decided that it would be quicker to remove all the bolts at once (he had not been told why they were replacing the bolts). When he had removed 29 of the 42 bolts, the cover blew off and killed him. Fatality.

[maintenance, management system inadequate]

Lessons
The following recommendations were made:
1. The proper procedure would have been for the maintenance task, (i.e. removal of covers) to have been properly assessed by an engineer manager or supervisor before it started, and the appropriate safety measures specified.
2. These measures should then have been clearly communicated to both the fitters, with the reasons for them.
3. In communicating the safety instructions to the fitters, their supervisors should have asked the following questions:
   · What is the nature of the work to be carried out?
   · How is it to be done?
   · Why should it be done in the manner specified?
   · What could happen if it is done differently?
Abstract
A fire occurred at the suction filter of a recycle gas compressor in a catalytic naphtha reformer. At the time of the incident the filter was being boxed up following the routine installation of new filter cartridges. The source of flammable material was high purity hydrogen recycle gas leaking through the filter isolation block valves and to atmosphere through the partially closed cover of the filter casing. The source of ignition was impact sparks produced when a steel filter clamp was struck by a steel bar during the tightening operations. Note that the minimum ignition energy of hydrogen in air is 0.02 mJ which is much lower than for hydrocarbons.

The fire was extinguished using a 150 lb, dry chemical extinguisher and no damage resulted. At the time of the incident, the plant had been on stream for about three hours and the recycle gas contained an unusually high concentration of hydrogen (estimated to be 90%).

The significant feature of this incident was the ignition of hydrogen rich gas at ambient conditions by the impact spark produced by steel striking steel. From the observed condition of the filter and steel bar, the ignition mechanism was not considered to have been a thermite reaction (impact of rusty steel on an aluminium painted surface).

Lessons
[None Reported]
Several out-breaks of fire occurred, following spillage of a liquid containing ethylene glycol onto the lagging of an autoclave. The autoclave was heated to 2500-300 degrees C, by a heat transfer fluid and it was thought, initially, that there was an ample margin between the auto-ignition temperature of ethylene glycol, 398-440 degrees C, and the temperature of the autoclave and lagging. It was subsequently demonstrated that the lagging, if soaked in ethylene glycol, could fairly quickly take fire in a slow stream of air from a temperature as low as 150 degrees C.

[lagging fire]

Lessons
[None Reported]
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.

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.
A fire occurred in the hydrogen purification section of a naphtha cracker. There were no casualties and nobody was injured, but a part of the hydrogen purification installation was damaged. The accident is attributable in particular to the absence of an automatic high-temperature and high-level protection system in the methane/hydrogen separation drum of the refrigeration section.

Lessons

[None Reported]
Abstract
A fire resulted from the ignition of about a tonne of vaporised hydrocarbon which had been released through a water drainage system. The source of ignition was a transfer line exchanger associated with a cracking furnace. The flash fire caused a number of other fires. One such fire, on an ethylene hydrogenation area heat exchanger joint, rapidly escalated due to relaxation of the bolting. This led to failure of an ethylene line and the subsequent rupture of other lines in an overhead gantry. These lines provided the energy for the fire responsible for the major damage.
The response of the operating and fire fighting teams was prompt and efficient and the image was contained within a small area of the plant. The initial hydrocarbon release is attributed to the operation of an automatic water dump valve, on the fourth stage suction drum of the cracked gas compressor, which failed to close before releasing hydrocarbon to the drainage system. The delayed response from the interface level controller followed from emulsification and/or vortexing in the drum. The local hydrocarbon monitors alarmed but ignition followed very rapidly.

Lessons
[None Reported]
For routine production of a batch of tetrabromopyranthrone, two operators had to charge a reaction kettle first with 560 kg of chlorosulphonic acid and then with 500 kg of sulphuric acid. One of the men was working for the first time on this process and forgot to switch on the agitator prior to charging the sulphuric acid. When both acids had been charged this omission was noticed and the agitator was switched on. After a short time, a violent exothermic reaction took place and acid splashed out of the drum charging chute which had already been installed on the manhole. Both operators sustained acid burns to the face and the area with in a range of two to three meters became contaminated.

Chlorosulphonic acid can form a liquid layer over sulphuric acid 98%. When both layers are mixed hydrochloric acid gas will develop spontaneously due to the water content of the sulphuric acid. The correct sequence of kettle charging operations, including starting of the agitator was clearly described in the operating instructions. Shortly before the incident the supervisor had discussed these instructions with the operators and stressed the importance of strict adherence to them.

Lessons
It is not easy to decide what measures to take if, e.g. due to failure of the agitator, reactants in a laboratory or production batch might start a dangerously exothermic reaction when mixing. Normally, the location should be evacuated. If careful gradual mixing is attempted two men with adequate protection (gas mask and fully protective suit) may try to move the agitator at intervals, but it must be anticipated that the reaction will get out of hand due to thermal effects or due to the mixing action of developed gases. Another possibility would be to drain off, or siphon off either the upper or the lower layer prior to starting the agitator.
Abstract
During the highly exothermic condensation of o-nitrotoluene to 2,2-dinitrodibenzyl, the rate of addition of the nitro compound is controlled to keep the temperature of the batch between 5 and 10 degrees C. When the temperature alarm, which was set at 15 degrees C, was activated, the operator observed that the agitator was not running. The agitation monitor had already stopped the addition of nitrotoluene. Jacket cooling with brine was at its maximum. First, the temperature of the batch rose slightly higher, then it remained constant. The agitator was moved twice for a very short period (1 revolution). This caused again a slight rise of temperature. At 20 degrees C, the building was evacuated. When the temperature had fallen back to 16 degrees C, the agitator was again moved for short periods. Two hours later the temperature was down to 12 degrees C, and the agitator could be switched on permanently and all operators came back to continue their regular duties. When normal reaction temperature was reached the remaining 20% of nitrotoluene was added and the batch was completed without any loss. Most probably the failure of the agitator was caused by an electrical equipment failure - worn out electrical switch on the motor.

Lessons
[None Reported]
Abstract
An acidic effluent was neutralised with chalk slurry in an agitated tank. The operator noticed that the effluent passing to drain was too acidic. He found that the agitator had stopped and switched it on again. The accumulated un-reacted chalk reacted suddenly and violently, blowing off the manhole cover and lifting the bolted lid off the tank. There was a massive evolution of carbon dioxide. Fortunately no one was hurt.

A similar accident had occurred previously, following which a standing instruction was issued detailing action necessary when the agitator stops. The operator did not follow the instruction, he was not aware of its existence and no copy of the instruction could be found on the plant. It was in the foreman's office.

Lessons
[None Reported]
A tank had been charged with oil for processing. Before any further addition was made the operator started the agitator. The charge boiled up and the 24" diameter manhole could not handle the rate of oil discharge. The tank top ruptured but no-one was injured.

Subsequent enquiry revealed that there was a leaking steam coil in a storage tank at high level. This tank outlet valve was passing, which would allow condensate to enter the lower tank. The condensate would lie stratified below the charge.

It was also found that one of the three steam coils in the lower tank had recently been left turned on for several hours before the agitator was started. As soon as the layers of hot oil and water mixed, steam evolution lifted the whole charge.

Lessons

[None Reported]
Abstract
During milling, a chemical caught fire in a mixer installed directly after the mill. The cause was probably a piece of metal which passed through the preliminary crusher and entered the mill. The fire was extinguished immediately by the permanently installed quenching system, so that no serious damage was done. Although the primary cause of the fire was frictional impact in the mill, the fire was established in the next unit. It is common for fires or explosions originating in mills to produce their most damaging effects in other plant units downstream.

Lessons
[None Reported]