



Pipe fittings and joints



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@ Explosion of hydrogen in a fertilizer plant

ARIA 31821 – 01/06/2006 – UNITED KINGDOM - BILLINGHAM

20.15 – *Manufacture of nitrogenous products and fertilizers*

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Shortly after midnight, a highly flammable gas leaked in an ammonia manufacturing unit of a chemical plant producing nitrogenous fertilizers. The gas, mainly comprising hydrogen, leaked from a valve at a pressure of 220 bar and a temperature of 120°C. It spontaneously ignited forming a fiery stream directed towards the pipeline carrying the gas. Due to the heat, the pressure in the pipeline increased; the top portion of the pipe ruptured releasing the gas that exploded.

The alert was sounded and the police implemented an emergency plan: traffic was stopped in the roads in the vicinity of the plant and residents were asked to stay indoors.

The rest of the gas burnt at the rupture point for 2 hours. The leak was plugged and the fire brought under control at 2.45 am. The site was secured. Human casualties included 2 employees who suffered mild concussions and sustained cuts. They were treated onsite. The plant operations were stopped during the enquiry.

The accident occurred due to a gas leak at the joint of a valve (in open position and at maximum flow). There was no leak-proof joint between the two metal parts in contact. The internal metal surface of the valve was not compliant with the specifications in terms of quality. The valve, replaced in 2002, was not considered to be an element critical to the safety even though the process was classified in the high-risk category. Only price was taken into consideration while selecting the maintenance supplier. There was no exchange of information between the operator and the subcontractor during the operation and no acceptance of work was done (especially inspection of the valve bolting).

The operator revised procedures, optimised management of maintenance and subcontractors (qualification, information, follow-up, etc.). The emergency operation conditions were also reviewed (appropriate number of trained staff even during low activity periods).



Source exploitant

@ Chlorine leak during transfer

ARIA 34397 – 14/02/2008 - 04 - CHATEAU-ARNOUX-SAINT-AUBAN

20.14 – *Manufacture of other basic inorganic chemicals*

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In a chemical plant, 11 kg of chlorine leaked around 9.30 am while being transferred in liquid phase from a tanker. The leak lasted for 30 seconds and led to the formation of a 50m cloud at the ground level that drifted with its visible part confined to the site premises. The technicians closed the valves by shutting off the supply of compressed air, sounded the alarm, and activated the water curtains.

The technicians who were not equipped with their self-contained breathing apparatus were poisoned by the fumes and taken to the infirmary.

The accident resulted from the rupture of the flange joint of a transfer hose during the tightness test. The joint was deformed because of the use of two 2 mm joints instead of one 4 mm joint. The operator who performed the tightening operation was undergoing training: The tightening operation was not properly carried out with the bolting machine. Lastly, the tightness tests were carried out in a chlorine atmosphere instead of nitrogen.

Since the flanges were not damaged, the transfer from the tanker was smooth during the afternoon.

The operator took several measures after the accident: strict compliance with the safety instruction on wearing a self-contained breathing apparatus, ensuring consistency in issuing permits for various industrial operations, updating technician training on tightening operations, exclusive use of 4 mm joints.

Pipe fittings and joints

The chlorine leak at Château-Arnoux-Saint-Auban once again illustrates the risk related to transfer operations and more generally all transfer operations involving connecting pipes with fittings. This accident occurred due to a combination of errors during the operations (technicians undergoing training without PPE, wrong choice of joint, poor bolting etc.) along with organisational failures such as non-compliance with guidelines and carrying out the tightness test in a chlorine atmosphere.

It is important to properly prepare all transfer operations. Several fittings along the length of a pipe must be avoided. The diameters of all pipes used must be uniform and in line with the diameters of the fixed or mobile storage tanks. Besides accidental mixing of incompatible products, assembly errors may also result in several incidents of leakage. All joints, flanges and hoses must be firmly secured and their suitability verified (ARIA 4982, 6958, 10165, 17740, 23545, 26918, 29885, 32174, 32145, 32817, 32966, and 34397). All bolts must be present and properly screwed in (missing or poorly screwed bolts: ARIA 11441, 12574, 14500, 17740, 34397, poorly screwed or upside down pipe fittings: ARIA 15660, 27207, 31667, etc.). Flanges and buffers must be correctly positioned to avoid joints from sticking out of their grooves (ARIA 14675, 10783, 18920, 17740, 30507, 30486 (not re-assembled), 31667, 32145, etc.).

Lastly, the material and size of joints and hoses must be verified as early as the design stage and their condition regularly checked during use. Material incompatible with the transported product can quickly lead to tightness problems (ARIA 4995, 5872, 25477, 29603, 31489, 33311, etc.). Similarly, corrosion, thermal embrittlement or ageing of joints / flanges / nuts considerably accounts for rupture (corrosion and ageing: ARIA 4989, 4323, 454, 5872, 12574, 14675, 21123, 21282, 25477, 25683, 27207, 33311, freeze/freeze thaw embrittlement 10331, 29096 or thermal action of the transported fluid: 24064, 28762 and 32174). This is why preventive maintenance must be carried out on all equipment.

The accidents also underline the importance of organisational aspects, even for phases considered 'simple' such as transfer. Training and qualification of technicians even their accreditation to perform a specific function is crucial in carrying out safety operations. The importance of the involvement of supervisory staff, employees and subcontractors understanding guidelines, as well as the crucial role of upkeep of facilities no longer needs to be proved (ARIA 14500, 30486, 34397, 32796, 33311, etc.).

With particular reference to transfers, pressurisation tests must be carried out with an inert fluid (often nitrogen). These tests help detect and resolve all tightness problems beforehand. The absence of such tests is often the reason for accident (ARIA 4982, 17740, 25683, 31337, 32796 and 34397, 31251 test poorly conducted).

Efficient preparation guarantees smooth transfer while any shortcomings in procedures invariably lead to accidents. Once the pipes have been properly installed, an inert fluid must be used for verification. However, while using compressed fluids (ex. N₂), the gas must be allowed to expand before being injected into the circuit failing which the equipment can sustain serious damage due to an abrupt increase in pressure (ARIA 22941).

The accidents whose references are not underlined may be consulted at:
www.aria.developpement-durable.gouv.fr

  **ARIA 12574 - 19/01/1998 - 01 - SAINT-MAURICE-DE-BEYNOST**

22.21 – Manufacture of plastic plates, sheets, tubes and profiles

 The French railway staff noticed five litres of methanol leaking from a tanker drawn outside the sender company 48 hours after being filled. The leak occurred at one of the lateral plugs of the tanker's drain pipe that was not correctly secured. The plug was screwed back properly and the tanker sent back to the sender company to be emptied. The accident occurred due to the failure of three cut-off elements assembled in series (poor tightness of the operating spindle at the bottom even though leaded, insufficient tightness/closing of the control valve and poor tightening/degradation of the safety plug joint. The operating modes were checked and the various players involved were briefed on the same, the checks on tankers leaving the company were tightened and customers were made aware on the need to regularly inspect the state of their tanks.

  **ARIA 14500 - 03/12/1998 - 01 - SAINT-VULBAS**

21.10 – Manufacture of basic pharmaceutical products

 In a fine chemical plant, a toluene leak in a solvent reception tank (300 litres) connecting a dryer (3 000 litres) caught fire while the facility was being cleaned with toluene. The solvent (whose temperature was close to room temperature) present in the reception tank and pipes (including the liquid seal) leaked from the cover joint and caught fire. The ensuing flash opened the doors of the premises. The internal contingency plan was triggered. A dozen employees who sustained light burns were evacuated. The person who suffered the most injuries (3 days stoppage of work) was closest to the reception tank at the time of the incident. The accident took place during the first production cycle. The drain pump of a tank failed to start following an electrical defect in a terminal board (poorly secured lug). This led to the excessive filling of the tank that gave in to the hydrostatic pressure (cover not airtight). The unit was newly installed and had several faults in the design: reception tank without retention unit and undersized compared to the centrifuge volume which meant that the pump had to be started several times, non-redundant level alarm, plastic making up the tanks and pipes not adapted to the dielectric properties of toluene, tank made of fragile plastic material, poorly secured cover, etc. During a visit, the inspection authorities of classified facilities observed anomalies in the pipe of the installation: Time / operation log book pre-filled by operator until 10.00 am where as the accident took place at 8.00 am, only seven bolts to secure the cover of the reception tank instead of eight, the eighth bolt was replaced with a clamp; only four bolts were mentioned in the original plans. Various measures were taken: some portions of the pipes were changed, dryer's drain cones maintained under pressure and instrumented, explosive atmosphere detection improved of, overflowing during automatic delivery of solvents prevented via the tank storage area, safety mobile valve on the reactor power supply bypassed. The accident is illustrative of organisational errors and design faults.

  **ARIA 15660 - 29/05/1999 - 03 - COMMENTRY**

20.14 – Manufacture of other basic organic chemicals

 In a chemical plant, 1 litre of chlorine leaked out of a container in a non-confined canopy depot housing 16 1-tonne tanks (including two being emptied) and a drawdown station in vapour phase. The Cl₂ detector of the depot was triggered and fire fighters wearing self-contained breathing apparatus arrived on site. Two leaks were detected: one at the nozzle flange and the other at the body flange. The tank was cooled, put away in a shaded place and a cover was placed on the nozzles to isolate them. The container was bled and the chlorine was transferred to a production unit 30 min later. The toxic cloud remained confined to the storage area and its immediate vicinity. No effects were observed outside the plant. A technical expertise of the tank revealed that the Cl₂ leak undoubtedly resulted from a stuffing box that might have been loosened by a plant technician. Some valves have a reverse pitch.

  **ARIA 17740 - 15/05/2000 - 60 - VILLERS-SAINT-SEPULCRE**

20.16 – Manufacture of basic plastics

 340 kg of butadiene leaked from a 55 m³ reactor in a plant manufacturing ABS resins. Following pre-polymerisation tests (safety systems, reactor pressure test), 25 tonnes of water, emulsifying agent, an initiator and 15 tonnes of liquid butadiene under a pressure of 8 to 10 bar were added to the reactor. .

 The water temperature was raised to 80 °C.

The pressure inside the reactor normally goes from 10 to 3 bar with the reaction going on. The partial pressure of 3 bar indicates the end of the reaction and the butadiene that did not react is recovered by stripping. The reaction normally last up to 15 hours.

At 3.45 pm, while the polymerisation reaction had been underway for 90 minutes, a butadiene leak occurred in the lower part of the reactor at the blind flange located just after the pneumatic waste valve. The technicians in the control room are alerted of the sudden opening of the valve via an indicator. This was not a major problem for the operator as the circuit was closed by a protective cuff and a blind flange. The technicians tried to close the valve but did not succeed. One of them went to the reactor to manually close the valve but could not reach it due to the foam released from the lower part of the reactor. He smelt the characteristic odour of butadiene. At the same time, the leak activated the gas detector network, one of the gas detectors being situated vertically above to the reactor. Some detectors crossed the upper threshold of the alarm (40% of the LEL). The internal emergency plan was triggered and the operator decided to open the pressure relief valve of the reactor towards the flare circuit located on the reactor's containment dome. The pressure of the latter decreased, stopping the leak in less than 30 min. The flaring lasted for 1 hour and 15 minutes. The detectors returned to their original state one hour after the start of the accident. The measurements made around the site revealed no contamination.

The accident analysis highlighted three concomitant factors: failure of the pneumatic waste valve with leakage at the O-ring of the push button controlling it resulting in a pressurisation and opening of the valve; the defect in the blind flange joint just after the valve; the inappropriate assembly of the blind flange with the wrong number of bolts and insufficient tightening. Moreover, no pressure test had been undergone on the equipment before. Subsequent to this accident, the facility was not re-commissioned. Polybutadiene production was carried out at another site of the group. Ever since, polybutadiene was supplied by road tankers. However, the prefectural order dated 14/11/2000 subjected the possible re-commissioning of the unit to compliance with certain provisions on risk prevention planning, implementing clear operating guidelines, preventive maintenance of facilities, regular inspection of safety devices, piping network of the facilities and vital safety equipment..

ARIA 25477 - 14/08/2003 - 69 - PIERRE-BENITE**20.14 - Manufacture of other basic organic chemicals**

In a chemical plant, 33 % hydrochloric acid solution leaked out of a transfer pipe connecting a production unit to a waste water treatment pit. The fire-fighters on site neutralised the acidic vapours with a deluge gun, two water shield nozzles in the immediate vicinity of the leak and one adjacent to the site. Water curtains in a neighbouring production unit were deployed to protect a nearby motorway. The leak was stopped after an hour and thirty minutes (after isolating the pipe) and had resulted in a loss of 20 m³ of hydrochloric acid, mainly recovered along with the fire water in the site's neutralisation pit. Heavy corrosion was seen at the sides of the pit. The facility was repaired overnight and re-commissioned. According to the operator, the acidic cloud did not interfere with the neighbouring motorway traffic. The accident was due to a rapidly corroding flange joint on the vent supplying hydrochloric acid to the neutralisation pit. The bolting that was rapidly corroded by the acid gave in and led to the leak. The pipeline was made of surface-treated PVC, the joint used was in expanded PTFE with a zinc-plated/bichromate bolting. The operator sought a feedback on adapting the type of joint used in presence of HCl and studied the possible impact of vibrations on the tightening of the joint. Moreover, an instruction to isolate the acid pipe had been put in place.


ARIA 30486 - 16/08/2005 - 02 - CHAUNY
20.14 - Manufacture of other basic organic chemicals

During a transfer operation from a barge in an upper tier SEVESO chemical site, 60 m³ of orthoxylene spilled onto the barge. The spill lasted for 45 minutes and polluted the OISE river. The operator reported the presence of a 300 m long hydrocarbon layer on the water surface. The internal contingency plan of the site was triggered. The inspection of the facilities classified, navigation department, local authorities and health authorities were informed. Air samples were taken to detect any possible formation of an explosive atmosphere. The measured xylene concentration near the river banks was in the order of 200 ppm (LEL 10 000 ppm). Four oil booms were installed downstream to the spill: two installed by the operator near the plant, two by the fire-fighters at 5 and 10 kms. However, they could not recover the products due to dilution and volatile nature of xylene. No death of fish was reported. The residents and especially local farmers were warned. They were advised against using the river water for animals. The infiltration of pollutants from the river bank into the river caused pollution to resurge on the following day at the site of the spill. An oil boom, pumping device, and site cleanup operations will be required to clean the soil polluted by xylene. The accident was caused due to a missing stop on the inspection flange of the transfer pipe: It was the 1st transfer operation after the pipe was de-commissioned for maintenance. While inspecting the pipe with a camera, the stop on the inspection flange has been removed and not re-assembled. This operation was carried out by a subcontractor who had only received verbal instructions from the operator instead of a concise written procedure. This oversight was not detected even during the inspections carried out upon site completion. The inspection authorities made note of the facts. The operator must modify the transfer facilities to detect leaks in transfer pipes and improve the safety management system.

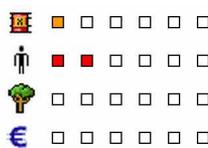

ARIA 32174 - 24/04/2006 - 76 - GONFREVILLE-L'ORCHER
20.15 – Manufacture of nitrogenous products and fertilisers

While re-starting an ammonia production unit in a chemical plant following a technical breakdown that lasted one hour and 30 minutes, a synthesis gas leak (50% hydrogen, methane, nitrogen and 17% ammonia) ignited on a flange (O-ring joint) located just after the synthesis reactor. The operator triggered the emergency shutdown after the unit's alarms were triggered, isolating and depressurising the synthesis cycle. Steam was sprayed on to the leak using mobile fire nozzles to extinguish the fire that was brought under control 55 minutes following its start.

Material damage was estimated at 60 K euro and concerned the thermal insulation of pipes, louvers protecting the reactor against atmospheric action, fire-proof concrete of the reactor frame and the instrumentation cables within a radius of 3 m. The blaze did not damage the reactor that was protected by a deflector. Operating losses stood at 300 k euro.

The tightening torques of the bolt on flange where the leak occurred is responsible for the accident: they were not adapted to the exceptional conditions prevailing during the accident (significant temperature difference between the bolt and the flange resulting from the abrupt temperature variation due to the short technical breakdown.)

The implemented corrective actions involved redefining the tightening torques, improving the tightness of the drip collar on the flanges (defective at the time of the accident), designing a nitrogen injection system in drips collars and installing a steam injection crown to protect the bottom of the synthesis reactor.


ARIA 32796 - 12/02/2007 - 06 - GILETTE
20.14 - Manufacture of other basic organic chemicals

At around 6.00 am, a flash was produced during operations in a chemical plant. The accident took place between two production campaigns. On the 7 and 9 February, the hydrogenation reactor was cleaned, deodorised and dried to eliminate residual waste from the previous production cycle and prepare the reactor for the following one. On 12/02 at 5.00 am, the production supervisor issued specific instruction on a new production cycle to a technician. The technician did not follow them in the right sequence as indicated in the verification instructions before starting production: to save time when pressurising the device at 9 bar of nitrogen, he simultaneously made several adjustments and carried out several checks (opening the manual hydrogen valves of the storage tank, the emergency shutdown valve just in front of the workshops, etc.). The reactor and safety process valves in front of the reactor were protected by a check valve that remained closed. The reactor was pressurised using nitrogen. The operator observed N₂ leaking from a manhole. He decompressed the reactor and removed the fastening bolts from the lid to change the joint. During this operation, he heard a leaking noise at the joint. Believing it to be a H₂-leak, he blocked the reactor and triggered the emergency shutdown of the workshop. He was convinced that the reactor was clean and the residual volume in the pipe was low and proceeded to change the joint with assistance from a fellow technician. The two technicians were projected backwards in an explosion that ensued. The internal contingency plan and ETARE plan (emergency plan drafted by the regional fire service) were triggered. Both the technicians sustained burns on their faces and hands and were initially hospitalised in Nice and subsequently transferred to a specialised unit in Toulon. A safety alert was sounded in the workshop. The gendarmerie (French military police) carried out an enquiry to determine the cause of the accident. The news was published in the press. The operator decided to shut down the site for 48 hours. The commissioned expert explained that the explosion occurred as a small quantity of H₂ ignited upon contact with the catalyst in presence of oxygen coming from the manhole. He also noted that the tightness of the reactor was checked and the pipe pressurised at the same time without following the guidelines, no tightness test was planned on the valves of the H₂ pipe and that there was not specific instruction on opening the manhole during normal or degraded mode as well as for changing the joint. The current Le montage H₂ sampling and introduction assembly increases the risk of leak on valves before the reactor and in the presence of a catalyst in the reactor. The drying conditions may have contributed to have increased the pyrophoric nature of the catalyst. Changes have been planned in the hydrogenation equipment (installing pressure sensors, flame guards on regulator vents, etc.) and procedures (risk analysis, verification of H₂ pipes, de-commissioning the H₂ pipe before opening the manhole).

ARIA 32817 - 29/11/2006 - 77 - GRANDPUITS-BAILLY-CARROIS

20.15 - Manufacture of nitrogenous products and fertilizers

In a chemical plant, there was an explosion and a leak that ignited at the flange of a relief valve on the turbocompressor of an ammonia (NH₃) manufacturing workshop being re-started. The hydrogen detectors and the fire alarm alerted the control room and sounded the safety alert in the plant. The rescue team gained control of the situation in a few minutes. The internal emergency plan was not triggered.

No victims were reported. A technician in the vicinity managed to escape just before the explosion after hearing a hissing sound made by the escaping synthesis gas composed 70% of hydrogen (flow-15,000 Nm³/h). The material consequences were confined to the immediate surroundings of the turbocompressor: electrical wiring and cladding melted down, insulating of pipes severely damaged, etc. The ammonia manufacturing unit was stopped for over a month.

Five days before the accident, the failure of CO₂ absorption in the decarbonation column of the NH₃ production plant being re-started led the technicians to open the vent downstream to the column before triggering the high temperature safety device. This rather excessive venting (operating error) led to the fall of the suction pressure of the NH₃ synthesis turbocompressor and activation of the emergency shutdown of the workshop. The valve on the line between the turbocompressor and the methanisation reactor opened under the effect of the high pressure without the knowledge of the technicians.

Production resumed in the following days but an abnormal balance in the synthesis gases led the operator to carry out detailed investigations only to find that the valve previously under stress was no longer air-tight. Gas escaped via a 47 m high stack. The workshop was shut down one again to replace the valve in question.

The unit re-started again. The methanation reaction was triggered at 10.00 pm. The NH₃ synthesis turbocompressor started at 1.30 am. The accident occurred at 3.14 am at the flange of the newly assembled valve (6" diameter, i.e. about 50 mm).

The accident occurred due to insufficient valve loading upon start-up that may have caused vibrations that loosened the flange screws. Moreover, the screws were undoubtedly not tight enough. The lack of traceability of the jointing operations (tightening torque) was also highlighted.

The accident feedback included the company in charge of valve reloading requiring certification from the inspection department of the plant, jointing procedures improved, specifications on jointing and valve overhaul made more stringent and an additional pressure sensor installed.

ARIA 32966 - 20/04/2007 - 38 - LE PONT-DE-CLAIX

20.14 – Manufacture of other basic organic chemicals



In the containment of a chemical unit, a phosgene (COCl₂) sensor was triggered at 6.40 am after



maintenance operations resumed as part of a technical shutdown.



This detection is further to a COCl₂ leak that occurred (ARIA32965) the previous day in a valve upstream to an exchanger being replaced. Only one out of the thirty sensors fitted in the containment reacted. The staff was evacuated. None of the detection badges worn by the technicians reacted. Operations were suspended. The working group set up the previous day was reconstituted and the facilities were inspected again.

The sensor that sounded the alert was close to the outtake of an air duct whose air intake was near the leak site. The accident occurred due to the release of COCl₂ at the joint upstream to the valve that leaked.

Several corrective actions were implemented:

- strengthening bolting of stoppers (during stop phases, bolting is reduced to save time)
- coating joints with adhesive to increase air-tightness
- stopping supply of nitrogen to pipelines to reduce pressure (weather conditions reduce the chances of humidity setting in facilities).



ARIA 33311 - 21/06/2007 - 76 - LE GRAND-QUEVILLY

20.15 - Manufacture of nitrogenous products and fertilizers



In a fertilizer plant, 62% nitric acid leaked around 8.10 am from a sectional valve at the inlet of calcium ammonium nitrate saturator in stable operating mode.



The 20 min leak resulting in the loss of 1 tonne of acid led to the release of significant quantities of nitrous vapours in the unit upon contact with the insulation of a steam pipe below.



The alert was sounded by an employee in the vicinity of the facility who noticed thick smoke being released from the unit buildings. The internal emergency plan was triggered at 8.12 am and lifted at 9.47 am.

The operations in the unit were stopped. The released acid, as well as the 2 m³ of water used to cool the facilities and reduce acid evaporation were collected in a retention tank and channelled to a pre-isolated recovery tank.

The economic consequences further to the stop of operations in the unit were limited.

The leak occurred due to the premature corrosion of the metal joints of the sectional valve. According to the operator, the material of the joint assembled a few days back did not match the specifications indicated in the purchase slip of the article.

Moreover, the inspection authorities for classified facilities noted that the nitric acid flow meter located downstream to the sectional valve and at the saturator inlet showed no variation in the inflow in the saturator despite the acid leak taking place upstream. The flow meter fitted with alarm and safety devices triggered at various thresholds by the closing of nitric acid valves failed to detect the leak and warn the technicians. No other safety device alerted the technicians of the leak. The unit was in fact not equipped with a sensor likely to detect such a leak.

Further to this accident, and before re-starting the unit, the operator had to carry out an exhaustive inspection of similar joints likely to have been replaced during recent maintenance operations. In addition, the operator also had to conduct an inspection and overhaul of all facilities likely to have been damaged due to the acid spill.