

Explosion of a hydrogenation reactor

27th December, 1995
Le Pont-De-Claix (Isère)
France

Chemistry
Toluenediamine / Dinitrotoluene
Reactor explosion / Fire
Washing
Human error
Organisation / procedures / control
Victim

THE FACILITIES INVOLVED

The site:

The Pont-de-Claix plant was operating a toluenediamine (TDA) production unit associated with the facility fabricating diisocyanate toluene (a polyurethane foam-based product). This installation had been classified as requiring operating authorisations subject to easements.



Specific unit involved in the accident:

The given workshop comprised 2 independent installations for dinitrotoluene (DNT) hydrogenation into TDA, as well as one shared facility for compressing hydrogen and separating finished TDA product by means of distillation. These 2 hydrogenation installations, denoted series "A" and "C", were located 50 m from one another.

The TDA fabrication process:

Means of production:

The process adopted (series "A") introduced the following components:

Isopropanol (solvent), Raney nickel (catalyst) and dinitrotoluene (DNT), which were made available in a mixing tank (R907a) installed on a weight indicator, then transferred by pump into an injection tank (R907b) in order to continuously supply a series of 5 reactors (G901a through G901e) under a pressure of 100 bar.

Upon production start-up, pure DNT was input directly at the level of the injection tank (R907b) via a dedicated pipe.

During normal operations, the mix was injected into the first 4 reactors, with the 5th being used as a finishing reactor. Hydrogen was only injected (at 100 bar) into the first reactor.

Washing:

The equipment was washed upon completion of each production run:

The mixing and injection tanks (R907a and 907b) were cleaned using isopropanol.

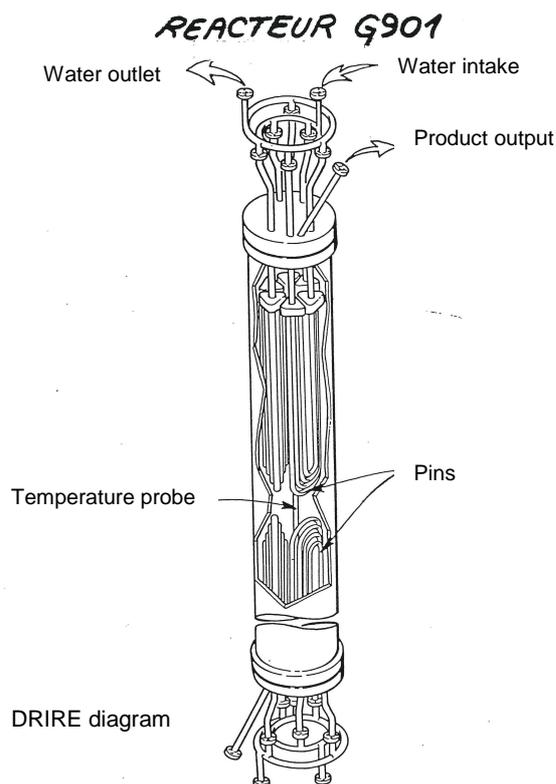
Reactors: Only reactor G901a was equipped with heating/cooling pins. A predetermined quantity of isopropanol loaded in the injection tank (R907b) was conveyed to this reactor, where it was subsequently heated to 150°C to make the TDA and tars soluble before being flushed by hydrogen at 100 bar to the 2nd reactor, where they underwent cleaning. After balancing pressure between the 2 reactors and climbing back to 100 bar, the reactors were emptied through the general reactor drainage line. This operation was repeated between the 1st and 3rd reactor, then between the 1st and 4th reactors and lastly between the 1st and the finisher.

The damaged reactor:

Damage occurred to the first reactor (G901a), as a hollow vertical cylinder 6.80 m long with an external diameter of 0.414 m and thickness of 0.039 m. This reactor was fitted with piping (in the form of pins) that enabled heat transfer fluids to circulate. Hydrogen and the reactive mix were injected at the reactor base. A temperature probe was inserted in order to monitor reaction evolution.

The reactor was fed by the injection tank (R907b); the hydrogenated product was then channelled to reactor G901b.

Reactor G901a had been removed in January 1995 for washing and placed back online in March of the same year. This device had been classified under a special regulation dedicated to pressurised facilities.



THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

Details of the accident:

On 27th December, at 5:15 am, an explosion occurred at the level of the first reactor (G901a) during a washing operation performed on series "A" reactors. A fire ensued, though it could be extinguished at 5:50 am by the plant's internal fire-fighting crew.

Chronology of accident events:■ **End of reagent injection:**

2:19 am: last transfer of mixing tank R907a to injection tank R907b. Beginning of the flow of the final mix.

2:51 am: end of the flow of the final mix.

■ **Washing of pipes, end of reaction, and drainage of reactors:**

2:55 am: addition of 800 kg of isopropanol in R907b. Relay into the pipes of reactor G901a for rinsing.

3:11 am: end of reaction on G901b, c, d; addition of hydrogen in G901a.

3:18 am: triggering by low H₂ pressure at the top of G901a. End of pipe rinsing with isopropanol. Beginning of the static hydrogenation phase (cut-off of fresh H₂).

4:23 am: end of static hydrogenation.

4:23 to 4:34 am: drainage and decompression of all 4 reactors and the finisher. Reactors cooled to 70°C and insulated from one another.

■ **Washing of the reactors:**1st sequence of washing: washing of G901a and G901b reactors:

4:38 to 4:41 am: washing of G901a: Injection of 150 kg of product (isopropanol + DNT instead of pure isopropanol, according to the analysis of accident causes) in G901a; in parallel, the bottom of the reactor was heated with steam.

4:55 am: pressure rise in reactor G901a to 100 bar with H₂.

4:55'28" am: drainage of reactor G901a into G901b. Pressures inside the two reactors became balanced then rose to 100 bar.

4:58'18" am: shut-off of the hydrogen inlet valve as well as the G901b bottom valve.

4:59'01" am: degassing of G901a: Opening of the general drainage valve to storage tank R915a.

5:00'41" am: closing of both the general drainage valve and G901a bottom valve. Opening of the G901b bottom valve, to allow for its drainage and degassing.

5:01'38" am: shut-off of the G901b bottom valve and the general drainage valve. All bottom valves were closed.

2nd sequence of washing: washing of G901a and G901c:

5:04 to 5:07 am: transfer of 170 kg of product (isopropanol + DNT instead of pure isopropanol) from R907b to G901a.

5:07'28" am: opening of the hydrogen inlet, raising the pressure in reactor G901a to 100 bar.

5:08 am: explosion of reactor G901a.



Photo credit: DRIRE

Four injuries were reported; one of the victims, with burns sustained over 40% to 50% of the body, died 15 days later. Two of the injured returned to work full time in January 1996, while the last victim resumed part time in March.

Fragments from the reactor and supporting structure were projected by the explosion.

During the fire-fighters' response, water from the plant's collector pipe was diverted to the site's emergency basin until official observation of the absence of amine (i.e. a pollutant characteristic of shop operations).

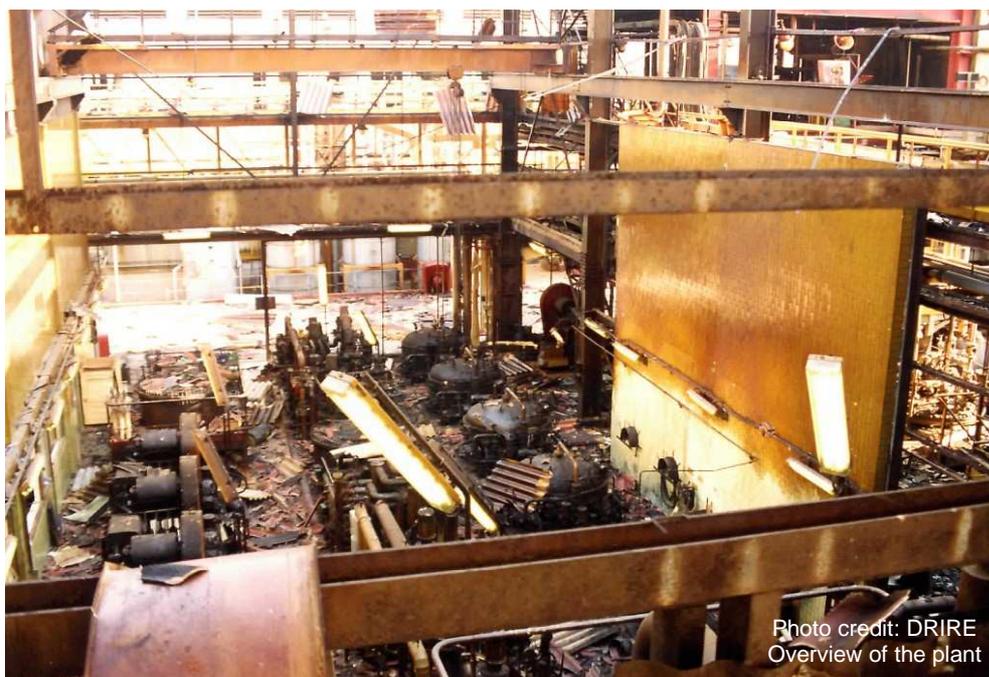
Consequences of this accident:

The damaged reactor was required to comply with conditions stipulated in the regulation devoted to gas pressurised devices. Placed into service in 1963, this reactor contained an interior volume of 440 litres, which had to resist a 5-year hydraulic test pressure equal to 240 bar, for normal use at a level of 160 bar maximum. Given the device specifications, it would appear that hydraulic testing had been regularly conducted and moreover the device inspection reports had not uncovered any major anomaly.

The explosion of a pressurised device most often leads to a rupture of the capacity with little or no spraying of debris; in the present case however, this reactor fragmented into some 15 pieces. The clean breaks on this device suggested that it had been exposed to a pressure considerably above the 240 bar test pressure and undoubtedly in excess of 1,000 bar.

One employee was killed and three others injured.

Property damage was very extensive: the TDA plant was unusable; the control room severely damaged; the reactor and a portion of the other facilities located in the bunker were destroyed. The masonry, showing signs of complete rupture in spots, along with twisted rebar attest to the violence of this explosion.



The blast of the explosion and projection of metal fragments resulting from the reactor destruction deformed the bunker insulating the chemical installation. Fragment projections outside the bunker reached adjacent facilities, as the shockwave destroyed a wall made of breeze block inside the catalyst preparation zone while deforming the control room building structure and cracking walls.

In the distillation unit, bordering the bunker, the effects from the explosion caused a loss of confinement and product ignition (isopropanol and TDA). Milder structural deformations of buildings were also observed at a neighbouring industrial site 150 m from the scene of the explosion.

The natural environment was not adversely affected thanks to the collection of water dispersed in the plant; the controls carried out on the morning of the accident in the DRAC River water yielded a value below 0.1 mg/litre of amine content.



Control room



Photo credits: DRIRE

Exterior of the building



Close-up of the damaged reactor

The European scale of industrial accidents

By applying the rating rules applicable to the 18 parameters of the scale officially adopted in February 1994 by the Member States' Competent Authority Committee for implementing the 'SEVESO' directive on handling hazardous substances, and in light of information available, this accident can be characterised by the four following indices:

Dangerous materials released		<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Human and social consequences		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Environmental consequences		<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Economic consequences		<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

At the time this accident occurred, several SEVESO substances were involved, namely DNT, hydrogen, isopropanol, nickel and TDA. The exact quantities of these substances released during the explosion were not known with certainty, in which case the index relative to quantities of dangerous materials released was scored a "1" as a default value (see Parameter Q1). The accident caused the death of 1 employee and injured 3 others, which leads to a "2" rating on the

human and social consequences index (Parameter H3). No environmental consequence was observed, thus resulting in a "0" score for the index relative to environmental consequences. With no precise evaluation of property damage costs, the economic consequences index could not be rated.

The parameters composing these indices and their corresponding rating protocol are available from the following Website: <http://www.aria.developpement-durable.gouv.fr>.

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THIS ACCIDENT

An analysis of product samples extracted from onsite equipment demonstrated that DNT had been introduced into the first reactor (G901a) during a washing operation via the injection tank (R907b). Indeed, this reactor contained 400 kg of crystallized DNT. Trace amounts were also detected in the reactor, pump P904a and ancillary piping. Moreover, traces of isopropanol were present above the crystallized DNT. Analyses performed in tank R907a did not reveal the presence of any such elements. Some catalyst could be found in reactor G901a.

Tank R907b was equipped with a DNT supply line that was only being used to prepare the synthetic mix for hydrogenation during unit start-up after extended downtime. This operation gave rise to a specific set of written procedures. The last shutdown prior to the accident occurred on 22nd December.

After the accident, the 2 valves in series installed on this line were found to be partially open (with a 10° opening). A verification in the presence of an appointed judicial expert indicated that, in this position and under operating conditions identical to those of the unit before the accident, these valves allowed 500-700 kg/hr of product to flow through; moreover, they were located respectively at 0.60 m and 1.50 m from the ground. A key was necessary to proceed with the handling manoeuvre, thus minimising the likelihood of mishandling as a reason for unintended equipment opening.

On 23rd December, between 7 and 8 pm, the hydrogen supply line was inadvertently cut. The weight recordings of injection tank R907b remained horizontal, given that the valves had been closed during this period.

The weight recordings of tank R907b, conducted on 27th December, indicated that the tank had been gradually filled during the static hydrogenation phase, concluding at 3:25 am. At 4:38 am, a complement was added, followed by an injection estimated at 150 kg of product in reactor G901a; afterwards, the tank kept filling up.

The instructions called for 2 washings of reactor G901a, with transfer of the first washing liquid to tank R915. Progress achieved on the catalyst loop had nonetheless made it possible to reduce reactor clogging and, consequently, eliminate one of the two washings. Reactor G901a thus underwent just a single washing, and washing products were conveyed to reactor G901b instead of tank R915. This change, though justified, was not transcribed into any of the written procedures. The elimination of one washing step resulted in a 2,500-kg reduction in the quantity of isopropanol introduced into injection tank R907b, thereby preventing adequate dilution of pure DNT input via the 2 partially open valves, even though such a level of dilution would have averted the explosion.

The safety report issued relative to the TDA production unit stated the prohibition of having pure DNT react with hydrogen since the resulting reaction would be too violent. Diluting DNT with isopropanol and a hydrogenation crude mixture was necessary prior to product introduction into reactors. The plant operating protocol took this restriction into account in its implemented (Bayer) process, with DNT only existing within a solvent medium and never in a pure state.

The site operator replicated the pure DNT explosion in the laboratory under operating conditions resembling those of the washing step at the time of the explosion: hydrogen pressure of 140 bar, and temperature of 140° to 150°C in the presence of the catalyst. The test concluded with a quick rise in both temperature and pressure and rupture of the autoclave safety disc preset at 350 bar. This simulation exercise confirmed the hypothesis that the heat release associated with the hydrogenation of a small portion of DNT triggered the abrupt decomposition of remaining DNT by suddenly reheating the reactive medium.

ACTIONS TAKEN

Subsequent to this accident, the zone surrounding the series "A" bunker was closed to access. This prohibition was then extended to the covered parts of annex buildings, where materials were at risk of falling, as well as to the distillation section adjacent to series "A". With judicial expert agreement, the prohibition was lifted, by virtue of court order, and after removal of the unstable material supply. The bunker was reopened following reinforcement of its upper structure by a metal frame along with installation of a concrete access tunnel.

The "A" and "C" series, located just 50 m from one another, were both shut down after the explosion. The distillation section, exposed to the onset of fire, was also closed for safety reasons with a curtailment of all transfers and heating.

Beginning on 2nd January, the water held in the site's retention basin, containing 10 mg/l of amines, was discharged at a slow rate together with the site's wastewater effluent in the direction of the DRAC River, as amine content remained less than 0.1 mg/l (i.e. a flow rate of 160,000 m³/day). The wastewater trapped in the plant's retention basins (100 m³) was incinerated onsite, as were all organic products recovered in devices and rinsing products.

Some 60 m³ of roof and wall debris, including sheets of asbestos cement roofing, were discharged to a certified dumpsite following verification of zero organic pollution content. Demolition wastes from the bunker were treated similarly. The solid organic wastes stemming from all of the various cleaning operations were placed in drums for subsequent incineration at a certified treatment facility.

An emergency order was adopted on 28th December, 1995 as a direct result of this accident.

In seeking to restart service of series "C" (i.e. mixing tank R907e and injection tank R907f), which were not affected by the explosion (given distance from the blast and protection features installed at the bunker) yet still equipped with some of the same machinery as series "A", the operator proposed the following measures:

- verifying all equipment installed on the TDA production line intended to be restarted;
- maintaining DNT intake on mixing tank R907e, but removing the intake on injection tank R907f;
- closing the connection, by means of an automatic on-off valve, between the mixing tank and the injection tank during reactor washing;
- scheduling closure of 2 automatic valves placed in series on the DNT feed line in the mixing tank and shutdown of the mixing tank transfer pump to the injection tank during reactor washing;
- installing an additional tank upstream of mixing tank R907e in order to directly supply the 1st reactor after extended downtime (complement of DNT);
- modifying the reactor cleaning protocol: series washing steps instead of a successive washing pattern.

More specifically, the washing step was only allowed to proceed after physical insulation of tank R907e. This measure implied reconfiguring all reactors at the level of the pins, in order to ensure cooling or heating, in addition to performing measurements at the valves to be opened/closed. The transition from a discontinuous to continuous process avoided requiring personnel to enter the bunker to handle the valves controlling transfers from one reactor to another.

Restart of series "C" was to be preceded by a thorough verification of TDA fabrication facilities (outside of series "A" and specific annexes) and the control room. The equipment intended to prevent introducing pure DNT into the reactor was implemented. The classified facilities inspectorate took note of the modifications adopted for the washing process. Weighing of the various products (DNT, nickel, isopropanol) was supplemented by a measurement campaign that enabled comparison with current weighing system recordings through to the present time. This restart however did not return the system to the previous level of TDA production. To resume production like before, the company devised a plan to install a reaction line using a different technology: according to this so-called "*Tolochimie*" process, the 5 Bayer reactors were replaced by a single reactor plus its backup units. With this process, the reaction could take place without any solvent, as the reactive medium contained 1 mole of TDA for 4 moles of water, and under hydrogenation velocity conditions such that practically no DNT was present in the reactor (i.e. a concentration on the order of 100 ppm). While TDA is produced in the same manner by pressurised DNT hydrogenation, still the fact of working without an inflammable solvent and at lower pressure (20-25 bar instead of 100-130 bar) was nonetheless intrinsically safer.

Lastly, given the reactor's appearance after the explosion (ripped into 15 pieces, with clean breaks) and the high pressure attained, a number of metallurgical analyses were conducted on the recovered parts.

LESSONS LEARNT

Organisation and controls:

Risk prevention is based for the most part on the juxtaposition and comparison of procedures established from guidelines and from automated mechanisms intended, at times, to render certain operations more reliable. In the present case, explicit guidelines dating from 2nd May, 1994 were not respected (i.e. no additional DNT during washing operations). Routine, old habits and experience are not justifications for waiving current rules.

Moreover, a visual inspection of the entire set of valves should have led to observing the opening of both valves. An extra barrier, such as servo-controlled valves on this DNT line, would have prevented eventual DNT introduction into reactor 901a during the washing sequence.

Identification and evaluation of accident risks, process supervision:

In light of the high exothermicity of the DNT hydrogenation reaction, several elements were capable of leading to this accident, namely:

- the washing sequence using a discontinuous process,
- the installation configuration, particularly the DNT line,
- the washing sequence modification subsequent to process improvements (less reactor clogging). This modification, wholly justified yet not transcribed in the guidelines, prevented DNT dilution.

All these points led to an insufficiently diluted DNT concentration in the reactor. Reaction conditions, as verified in the laboratory, caused the pressure and temperature rise required to trigger the accident.

An assessment focusing on the risks related to opening DNT pipe valves during reactor washing with isopropanol under H₂ pressure, along with in-depth knowledge of the process, would have allowed evaluating these risks and then modifying the installation prior to the accident. The risk analysis performed for this plant seems to have been inadequate.

Feedback management:

The modifications proposed to the "C" series by the site operator were intended to prevent a repeat of such an accident, with special emphasis on eliminating the DNT intake line on the injection tank. This line, which proved necessary during production restart (by providing an additional supply of DNT into the first reactor), was replaced by introduction of an extra tank upstream of the mixing tank. The installation of additional valves, notably those between the mixing and injection tanks, helped make this process safer.

As a final consideration, the washing process modification served to strengthen process safety by enhancing operational continuity through laying out the reactors in series. This step made it possible to avoid both handling many different valves and requiring personnel to enter the bunker. The transition from discontinuous to continuous washing necessitated reconfiguring all reactors in order to monitor and ensure their constant temperature.