

Butadiene leak in a chemical plant.

December, the 4th, 2000

Bassens – [Gironde]

France

Gaseous release
Polymerisation
Valve
By-pass
Overpressure
Organisation
Nuisances
Intervention plans
Crisis
Information

THE INSTALLATIONS IN QUESTION

The site :

The plant employs 425 people. It produces 120,000 t/year of synthetic rubber derived from butadiene and styrene. The procedure used is a solution-type procedure, the solvent being toluene. The plant is almost the only one which manufactures high-viscosity butadiene, which is essential for the other plants within the group.

The establishment is covered by the AS (SEVESO) regime of the nomenclature for installations classified for the storage of inflammable gas (butadiene) that is liquefied and refrigerated (5,000t) and pressurised (1,790 t). The last prefectorial order, which followed a public enquiry dates back to December 4th, 1996.

Within the framework of the PPI (Plan Particulier d'Intervention, special intervention plan), the instructions issued to the population include evacuation within a 600m radius and sheltering in a "restricted zone" between 600 m and 1,200 m.

THE ACCIDENT, ITS BEHAVIOUR, EFFECTS AND CONSEQUENCES

The accident

On December 4th, around 6.30 p.m., on the U400 high-viscosity polybutadiene manufacturing unit, a valve ruptured downstream from a 12m³ tank, releasing its contents, 5m³ of pressurised liquefied butadiene, in 15 minutes (1,250m³ of gas). The cloud of gas drifted towards the west of the site during the first hour, then towards the south-west, in the direction of the Paris-Bordeaux TGV (French high-speed train) line. The POI (Plan d'Organisation Interne, internal contingency plan) was put into action, and a control unit was installed on the site. The production units were stopped and water curtains were installed around the tank. The SDIS (Service Départemental d'Incendie et de Secours, fire and emergency services) arrived at approximately 6.50 p.m. The road was closed to traffic south of the site at 7.10 p.m. and in the south east at 7.35 p.m. The TGV line was closed at 8.p.m.

Explosivity measures were taken in the area around the establishment as of 7.10 p.m, first in a random manner by the operator and then from 8.p.m. onwards, in an organised manner by the fire and emergency services and teams of firemen from the plant.

All of these security measures were called off at approximately 10.30 p.m.



Source : DRIRE Aquitaine

The consequences:

There were no victims as a result of the accident. Residents of Bassens complained about the smell following the leak. Olfactory perception of butadiene is possible as of 2 ppm, while the lower explosive limit (LEL) is 20,000 ppm. According to the operator, the explosimeter detection threshold set at 10% of the LEL does not appear to have been reached.

European scale of industrial accidents

By applying the rating rules of the 18 parameters of the scale made official in February 1994 by the Committee of Competent Authorities of the Member States which oversees the application of the 'SEVESO' directive, the accident can be characterised by the following 4 indices, based on the information available.

Dangerous materials released		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" 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"/>

The parameters that comprise these indices and the corresponding rating method are indicated in the appendix hereto and are available at the following address: <http://www.aria.ecologie.gouv.fr>

At the time of the accident, 5 m³ or roughly 3 t of butadiene (an extremely flammable liquefied gas) were released, corresponding to 1.5% of the Seveso threshold (200 t). The "dangerous materials released" index of the industrial accidents scale is thus 3 (parameter Q1).

As public transport was interrupted for more than 2 hours, the "human and social consequences" index was given a rating of 2 (parameter H8).

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

Spontaneous auto-polymerisation caused a brittle fracture of the valve in question. The valve served as a by-pass for a remote-controlled valve on the pressure control circuit in the butadiene tank. The forming of this polymer, known as "pop", in the valve cover was due to :

- butadiene stagnation : the valve, which was closed at the time of the accident, constitutes an abandoned channel, with no circulation of the product
- the ambient temperature
- the absence of an inhibitor (tert-butyl cathecol): the tank did not contain any, as the butadiene is derived from a recondensed gaseous phase and the inhibitor is eliminated during this operation.

The increase in volume during polymerisation caused the internal pressure to rise sharply, thus causing the brittle fracture of the cast iron valve, the cover of which was torn off.



ACTION TAKEN

Over and above the analysis of the accident, the department of the DRIRE (French regional inspectorate for industry, research and the environment) that is responsible for the inspection of classified installations requested a plan of action from the operator, in order to prevent the same type of accident from occurring again.

The measures are as follows:

- ✗ Enumeration of similar configurations throughout unit U400, based on the following criteria:
 - ✓ Presence of dry or wet butadiene without inhibitor
 - ✓ Development of pop favoured by temperature
 - ✓ Development of pop favoured by the presence of a gas phase
 - ✓ Development of pop favoured if the output is low or nil ("abandoned" channel, upper taps of tanks in the gas phase, valves and fittings, etc.)
 - ✓ Cast iron valves and fittings
- ✗ Analysis of the risks of the installations based on the following criteria:
 - ✓ Output conveyed
 - ✓ Nominal diameter
 - ✓ Line or tank pressure
 - ✓ Volume involved in case of confinement
 - ✓ Isolability: is there a means of insulating the critical point, is it accessible in the case of a leak?
- ✗ Site inventory and analysis: machine checks, verification of the upstream/downstream pressure levels of identified points, manoeuvrability tests of valves and fittings at risk.
 - ✓ Similar configurations have either been removed for verification of the absence of pop, cleaning where necessary and replacement in certain cases, or a manoeuvre test has been carried out on the valves and fittings, allowing seizing or pop to be detected. In the case of a negative test, the valves/fittings were removed and cleaned.
 - ✓ The [quarter-turn] valve in question has been replaced by a steel ball valve, pending a detailed study of the problem with the by-pass. Two other cast iron valves have been replaced.
 - ✓ The offending valve was not referenced as critical. At the request of the DRIRE, a "critical valves/fittings" inspection plan has been completed by valves and taps which could present a risk of blocking by pop.
- ✗ In addition, the following preventive measures have been taken:
 - ✓ Surveillance rounds (visual control, pressure and output controls) and a 2nd level control performed by the company's inspection department
 - ✓ Biannual manoeuvrability tests while in operation
 - ✓ Removal for biannual internal examination at the time of the two annual shutdowns. These last two points are staggered, in order to ensure maximum cover of the valves at risk
 - ✓ Replacement of critical gate valves and cast iron valves by steel valves, at the time of the July 2001 order
 - ✓ A study of each abandoned channel that has been enumerated, in order to carry out modifications to reduce the risk of pop, at the time of the July 2001 order

At the request of the Inspection des Installations Classées, the classified installations inspectorate, a study on the atmospheric dispersion of the butadiene cloud was carried out, in order to determine whether the cloud that was dispersed towards the south/south-west could have caused an explosion exterior to the site, and to evaluate whether the populations exposed to the passing cloud could suffer irreversible damage to their health.

1.3 butadiene is a highly flammable gas that can form peroxides. The explosivity of the vapours in air ranges between 2% (LEL) and 12% (upper explosive limit, or UEL).

It is an anaesthetic gas if inhaled in strong concentrations. Weak concentrations in the air (1%, or 10,000 ppm) do not have any noticeable effect on breathing, but this kind of exposure can cause quickening of the pulse or sensations of stinging or dryness in the nose and mouth. Inhalation at strong concentrations first cause eyesight problems, nausea and irritation of the eyes, followed by progressive anaesthesia. Respiration of an atmosphere containing 25% volume of butadiene for more than 20 minutes can be fatal. The recommended maximum allowable concentration of butadiene in the atmosphere of industrial premises, which allows for 8 hours' exposure per day, 5 days a week, with no detectable effect for most individuals, is 2 ppm. The IDLH (Immediately Dangerous to Life and Health) is a concentration value which was defined by the National Institute for Occupational Safety and Health (NIOSH) in the mid-1970s. It represents the threshold for irreversible effects after 30 minutes' exposure. For butadiene, it was set at 20,000 ppm. This value was reduced to 2,000 ppm in 1994. In addition, different studies have shown that 1.3 butadiene is a carcinogen.

Lastly, this gas has a density of 1.9. Heavier than air, it forms clouds which are then dispersed more or less rapidly, depending on the weather conditions.

This study concludes that the explosive area do not come out of the site's limits. Concerning the irreversible effect area (IDLH), it slightly comes out the site but does not impact outside residences..

LESSONS LEARNED

In terms of feedback, the phenomenon of spontaneous, uncontrolled polymerisation of butadiene is a reality which must be taken into account and is a scenario that must be analysed, particularly in valves that serve as a by-pass.

This accident revealed problems in the organisation and indeed in the culture of safety that are currently being analysed, and of which the analysis should result in an additional order within the framework of the order of May 10th, 2000 (SEVESO II), drawing conclusions in particular about:

- ✓ The failure to react, on the part of the personnel, at the time of the leak, and the failure to intervene on a manual valve located between the tank and the offending valve, which could have considerably reduced the quantity emitted into the atmosphere
- ✓ The absence of analysis of this scenario in the studies of the dangers, leading to a lack of training and practice on the part of the personnel and a doubt concerning the risk of explosion in the area around the site (culminating in the closure of the Paris-Bordeaux TGV line)
- ✓ The location of the operator control unit which could have been inside the butadiene cloud
- ✓ The anxiousness of some residents concerning the smell of butadiene, due to lack of information
- ✓ The ill-defined limit between P.O.I and P.P.I. depending on the drift of the gas in changing winds
- ✓ Improvement of crisis management (decisions taken after some delay)
- ✓ Interface of instructions with the railway company.

