Reactor explosion

3rd January, 1996

Sisteron

(Alpes-de-Haute-Provence)

France

Fine chemical manufacture
Thionyl chloride
Sulphur dioxide
Reactor
Explosion
Glass equipment
Organisation / procedures / instructions
Human factor
Victims / injuries

THE FACILITIES INVOLVED

The site:

The plant was manufacturing active ingredients for use by the pharmaceutical industry at an annual output of 400 tonnes of finished product; a total of 5,000 tonnes of organic solvents were being utilised on a yearly basis. The facility was assigned a Seveso rating for its storage of phosgene.

Site overview

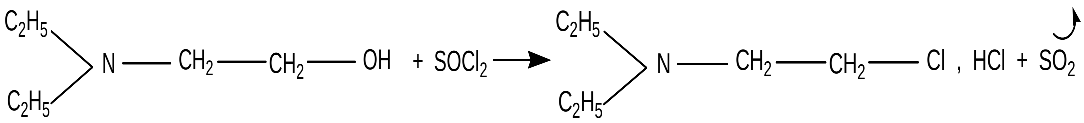
The specific unit involved:

The damaged building housed a multi-purpose, 6,000-litre capacity enamelled reactor used for the synthesis of various products. The reactor had been equipped with a glass superstructure that included a column, a Dean Stark distillation apparatus and a 200-litre loading tank. A valve calibrated at 2.5 bar was also installed on the reactor, and a rupture disc calibrated at 0.3 bar was placed on the glass column.

Example of an industrial reactor containing a glass column

Example of the Dean Stark apparatus: Topped by a condenser, this set-up allows recovering the densest product.

The accident occurred during synthesis of an intermediate product in the manufacturing of an active pharmaceutical ingredient, namely 2-diethylamino-ethane chlorhydrate, as obtained by the action of thionyl chloride ($SOCl_2$) on 2-diethylamino ethanol within a 1,2 dichloroethane (DCE) medium, according to the following reaction:



Initially, the reactor had contained 1,064 kg of thionyl chloride and 5,150 kg of DCE, to which 950 kg of 2-diethylamino ethanol were added in a controlled manner over a 30-hour period. Temperature was held at 70℃±5℃ by in jecting vapour into the reactor's double-containment structure. The reaction took place at a slight depression (10 to 20 cm of water), caused by an alkaline-hydro neutralisation system capable of gradually neutralising the sulphur dioxide (SO_2) generated by this chemical reaction.

According to the process design file, intermittent heating is necessary, as the slightly exothermic reaction does not allow maintaining the temperature at 70℃.

After 25 years of successful operations, this process had still been deemed robust and effective by plant technicians and executives.

Based on tests conducted in the operator's process safety laboratory, no major risk could be identified. Both the reagents and products used proved to be stable within the considered temperature range, and the level of exothermicity could not reach the runaway reaction zone. A series of tests then confirmed this limited reaction exothermicity.

THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident:

When the accident occurred at 10:30 pm, pouring of the 2-diethylamino ethanol (amietol) had been underway for 3 hours; this process was performed by means of individual 200-litre loads, with the first load not yet fully complete. The operation was being executed by 2 technicians, one of whom was still in training. The two process parameters, i.e. temperature and depression, had been regularly controlled every hour (7:30, 8:30 and 9:30 pm) without witnessing any anomalies; the last recording had indicated a temperature of 74.9℃ and a depression equal to 19 cm of water.

Around 9:30 pm, the more experienced technician turned off the control box selector for the spout used to insert powder used during the previous operation into the same reactor. The noise that accompanied rupture of the safety disc installed to protect the facility alerted this employee, who at the time also observed white smoke emanating from flange joints on the glass superstructure. He proceeded by closing the amietol injection valve and was heading to close the vapour injection device when he noticed that leaking on the glass column was getting worse. He decided to leave the unit and asked that his trainee colleague do the same. The whole sequence of events happened in less than a minute: the explosion occurred just as the first technician was exiting the premises, with the glass column bursting into small pieces and a thick white cloud permeating the workshop. Visibility was next to nothing and the air became unbreathable.

Consequences of this accident:

The rupture disc calibrated at 0.3 bar and the glass equipment on top of the reactor burst. Either the explosion or the toxic gases and vapours emitted once the equipment had been shattered were responsible for the death of the trainee technician, who was unable to immediately evacuate the premises.

The building housing the reactor was evacuated, and production was stopped while awaiting conclusions of the judicial investigation and technical appraisals conducted by the plant's in-house units.

From an environmental perspective, no impacts were observed, as the discharge of toxic gas (SO_2) had remained confined to the building.

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:

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

The reaction exposed 2-diethylamino ethanol and thionyl chloride, both of which are Seveso-rated substances, along with the solvent (DCE). Given the absence of data able to identify the quantities of substances involved in the accident sequence, the index relative to the quantities of dangerous materials released was scored a "1" as a default value (see Parameter Q1). This accident caused the death of an employee, which resulted in a "2" assigned to the human and social consequences index (Parameter H3). Given the lack of any environmental impact observation, the corresponding index received a "0" score. Since the extent of property damage could not be evaluated in cost terms, the index relative to economic consequences was not scored.

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THIS ACCIDENT

The analyses conducted revealed that:

- All substances used were compliant with specifications;
- The anhydrous heat transfer fluid supplying the condenser had not reacted with the reaction medium;
- No trace of sodium had been detected inside the reactor and the embedded tank, thereby excluding the hypothesis of a return of the hydro-alkaline neutralisation system implemented in order to neutralise SO_2 generated by the reaction;
- The volume remaining inside the reactor after the accident amounted to 1,500 litres.

As regards the installation's safety devices, the disc calibrated at 0.3 bar protecting the glass column had burst and moreover the protection valve placed on the reactor and calibrated at 2.5 bar had opened. When tested following the accident, this valve operated normally.

The material features (enamel, the reactor's double containment, control of measurement instruments) were also fully compliant with specifications.

A verification of valves and connections indicated that the water inlet channel was disconnected, as was the solvent supply hose.

The computerised reading of solvent quantities used during the day showed no unexplained consumption.

The powder insertion spout comprised 2 valves. Following the accident, an examination of this equipment revealed a closed upper valve (on the loading booth side) and an open lower valve (on the reactor side). The pneumatic control hoses associated with the lower valve had been reversed.

Given the full range of investigations, the most likely hypothesis forwarded is that of an accidental intake of water into the reaction medium via the powder loading spout used during the previous synthesis step, which was then rinsed with water though not recorded prior to start-up of the 2-diethylamino-ethane chlorhydrate synthesis. As a matter of fact, the simulation performed at the operator's process safety laboratory by adding water to the reaction medium under process conditions demonstrated the presence of hydrolysis, as reflected by a sudden pressure rise. The calculation displayed that 1 kg of water added to the reaction medium had generated 4.7 kg of gas nearly instantaneously, i.e.:

$$\mathrm{SOCl_2 + H_2O \rightarrow SO_2 + 2HCl}$$

Both the protection disc calibrated at 0.3 bar and its outlet were calculated in order to protect the glass superstructure from an overpressure due to an external fire, or loss of control over the vapour heating system, or else an unexpected change in the quantity of amietol injected. The accidental introduction of water into the reactor, as a result of hydrolysis, led to a substantial gas release that the installation's safety devices were unable to evacuate. This particular release was biphasic in that only 1,500 litres of reactive volume out of some 4,900 litres total were found inside the reactor after the accident (meaning over 3,000 litres had been dispersed during the accident).

ACTIONS TAKEN

Subsequent to this accident, which gave rise to a judicial enquiry, a number of specific measures were adopted, namely:

➢ Technical measures:

At the level of the powder insertion spouts:

- Replacement of fast couplings on pneumatic control hoses for valves via a set of screwed, but not interchangeable, fittings;
- Introduction of synoptic diagrams for positioning powder injection system valves, based on a series of limit switches;
- Mechanical logging system.

At the level of production machinery:

- Programme to replace the glass superstructures by enamelled steel superstructures for those reactors whose chemical reactions were generating gases;
- Systematic recording of process-related parameters (temperature, pressure).

At the level of the plant building:

- Reinforcement of signalling for backup equipment, intervention procedures and emergency exits;
- Installation of guide lamps (alternative mode of bursting on the emergency exits).

➢ Organisational or human measures:

- Inspection and layout of facilities prior to initiating any type of operation;
- Adoption, on a unit-by-unit basis, of a logbook for monitoring anomalies;
- Systematic and periodic audits performed of units/processes, with an in-depth assessment of the configuration and environment of the various installations, plus the set of production documentation serving as a guide;
- Mandatory wearing of the escape mask.

LESSONS LEARNT

Organisation and controls

The accident was due to a combination of several elements, including:

- reversal of the lower valve control hoses on the feed spout, yielding a position that contrasted with the logic of the local automaton;
- failure to log the spout during the change in synthesis, thereby leading to the accidental introduction of water;
- noncompliance with procedural instructions when one of the technicians was handling the spout control box.

The familiarity and execution of somewhat repetitive tasks frequently caused lapses in technicians' concentration when faced with the absence of strict protocols and clearly established procedural guidelines. Increased operator awareness of this hazardous tendency proves just as necessary when the process, even when deemed robust, involves exposure to sensitive operations and/or substances.

Feedback experience management

The measures adopted following the accident were intended to prevent such an accident from ever recurring, by making the hose reversal impossible and the couplings no longer interchangeable, as well as by strengthening equipment controls and introducing a logbook for tracking observed anomalies, thus making it impossible to start a new production run with a non-recorded spout.

The continuous recording of process parameters would allow technicians to control in real time the effective execution of synthesis operations. Whenever gases were potentially generated, the replacement of glass structures by enamelled steel at the level of the reactors offered additional protection in the event of a deviation in process parameters.

Moreover, measures such as the reinforced signalling of emergency resources, installation of guide lamps and mandatory wearing of escape masks were designed to avoid the occurrence of tragic human consequences during an accidental situation.

From a more general standpoint, greater attention must be paid to processes capable of generating large quantities of gaseous products or vapours, which in turn cause pressure to increase. It is therefore recommended to limit the use of glass equipment and replace it as quickly as possible with materials like enamelled steel. The technical options chosen will be required to integrate the possibilities of runaway reactions and moreover allow completing or interrupting the reaction under safe conditions: ice injection, quenching of the reaction, inhibitor, blowdown method, etc. The design and dimensioning of the rupture disc assemblies and associated safety valves must acknowledge the underlying pressure rise dynamics. Lastly, if an undesirable reaction is possible with residue from previous operations, then cleaning of the reactor and adjacent premises (feed hopper, etc.), along with their drying, becomes essential. These actions are to be carried out and verified in accordance with a procedure whose efficiency has been validated beforehand.