# Hydrogen explosion

## September 1, 1993

## Gennevilliers – [Hauts de Seine] France

**Fine chemistry**
**Discontinuous process**
**Sodium borohydride**
**Aluminium trichloride**
**Design**
**Automatic control / Regulation**
**Instructions**
**Alarms**
**Victims**
**Procedures**
**Organisation**

## THE INSTALLATIONS IN QUESTION

### The site

The fine chemical plant is located on 1 ha of land in the Villeneuve-la-Garenne / Gennevilliers industrial estate. It specialises in the synthesis of active substances for the pharmaceutical industry. The plant is not subject to the SEVESO directive, although has an internal contingency plan owing to the on-site storage and use of ammonia contained in tubes, and other dangerous substances and solvents (toluene, methanol…).

## THE ACCIDENT, ITS BEHAVIOUR, EFFECTS AND CONSEQUENCES

### The accident

On September 1st, 1993 at 6.45 am, an explosion and fire occurred in one of the plant's workshops during a chemical reaction. In this reaction, an imide is converted into an amine in anhydrous conditions and in the presence of aluminium chloride-activated sodium borohydride. The reaction, inerted with nitrogen, is performed in a triethylene glycol methyl ether (triglyme) and chloroform mixture. The synthesis was already performed at an industrial scale 21 times in 2 years.

Imide is introduced into the reactor by a flexible hose connected to a portable pneumatic metering pump. The operation began at 6.30 am, one half hour before the end of the shift. The procedure stipulates that the operation be conducted in at least 8 hours and that the temperature of the reaction environment not exceed 65℃.

At 6.45 am, as the setpoint temperature had been reached, the operators prepared to cool down the reactor to maintain it at approximately 65℃. The reaction continued br utally. The temperature and pressure in the apparatus increased.

The operator nearest the reactor noticed a highly unpleasant odour. Through the unit's glass window, he noticed a glow that normally precedes an explosion. Employees located 15 m from the reactor felt the blast effect. Flames crossed the workshop while others blew out from the reactor through a joint and damaged branch connections. Employees inside the building felt a blast just prior to the explosion. A flame measuring several meters high was visible for a few seconds at the exit of a stack which allowed the reactor to decompress should the rupture disc burst (calibrated at 0.5 bar).

### Consequences

Four of the eight people present in the workshop were hospitalised for burns and respiratory difficulties : 2 were discharged from the hospital the same day.

The cost of property damage was evaluated at 14 MF.

## 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.


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

Parameter Q1 is given a rating of 1 by default, as the quantity of chemical substances involved is not known.
As the effects of the explosion had not been characterised and windows were broken at distances less than 300 m, parameter Q2 was given a rating of 1.
The overall "dangerous materials released" rating is thus 1.

Two parameters are involved in determining the level of the "Human and social consequences" rating: H4 and H5.
- Parameter H4 reached level 2; 2 employees hospitalised more than 24 h (H4 between2 and 5 seriously injured).
- Parameter H5 is rated 1, as 4 employees were injured during the accident (H5 between 1 and 5 injured).

As a result, the overall "Human and social consequences" rating is 2.

The €15 of the "economic consequences" rating is 3: the amount of property damage is estimated to be 14 MF, or roughly 2.13 M€ (€15 between 2 M€ and 10 M€).

## ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

A material assessment showed that the imide transfer rate into the reactor was 8 to 9 times greater than intended. In order to control the transfer rate, the operators modify the number of pump pulses using an adjustment screw and by manually configuring the two valves located upline. After the accident, the pump's configuration corresponded to high output and the valves were wide open.

Reactions involving the reduction of imides using borohydride in an ether-type solvent are unusual in industrial applications and such reactions are classified as dangerous by the INRS. Furthermore, the aluminium trichloride and the sodium borohydride can decompose in water, even in the trace state, by possibly forming hydrochloric acid or hydrogen. Finally, diboride can be formed when the reaction catches fire spontaneously in air at 25℃.

When the accident occurred, the runaway reaction caused a significant quantity of hydrogen to form which was not consumed by the reaction environment. The sudden ignition of the gas may have been caused by static electricity, a hot point or the possible presence of diboride and traces of water.

The instructions do not provide the settings to be made during transfer operations. The latter are based primarily on the operators' know-how.

The agents that work on the shift were qualified but the operator, the newest arrival to the crew, was conducting the imide transfer operation for the 1st time.

The unit functions discontinuously and it is controlled manually for the most part. Considering the specific dangers involved in the process, it is essential to use a sufficient number of reliable equipment to safely ensure and control the operation of the installations. These conditions were not fulfilled at the time of the accident:

- Two pumps of different power could be used for the transfer operations and a measurement device was not provided to monitor the flow rate.

- Safety devices were not available to alert the operators in case of a deviation in the operating parameters (significant flow rate, high pressure in the reactor...).

- The unit was not equipped with a remotely controlled valve to quickly isolate the reactors. The reactors cannot be drained rapidly; "neutralisation" of the reaction environment is impossible.

- The installation is made fragile by certain equipment made of glass.

## ACTIONS TAKEN

The Classified Installations Inspectorate requested that the operator submit a written request, accompanied with all supporting documents attesting to the complete verification of the installations (pressure, electricity...) prior to resuming operations in the other installations of the workshop, and contingent upon the ruling by the judicial authorities. The internal contingency plan and the danger study had to be completed as soon as possible.

The operator must:

- define improve:
  - ✓ procedures, by completing detailed sheets of all manufacturing processes and for all repetitive dangerous handling operations, for each of its agents,
  - ✓ internal training of its employees.

- install new equipment (displacement pumps, replacement of glass vessels, temperature, pressure and pH controls, high temperature alarm, remote monitoring of reactor operation, loading of powders, diagram on washing columns, column outlet detector).

A complete overhaul of the authorisation order is planned in order to spell out the installations' field of operation, to require safety documents to be drawn up for each of the processes, to integrate any specific characteristics associated with a given process, an installation or organisation, to request the establishment of intervention instructions when changes occur in a process and to study the possibility of containing gaseous releases.

## LESSONS LEARNED

The multipurpose industrial units operate discontinuously and are generally automated or only to a small extent. Most often, the accidents are the result of human error associated with design or organisational errors or insufficient instructions or operating procedures.

The standard equipment called into question (double walled reactors, fractionating towers, piping...) often include glass components.

The processes used are rarely subject to a detailed danger study. The unit's safety essentially relies on the operators' training and experience, as well as the quality of the instructions and operating methods.