Release of hydrochloric acid by the manhole of a benzoyl chloride tank

February 5th , 2002

Persan – [Val-d'Oise]

France

Hydrochloric acid

Discontinuance of business

Benzoyl chloride

Tank drainage

THE INSTALLATIONS IN QUESTION

The company and the administrative context:

The company mainly produces additives for oils, antioxidation and anti-UV agents and sucroglycerides.

For reasons associated with industrial competitiveness and production optimisation, the company, despite restructuring of its activities at Persan over several years, decided to shut down this site in the summer of 2001 and layoff its personnel.

This establishment had two activities associated with the use and storage of toxic and very toxic liquid substances exceeding the "AS" levels according to the nomenclature of the Classified Installations Inspectorate. It is governed by a Prefectoral order of April 2, 1997. Several Prefectoral orders complete the operating provisions, namely concerning the processing of soil and water table pollution discovered at the site.

As the establishment is governed by the Ministerial order of May 10, 2000 relative to the prevention of major accidents, the operator was required to submit a danger study prior to February 3, 2001 and set up a safety management system within the same deadline. As the deadline was not respected, official notification was issued for the company to comply with this obligation before July 2001.

In early summer 2001, after having announced the closure of the site and the complete shutdown of manufacturing operations, the operator reviewed its position and showed its desire to maintain an industrial potential at the site in order to facilitate its possible restart or, in the medium term, contemplate different production activities in its installations. In a difficult situation in terms of laying off its personnel, the operator was also securing the site and removing the stocked products and raw materials.

In October 2001, the Prefect of the Val d'Oise département requested that the company officially confirm that it was either discontinuing its business activity or continuing an industrial activity in Persan. Faced with uncertainly and the lack of clarity in the company's decision-making, the Classified Installations Inspectorate proposed an additional draft order to the Prefect of the Val d'Oise on January 30, 2002, designed to regulate the installations of the Company during the manufacturing shut-down period.

The prescribed measures foresaw provisions relative to the following points:

- ✓ The clean-up and securing of the installations including the organisational aspect;
- ✓ The dismantling of structures, equipment or buildings;
- ✓ The precautions relative to special risks (asbestos or radioactive sources);
- ✓ The management of a site rehabilitation program in relation with the soil and water table pollution;
- ✓ The operation of the utilities, the management of emergency response means and site guarding.

Finally, several incidents occurred in early 2001, the first caused by the untimely shut-down of a gas scrubber which resulted in the release of HCl into the atmosphere, the second resulting from maintenance/servicing on the computer management system of an industrial process which resulted in the release of xylene into the natural environment.

The installations concerned:

The benzoyl chloride was used in the manufacture of an anti-UV and benzophenone. Due to a process change, this product had not been used for several years. It was stocked in a 30 m3 tank (C-95) located along the organic synthesis workshop. At the time of the incident, the tank contained 11.7 tonnes of benzoyl chloride, that had been delivered May 21, 1999.

Benzoyl chloride is a corrosive product to which risk phrase R34 is applicable (causes burns). It is a colourless liquid and has a pungent odour. Its density is 1.2 and its flashpoint is 72°C. It is unstable in the air under the action of humidity. It reacts violently with water and numerous components such as alcohol.

THE ACCIDENT, ITS BEHAVIOUR AND CONSEQUENCES

The accident:

Following the shut-down of production at the Persan site, GLCF began draining and cleaning the storage tanks. A few days earlier, the operator was unable to drain tank C95 due to solid benzoic acid deposits which most likely formed due to the slow decomposition of the product. The operator decided to disintegrate the deposits by adding solvent. Laboratory tests were conducted with methanol without detecting any abnormal reactions.

Following tests, tank draining operations were begun on February 5, 2002 at around 9.30 am. The operation, conducted by a technician from the company, and assisted by a fireman from an external company, consists of pumping 2 m3 of methanol into the tank then, circulating the product designed to homogenise the mixture, and then finally transferring the mixture into a tanker truck for subsequent destruction.

Having noted that the transfer pump was malfunctioning, the GLCF technician stopped the operation and began spraying down the tank with the sprinkler system. The personnel noted a small explosion, probably due to excess pressure in the tank, and a cloud of acid gas was released through the faulty flange seal on the upper dome of the tank.

The personnel attempted to bring down the cloud by setting up a water curtain and spraying down the tank.

The Consequences:

According to the testimonies gathered, an opaque cloud in the form of a "fluffy mist" was observed on the site and was moving towards the homes located approximately 150 m from the tank concerned. Residents complained of a prickly sensation in their eyes. An elderly person was effected and transported to the hospital for an examination and stayed a day under observation.

The phenomena lasted a few minutes. The cloud of acid gas coming from the tank moved by bursts in the direction of the wind although its dispersion was hindered by the presence of buildings next to the storage facility. There were no harmful consequences to the river which flows through the plant.

European scale of industrial accidents

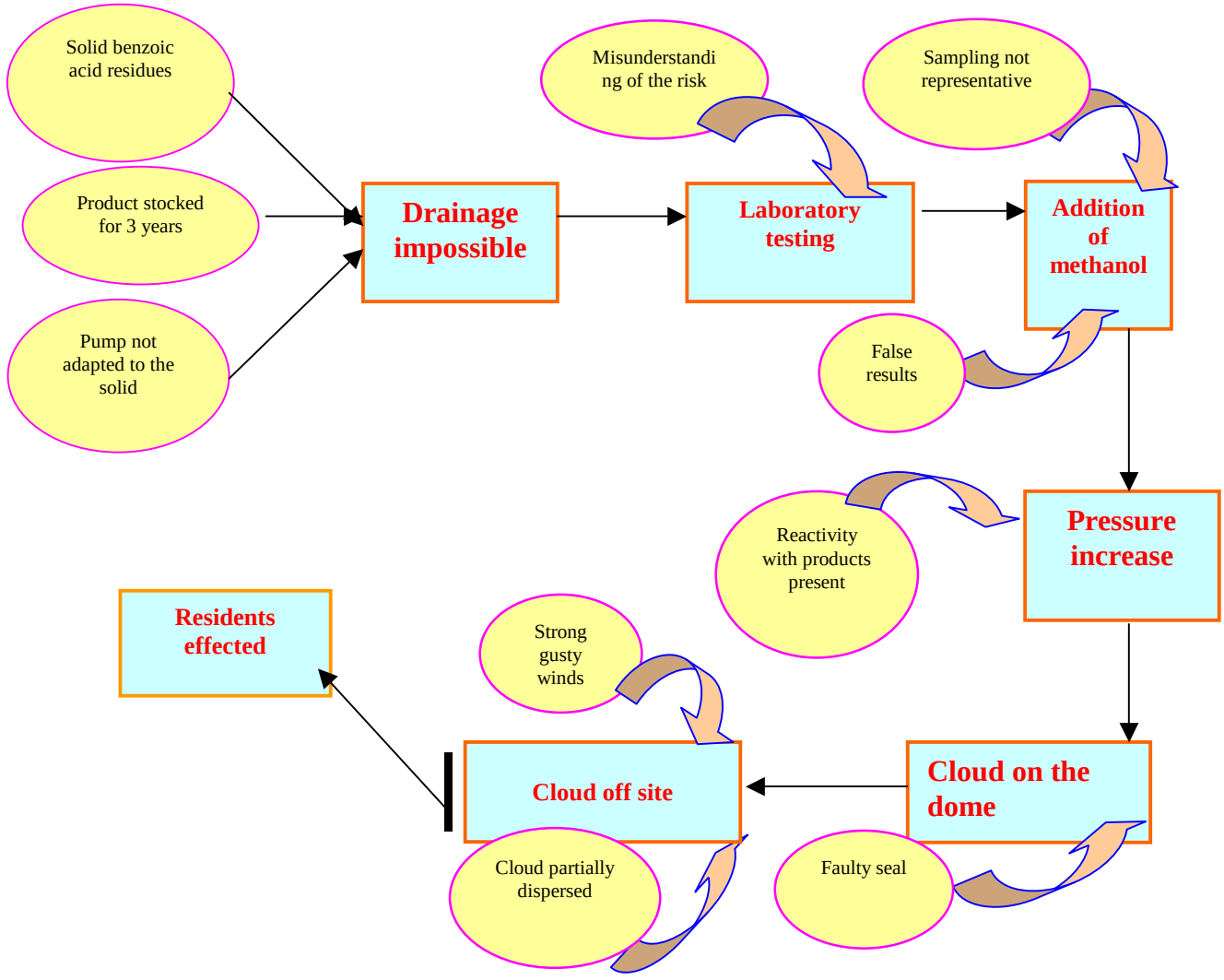
By applying the rating rules of the 18 parameters of the scale made official in February 1994 by the Committee of Competent Authorities of the Member States which oversees the application of the 'SEVESO' directive, the accident can be characterised by the following 4 indices, based on the information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

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

According to the estimates, 90 kg of hydrogen chloride were released during the reaction, i.e. 0.036% of the Seveso threshold (250 t). The "dangerous materials released" index of the industrial accidents scale is thus 1 (parameter Q1).
As an individual of the general public was slightly injured (hospitalisation less than 24 hours), the "human and social consequences" index is rated 2 (parameter H5).

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

Benzoyl chloride (C6H5-COCl) is a highly reactive acyl halide. Its hydrolysis is very exothermic and leads to benzoic acid (C6H5-COOH) with the formation of hydrochloric acid (HCl). A reaction also occurs with alcohols and leads to an ester and the release of HCl.
New tests conducted after the accident showed reactivity of the benzoic acid/methanol mix at temperatures above 30°C. The laboratory tests conducted by the company were thus not representative.
At the time of the accident, adding methanol (CH3-OH) to tank C95 thus caused a significant release of HCl (estimated at 90 kg, or 55 m3 of hydrochloric acid for 100 litres of methanol introduced into the tank and supposing that a complete reaction occurred). The reaction was accompanied by a heating up of the mixture.



ACTION TAKEN

Technical actions:

After plugging the leak on the seal, no release was visible on the tank the evening following the accident. The reaction was completed and the system returned to a stable state. At the request of the Registered Installations Inspectorate, the installations were monitored and a senior executive was placed on standby for the night and following days. A tarp was installed on top of the tank to protect it from the rain.

The Registered Installations Inspectorate requested that the operator prepare a technical file (upheld by an emergency prefectoral order) describing the security measures and precautions to be taken relative to the safety of the operations and the maintenance and back-up means needed to perform them. Prior to all further work, a new tank drainage procedure was compiled; this procedure was to be examined by a third-party expert.
The total drainage of the tank took place from the 22nd to the 30th of April, 2002, after the procedure used was approved by a third-party expert. The solvent used was xylene.

Administrative and penal actions:

Following this event, on February 13, 2002, the Prefect of the Val d'Oise established an order implementing article L 512-7 of the Environmental Code in order to prescribe the operator provisions concerning the installation clean-up and securing, their dismantling and the organisation of safety measures to prevent similar events from reoccurring given the existence of dangerous material storage facilities at the site. This order notably required the company to prepare and

submit procedures prior to draining the benzoyl chloride tank and a second tank containing aluminium chloride; a critical examination of these procedures was to be undertaken by a third-party expert.
The classified Installations Inspectorate requested that the operator also submit an accident report. Event analysis and the on site investigations showed the presence of the following anomalies:

DESIGNATION	*ANOMALIES REPORTED*
Accident declaration	• The accident was not declared to the Classified Installations Inspectorate
Safety organisation	• No senior executive at the site and failure in the management of the organisational and decision-making chain in terms of safety, • The internal contingency plan initiated too late • Lack of operator organisation in the management of events immediately following the accident
Management of benzoyl chloride storage	• Long term storage of the product – Unchecked and unused since 1999 • Corrosion on the outside wall of the tank • Tank high level disconnected in the control room • Poor condition of the seal on the manhole flange
Misunderstanding of the dangers associated with drainage	• Implementation of a drainage procedure resulting in risks of the personnel and the environment owing to insufficient prior analysis bearing mainly on the incompatibility of the substances used and an evaluation of the consequences of such action. • No danger labels on the methanol container.
Condition of firefighting means	• Poor condition of the site's firefighting hoses • Certain Dräger lines for searching for HCl were expired since July 1998.

Non-conformities were noted relative to the technical provisions required of the operator. An inquiry was conducted by the judiciary police at the request of the public prosecutor's office of Pontoise.

LESSONS LEARNED

Unused products must be removed in a reasonable time in order to avoid new risks (product deterioration, equipment condition, loss of information).

Special vigilance must be maintained during work performed following the shutdown of manufacturing operations or the dismantling of installations, notably in facilities at risk in which dangerous materials are used. In a similar context, the operator must provide an unambiguous statement relative to its intention to discontinue its business activities or continue operations.

This accident illustrates the importance of the internal contingency plan and the need to implement an operational organisation should an accident occur. The operator must have thorough knowledge of this document and the previously assigned roles of the persons concerned.