Toxic vapour (HCl) emissions due to overflow of a proportioner in a chemical plant

16th October, 1991

Chalon-sur-Saône (Saône-et-Loire) France

Fine chemistry (batch)
Management of change
Installation design
Procedures
Automated mechanisms
Risk mitigation measures (bypass)
Organisation / anomaly description

THE FACILITIES INVOLVED

The site:

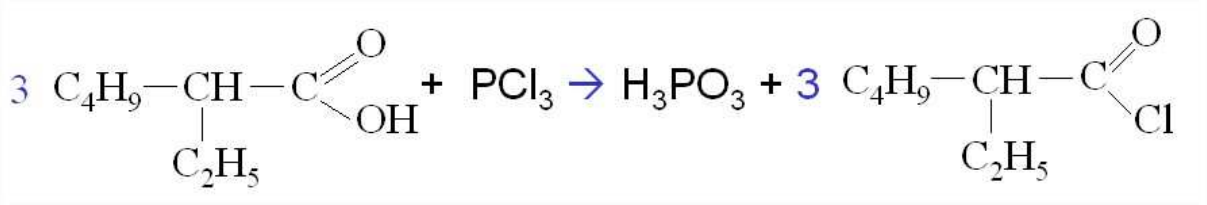
The plant, which was employing a staff of 28, was located in an industrial zone 1,500 m south-east of the city centre. It was manufacturing liquid organic peroxides, either by means of direct action of hydrogen peroxide on an acid chloride or else via tert-butyl hydroperoxide (T.B.H.P.).

The facility, which had to submit operating permit applications, was as of 1st June, 1991 required to comply with the Seveso I Directive for peroxide storage. As such, this plant was ordered to furnish a safety report and an internal operation plan by 31st December, 1993.

The nearest residences were located 200 m east of the site.

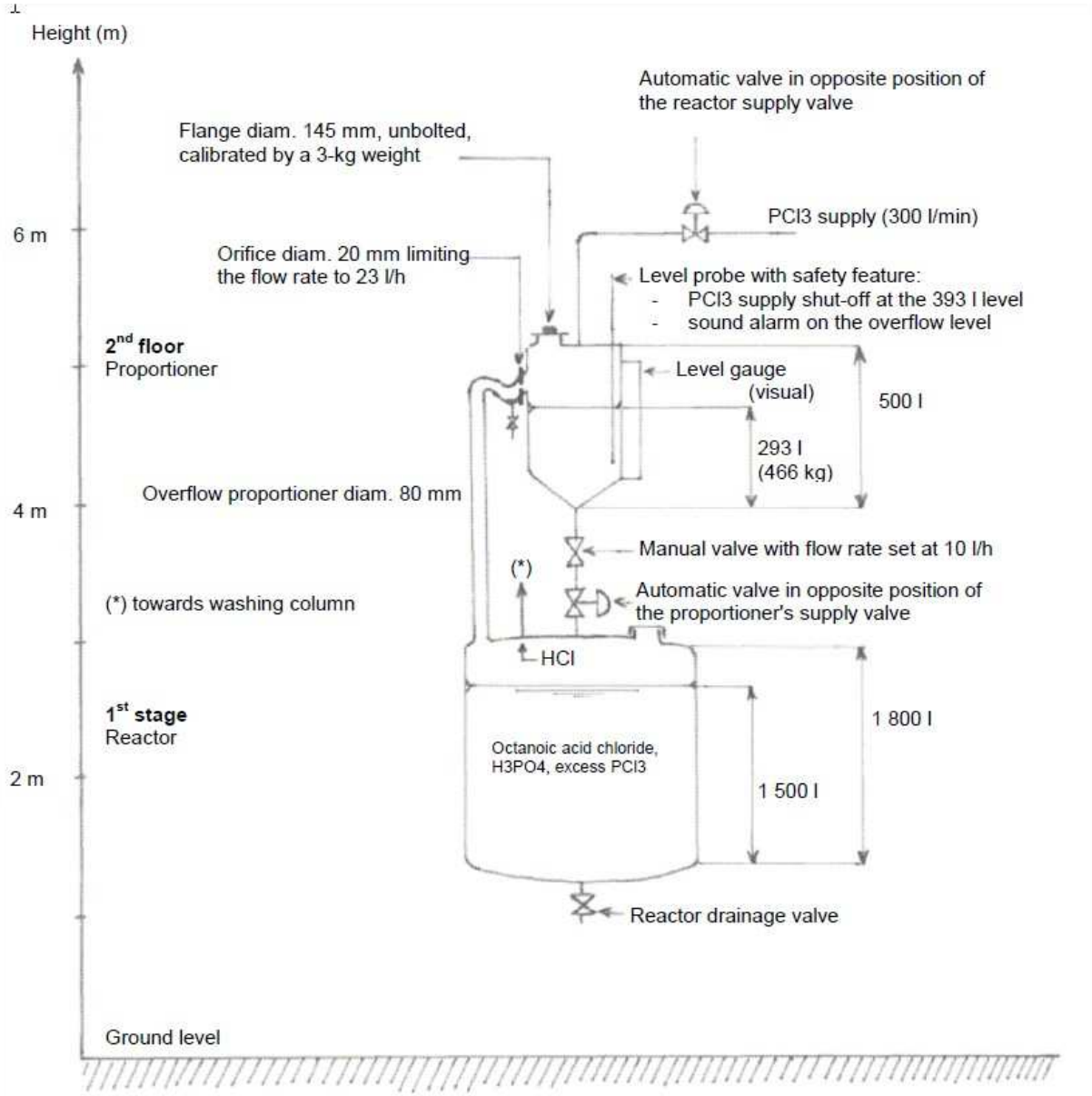
The specific unit involved:

The workshop, which had been operating for 25 years, comprised 2 octanoic acid chloride production chains running in parallel. The chemical reaction being implemented was practically athermal, i.e.:



The acid, which needed to gradually reach a temperature of 50°C, was introduced into a reactor the day prior. The next day, 466 kg of phosphorus trichloride (PCl_3) were added through a proportioner. The gravity-induced flow took 30 to 40 minutes without requiring any stirring; all of the acid was able to react within 5 hours at 60°C. Once the reaction was complete, the reaction mixture was cooled at 25°C until the following day. The phosphoric acid and acid chloride produced were separated by gravity when draining the reactor. Both these products were then prepared for sale.

Placed above the reactor (see schematic diagram on p. 2), the proportioner was connected by a pipe and pump to a 22-m^3 storage zone located 20 m outside from the workshop. This pump was activated for PCl_3 transfer to the production chains as well as all transfer operations for cisterns supplying the site's storage facilities. Hence, the maximum pump flow rate (300 l/min), designed to accommodate these transfers, was too high compared to both the proportioner's actual capacity (500 l) and the quantity needed to be introduced per batch (293 l, i.e. less than 1 minute of transfer).



Schematic diagram of the site installation

THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident:

The accident occurred upon restarting a portion of the installations after a 4-month plant shutdown and a series of many blank tests.

A well-experienced technician started his shift at 7 am. From the installation's pneumatic control console, he activated the PCl_3 pump in order to fill the proportioner on the 1st chain. He proceeded by verifying the level (using a glass tube and mirror), stopped the pump and then adjusted the chloride flow rate into the reactor (which had been prepared since the day before, in accordance with current procedure). He had returned to the plant's ground floor to prepare to drain the reactor on the 2nd chain, whose synthesis operation had been completed, when he was sprayed by PCl_3 (at around 7:10 am) that had overflowed from the proportioner subsequent to an unscheduled restart of the PCl_3 transfer pump.

The technician immediately left the building to activate, from the outside, the pump emergency shutoff button. A second technician verified that the pump had been stopped and removed the fuses from the pump's electrical control circuit to ensure that the pump had been turned off definitively.

The maintenance electrician, who was also a member of the site's emergency intervention team, wore the emergency gear and, equipped with a rope, entered the workshop filled with white acid (HCl) fumes to secure the facility by closing all manual and automatic valves on both installations.

PCl_3 had spread into the plant and then into the sewer system. Given the lack of a specific written protocol in the event of accident, it was decided to flood the sewer lines using fire nozzles, but this step wound up exacerbating the phenomenon of phosphorus trichloride hydrolysis. The ensuing toxic cloud, composed primarily of hydrochloric acid, headed towards the city centre due to unfavourable meteorological conditions in the presence of fog.

Local fire-fighters, who had received many emergency calls, provided treatment to the first intoxicated victims around 7:40 am. They telephoned 3 industries located in the zone likely to be the source of this toxic pollution; the plant operator confirmed incident occurrence at 8 am. Formation of an emergency unit was initiated and fire crews performed an analysis of the atmospheric pollutants emitted. Wind had dissipated the gaseous cloud within an hour. The local Prefecture issued a press release, and the city of Chalon requested its residents to contact a physician or the SAMU emergency medical services in cases of breathing difficulties, eye irritation, etc.

Consequences of this accident:

The effects of this accident were observed over a radius extending 1,500 m from the point of emission. The 2 employees exposed were hospitalised for observation and 17 individuals from outside the plant contacted emergency services; 11 of them were admitted to the emergency room for testing, and all were released a few hours later.

pH recordings at the site outlet revealed a significant drop in pH (pH = 3) between 7:30 and 8:30 am, yet no fish mortality could be detected.

CHALON

UN NUAGE TOXIQUE SURVOLE LA VILLE

La gorge irritée malgré un mouchoir sur la bouche et les yeux embués de larmes, il était impossible hier matin de ne pas ressentir les effets de l'émanation d'un produit toxique dans l'air ambiant.

CHALON — Une grande partie de la population chalonnaise était surprise pour la première fois de son histoire à une pollution industrielle de grande ampleur. Et si elle ne s'est pas à la panique, il n'en demeure pas moins qu'un grand nombre de chalonnais inquiets sont complètement le nez rivé à l'appel des sapeurs pompiers. Dans sapeurs pompiers ont gênés pour répondre à leurs questions. Et pour une raison simple : ils n'en savaient pas eux-mêmes plus qu'eux.

Les premiers symptômes se manifestent à 7 heures 40. Les personnes se rendant à leur travail, à la boulangerie ou au bureau de tabac, les lycéens gagnant leurs établissements sont étonnés par la manifestation de signes anormaux : Les yeux piquent et rougissent, la gorge est irritée et douloureuse et ils toussent. Pour y échapper, un seul moyen placer un mouchoir devant la bouche. Que se passe-t-il ? Personne n'échappe à ces désagréments et tout le monde s'interpelle. Les soldats du feu dépêchent dans plusieurs quartiers de la ville des véhicules de reconnaissance mais sans résultat. Il semble pourtant que le centre ville et la cité des Prés-Saint-Jean soient plus touchés par le phénomène. Le commandant Mariot (ci-contre) alors l'initiative d'appeler les entreprises industrielles pour connaître l'origine de cette pollution. C'est ainsi qu'il apprend qu'un accident est survenu à l'intérieur de la société Chalonnaise de Peroxydes Organiques situé au sein de la Chemaxal (ex Air-Liquide) implantée en zone industrielle sud.

M. Horn (debout) et autres dirigeants de la société

Débordement

7 heures 10. Un opérateur est chargé d'une opération de remplissage. Il doit déverser le contenu d'un « pulgeur » dans un réacteur. Soudain, sans qu'on n'en sache à l'heure actuelle la raison, le produit chimique, du trichlorure de phosphore, déborde du « pulgeur » et s'échappe à l'extérieur. Le contact avec l'air et surtout l'humidité résiduelle le produit à l'état liquide se transforme en gaz chlorydrique et se mêle à l'atmosphère. Par manque de chance les conditions réunies pour amplifier cette pollution sont réunies : un plafond bas, l'absence de vent et la présence de brouillard. Et quelques minutes plus tard, le nuage toxique se forme au dessus de la ville avec les conséquences que l'on sait.

Selon le docteur de l'usine, M. Horn l'opérateur s'aperçut rapidement du déversement puisque trois minutes s'écoulent entre l'accident et la fermeture de la vanne avec l'aide d'un autre ouvrier. Tous deux furent transportés au centre hospitalier et sont toujours gardés en observation. Leur état n'est cependant pas jugé grave. Il estime que deux à trois cents kilos de trichlorure de phosphore se sont déversés, chiffre qu'il évalue en fonction du temps et du débit de la pompe. On a beaucoup de difficultés à comprendre pourquoi, l'accident ne fut pas signalé aussitôt auprès des sapeurs pompiers qui auraient alors pris les mesures adéquates et renseigner la population des dangers encourus. L'explication, c'est M. Pélissier qui le tourne : « Ils ont perdu

Une vue de Chemaxal

qu'il s'agissait d'un problème interne à l'entreprise et qu'il n'y aurait pas d'incidences à l'extérieur ». Les événements leur donnèrent tort.

La Chemaxal et par extension la société chalonnaise de peroxydes organiques dès la signature dans quelques semaines de l'arrêté préfectoral devra se soumettre aux directives de Seveso qui exigent notamment de rédiger aux autorités tous les incidents se produisant dans l'entreprise. Dans un cas comme celui-ci, le plan particulier d'intervention serait alors appliqué.

En attendant, la Direction Régionale de la Recherche et de l'Industrie a entrepris une enquête sur place qui se poursuivra dans les jours prochains pour définir les causes de cet accident.

Cellule de crise

A partir de 8 heures 30, une cellule de crise est mise en place à la Caserne Foyot. MM. Grévet, Alexandre élus locaux y participent en compagnie de M. Dugourd, chef de cabinet du maire, le docteur Chavagnac, le commandant Mariot et M. Horn et deux de ses collaborateurs. « Il était trop tard pour employer le système CAMEO confié le commandant Mariot. D'ailleurs en dehors de nos reconnaissances, nous ne sommes pas intervenus. A 9 heures, le nuage s'est dispersé » Pourtant au cours d'une conférence de presse à laquelle assistèrent notamment MM. Pélissier sous-préfet et M. Pierre Arnaud, PDG de la société chalonnaise de péroxydes organiques, le docteur Chavagnac explique que dix neuf personnes intoxiquées s'étaient présentées au centre hospitalier pour y recevoir des soins dont treize furent admises au service d'urgence avant de regagner leur domicile. Sous les deux employés grave gardés en observation.

Ces chiffres n'entendant pas les patients ayant consulté leur médecin de famille.

La principale préoccupation de la cellule de crise et on le comprend fut de s'informer sur les dangers relatifs à ce produit. Un produit qui n'aurait pas à lui seul incité la préfecture à la classer cette société en entreprise à hauts risques.

Patrick RONGET

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.

In the presence of water (even simply through airborne humidity), approximately 489 l of hydrochloric gas were formed per kg of PCl_3. According to operator estimations, 267 litres would have overflowed into the plant, i.e. 530 kg, which in turn generated a hydrochloric acid volume of nearly 260 m^3. The hazardous substances released index therefore reached a level "3" (parameter Q1 equal to 2.6% of the Seveso tier for PCl_3).

The human and social consequences index was scored a "3", given that 2 employees and 11 members of the public had been slightly intoxicated.

Since no environmental consequences directly corresponding to the scale parameters had been reported, this index was set equal to "0".

Given the lack of information available on the amounts of eventual property damage or production losses, the economic consequences index could not be rated.

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THIS ACCIDENT

The investigation revealed a whole set of deficiencies, relative to both physical and organisational aspects:

Installation design

- Work station ergonomics were not well adapted. More specifically, the liquid level was difficult to distinguish inside the proportioner (requiring use of a mirror), and the control cabinet was not visible from the lower part of the installations.
- An (overly) complicated control circuit included many time lags capable of generating interactions. The only pump used for the PCl_3 transfers was being controlled by a set of switches distributed at 4 different points, none of which were mutually visible.
- The maximum pump flow rate (300 l/min) was too high compared to the proportioner's actual capacity (500 l) and the quantity to be introduced per batch (293 l, i.e. less than 1 minute of transfer!), thus forcing the technician to hurry to turn off PCl_3 supply prior to triggering the high level alarm.
- Due to the excessive PCl_3 supply flow rate (see above point), monitoring of the PCl_3 quantity introduced into the proportioner was too imprecise and the installation regularly switched into security mode. To avoid this phenomenon, the safety function was bypassed by altering the prescribed point to "end pump filling".
- Despite the presence of a highly corrosive atmosphere, the relay cabinet was not sealed. The control circuit copper pipes were covered with salt deposits, which increased the risk of property degradation.
- The installations using PCl_3 were not adequately confined. A manhole on the proportioner was blocked by an unfastened flange despite the indicated design locations. The PCl_3 that spread wound up reaching the sewer network via a low point sump in the building (inside a plant without retention).

Maintenance / repair phases

- Both safety mechanisms associated with the proportioner's level probe were malfunctioning, the first shunted following a series of repeated activations (see point under "Installation design" above), while the second (which was a malfunctioning or inaudible "proportioner high level" sound alarm) was never repaired.
- An orifice, used to limit the proportioner supply flow rate at the source to 50 l/min and provide the time necessary for the technician to handle reagent loading, had disappeared several years prior for no apparent reason. Moreover, an orifice in the tank's overflow duct reduced, again for no apparent reason, its diameter from 80 to 20 mm. The overflow discharge rate was thus limited to 23 l/min, a value much lower than the pump flow rate, which as a result prevented the overflow from performing with an activated safety function. The

operator explained these modifications by an eventual assembly error committed during maintenance. Such modifications did not appear on the installation drawings and were seemingly unfamiliar to the site's technical staff.

- A detected air leak the day prior on the pneumatic control circuit had not been repaired before restarting the unit. A temporary modification was provided instead on one of the installation's control boxes. A "fill" pushbutton and its cell, which were out of stock, had been replaced on a "floating installation" by a dial with a different operating mode. This modification, performed without updating the operating guidelines and without analysis of its potential impact on safety, led to circumventing 2 successive "AND" gates on the automaton.

Organisation / Protocol / Supervision

- The operating plans and protocols were not systematically updated, especially when introducing modifications.
- No modification management procedure had been formalised for the preparation, monitoring or verification of equipment modifications.
- The protocols did not outline appropriate conduct in the event of a degraded situation, such as the spreading of a hazardous product like PCl_3. The water used during the emergency intervention had, as a consequence, magnified the size of the toxic cloud.
- Apparently, the hierarchy remained unaware of many plant malfunctions. Such was the case with the orifice modifications, as well as the alteration of recommended operating points and improper functioning of the sound alarm.
- A similar incident (unscheduled pump restart) had previously occurred at the same site a few years prior during a transfer step, though without seeming to initiate any special remedial actions of modifying the installations or their operating system (due to the lack of exploitation of experience feedback).

ACTIONS TAKEN

The site operator decided to discontinue this production line.

LESSONS LEARNT

The accident arose on an older installation subsequent to several modifications performed without adequate information provided to users or management. Moreover, many human errors were committed, some of which made possible due to poor ergonomics designed into the installations and their control systems.

Given the remarks delivered regarding the pneumatic control devices (circuit complexity, reliability of certain components, location of the control cabinets, etc.), special attention must be paid to the following:

- consequences stemming from the eventual pollution of the air control and command circuits;
- the risks of malfunction in a corrosive atmosphere among certain devices that may not be sufficiently protected (in particular the pneumatic cells);
- stable vs. unstable states of the automated mechanisms, in order to take into account time lags or the eventual effects of a simultaneous action on several switches. In the present case, the operator had noted that a transfer pump restart after shut-off was capable of occurring when 2 technicians intervened simultaneously;
- ageing of certain components (e.g. cells) that may cause malfunctions capable of compromising installation safety.

This accident highlights, in addition to the importance of an effective installation design (pumps with capacities different for the storage and plant supplies, buildings under retention, control system ergonomics, etc.) and their maintenance over time, the need for strict organisation with oversight of actual applications and a strong involvement from facility executives (safety management system subject to executive review, internal emergency plan, change management procedures, protocols, etc.). In fact, the anomaly observed by the technician necessitating, subsequent to onsite works, running to a location where he could shut off the pump in time should have been targeted for further analysis (as a precursor). Similarly, the repair works should have been officially accepted and inspected, a step that would have allowed noticing the poor orifice assembly.