Fine chemistry
Enamelled reactor
Dichloromethane
Hydrogen
Corrosion
Static electricity
Blow-out disc
Design / Dimensioning

# Blast in a reactor on a fine chemicals site

## September 3, 2002

## Marans – [Charente-Maritime]
## France

## THE INSTALLATIONS IN QUESTION

### The site

The establishment, located in Marans, in the Charente Maritime département, was created in 1959 to manufacture medical imagery products – and fine chemistry specialty products (iodine based chemistry). In 2002, it had 90 salaried employees and reported turnover of 16 million Euros, distributed among two main activities:

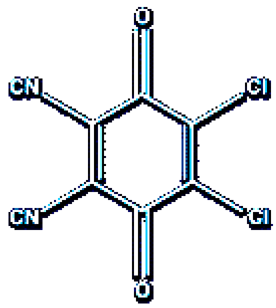
- ✓ 60% for group products, medical imagery,
- ✓ 40% for custom-made chemical specialty products.

The site operates various reactors with enamelled walls, with capacities ranging from 50 litres to 6.3 m3.

This establishment is an installation subject to authorisation. it is classed as low level "SEVESO" for the products that it uses. The last prefectoral order authorising the establishment to operate dates back to February 20, 1990.

### The unit concerned:

The plant's manufacturing unit No. 1 is regularly used to produce 2,3 DICHLORO 5,6 DICYANO BENZOIQUINONE (D.D.Q.). This product is most commonly manufactured by the company and used in the field of medical imagery (MRI): the selective reduction of this product allows certain ailments to be detected (cancers).




The reduced form (DDQH) may also be regenerated by oxidation at low pressure (2 bar) in a reactor with enamelled walls: the DDQH is put in solution with nitric acid, gaseous oxygen and a solvent, dichloromethane ($CH_2Cl_2$). The reaction temperature is between 20 and 32°C. The DDQ produced is then dried and packaged.

The accident occurred during the regeneration reaction in a 1,500 l reactor. It also involved the transfer line after the blow-out disc and the upline crash tank. Prior to the accident, the operator had performed more than 200 regeneration cycles without any particular difficulty.

## THE ACCIDENT, ITS BEHAVIOUR, EFFECTS AND CONSEQUENCES

### The accident:

**On September 3, 2002 at 9 pm**, the hydrogenated DDQ (DDQH) regeneration reaction was launched in the enamelled reactor.

**At 9.30 pm**, the mixture displayed abnormal behaviour: the operators were required to degas twice in order to mitigate the increases in pressure in the reactor.

**At 9.55 pm**, the reactor slowly began to increase in pressure, an operator was ready to degas. While his hand was on the vent control valve, a blast occurred in the reactor and in the associated crash tank via the vent pipes and valves.

A second operator at the scene evacuated his co-worker and sounded the alarm. The site was secured after the firemen and standby crews arrived. The alert was lifted at **11 pm**. The neutralisation of the process began at **00.30 am** by slowly pouring in diluted hydrochloric acid, and was completed at **1.30 am.**

## The consequences:

The first operator suffered superficial burns to this forearms, a nose injury, enamel fragments in the hands, eye irritation and a sore eardrum.

In terms of equipment damage, at the building level:

- ✓ Twenty square meters of the ceiling were blown out, mainly on the span of clear sheeting (the sheeting was folded although it remained in place),
- ✓ The siding on the upper part of the building, to the west and to the north, was blown out over 5 m with partial tearing away of the sheeting,
- ✓ Traces of product projection was visible on the northern part of the wall, up to heights of 2 m,
- ✓ Impact holes (possibly due to pieces of PVDF) were observed on the clear siding.

At the level of the crash tank zone, located outside the building:

- ✓ The crash tank's plastic cover was completely ripped away, as well as all of the connecting pipework,
- ✓ 30 cm of liquid is present in the tank,
- ✓ A piece of broken plastic was projected through a window in the administrative office.

At the reactor level:

- ✓ Several gaskets exited their seats (manhole, cover and vent outlet), and their metal reinforcements are were partially torn,
- ✓ Yellow traces indicate that product exited by the cover gaskets and manhole,
- ✓ A change in appearance of the PVDF piping and the valve was noted,
- ✓ Numerous enamel fragments were present on the reactor and in its immediate proximity
- ✓ The lower part of the metallic protection of the mixing shaft is caved in.

On the outside of the site,

- ✓ A flange weighing approximately 1.2 kg was found by a neighbouring resident 70 m from the building in question,
- ✓ Several other elements of the installation (PVDF valve, crash tank cover…) were found at different locations around the site (other workshop, administrative building…)

The blast effect was limited to the immediate vicinity of the building, although the explosion was heard up to 300 m away. Projections of DDQ were observed in the immediate environment of the building and in the establishment. Local residents reported neither a cloud (although it was night time), or deposits of DDQ.

## 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

As the effects of the explosion had not been characterised and windows were broken at distances less than 330 m, parameter Q2 (explosive substances) was given a rating of 1.

The "human and social consequences" index is 1 as the accident resulted in an operator being slightly injured (parameter H5).

In addition, the lack of precise quantified data does not allow the "economic consequences" index to be completed.

## ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

Various investigations were conducted on the products and the process in order to determine the causes of the accident. All of the checks made on the materials used for the synthesis showed no sign of anomaly. Laboratory tests in similar conditions showed no particular instability or abnormal reaction behaviour.

Searches conducted after the accident proved that the blast concerned only the gaseous phase of the reaction environment. The gaseous phase was significantly oxygen-enriched in relation to the habitual mixture owing to the successive degassing operations conducted by the operator to control the increase in pressure.

This research did not provide formal proof as to the exact origin of the phenomenon that initiated the blast. The most probable hypotheses are as follows:

The combustion of the dichloromethane ($CH_2Cl_2$) / oxygen ($O_2$) pair was initiated by an electrostatic discharge. A static electricity initiation point was observed on a Teflon-coated valve located on a tube of the cover that may have acted as an insulated conductor.

The self-detonation of an oxygen (O2) / hydrogen (H2) mixture, the hydrogen being produced by the acid corrosion of an unprotected metal surface. A corrosion spot was observed at the top of the mixing shaft. This defect on the coating of the enamelled surface of the reactor's mixing shaft happened when the mixer was being installed after inspection, an impact to which the operators did not pay any attention. As such, a gaseous mixture of dichloromethane and oxygen, sufficiently enriched with hydrogen in order to be self-detonating, may have formed in a recess of the reactor, created by the tube. The results of the tests, the extent of the damage associated with the blast and the observation of an enamel corrosion spot, backs the hypothesis of hydrogen being present in the environment.

In addition, it should be noted that if the rupture valves and discs had functions as intended, they were not designed for such a blast; the same is true for the transfer pipes leading toward the crash tank.

## ACTION TAKEN

The operator suspended this manufacturing process pending the results of the various expert evaluations conducted. It was then decided that the process be abandoned all together. Studies were conducted to find alternative solutions to this process.

## LESSONS LEARNED

A process, even very often implemented, may still be at the origin of the accidents.

Further to post-accident investigations, the operator determined that a process conducted in a gaseous oxygen and $CH_2Cl_2$ solvent environment required that the following conditions be controlled:

- ✓ Do not reach the explosive limits of the solvent/$O_2$ mixture in the gaseous phase,
- ✓ Guarantee the strict absence of hydrogen resulting from acid corrosion of a metal surface in the reactor's gaseous phase,
- ✓ Control all risk of static electricity discharge in the reactor, particularly at the gaseous phase level,
- ✓ Avoid all possibility of nitration of the sealing fluid (alcohol or glycol) in the mixing system's seal packing.

The enamelled walls are very efficient in terms of corrosion protection, but they are also very fragile: they are sensitive to mechanical and thermal shocks. The process evaluation studies must consider the risk of damage to the protection of these walls and regular inspections must be conducted (by analysing with high voltage current, for example).

Finally, the dimensioning of the protection accessories of the reactors and the associated pipework must be adapted. In this manner, the rupture disc / safety valve assemblies must be designed and dimensioned to also take the pressure increase dynamics into account, primarily during thermal runaway or the formation of significant quantities of gaseous sub-products. It is also recommended to take into account the risks of vesicular entrainment or condensation in the connections equipped with safety devices of this type (see "Les recommandations de la chimie fine" (*Recommendations in the field of fine chemistry*) by the UIC, available on the internet site www.aria.environnement.gouv.fr).