

## Explosion in a chemical reactor

January 29, 2002

Calais – [Pas-de-Calais]

France

Fine chemistry  
Catalyst  
Methanol  
Washdown  
Nitrogen inerting  
Organisation

### THE INSTALLATIONS IN QUESTION

#### The site:

Involved in the fine chemistry industry, the company operates 8 shops specialising in the synthesis of intermediate products for the pharmaceutical industry. It was created in 1976 and employs 125 people. The site (covering approximately 7 ha) is located to the northeast of the city of Calais, in the Dunes industrial estate, and to the south of the Hoverport terminal.

The establishment is subject to the "Seveso II" directive: it was declared "High Level" Seveso in application of the additivity rule of the substances. Its last Prefectoral authorisation order is dated April 22, 1998.

The site has a production capacity of 140 m3 for reagent ranging from 1,500 to 8,000 litres. Annual production is in the order of 1,200 tons.

#### The unit concerned:

The reactor (R404) involved in the accident is located in shop U01, to the southeast of the plant. With a capacity of 2,800 l, it was new and in service less than one month.

### THE ACCIDENT, ITS BEHAVIOUR AND CONSEQUENCES

#### The accident:



**On January 27th at 1 pm**, a hydrogenation operation was completed in reactor R404 (this manufacturing formula is relatively infrequent, even rare, as the last series was performed more than 6 years ago). Six washdown operations with water were conducted to eliminate traces of reaction catalyst (Palladium) as well as two hot methanol stripping operations (30°C) to eliminate traces of organic compounds still contaminating the reactor.

**On January 28 at 2.40 pm**, reactor R404 was allowed to drain. **At 9 pm**, it was heated empty to 80°C for a period of 8 hours.

**On January 29 at 5 am**, the operator, before leaving his work station, shut down the heating, re-established the pressure with nitrogen and opened the air vent to allow the reactor to cool down naturally.

On January 29 at 10 am, the foreman cooled reactor R404 for its subsequent examination. An hour later, the foreman noted that the inside of the reactor was "a bit tarnished and a bit humid with a residual trace on the bottom". At 5 pm, following this assessment, the shop supervisor requested that the reactor be washed again. Analyses of the methanol wash solution confirmed that the previous washdowns were inefficient: synthetic and intermediate product was detected.

On January 29, 2002 at 6.45, an explosion occurred on R404 during the additional washdown operation that was requested during the day. A manhole had been opened to conduct the requested rinsing operation.



**The consequences:**

An operator was found lying next to reactor R404, and his face seriously burned.

The reactor and the related installations showed no signs of visible damage. The reactor's gasket had been ejected a few metres away. The reactor was immediately closed and injected with nitrogen.

**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.

Dangerous materials released		<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Human and social consequences		<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Environmental consequences		<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Economic consequences		<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

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 although the distances at which windows were broken was less than 330 m, parameter Q2 (explosive substances) was given a rating of 1.

The accident seriously injured an operator. The "human and social consequences" index was thus 1 (parameter H4).

**ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT**

The origin of the accident was most certainly due to the sudden combustion of an explosive gaseous mixture inside the reactor.

Following what appears to be a poorly executed drying operation, traces of methanol were still present in the reactor. While evaporating, these traces lead to a concentration of vapour consistent with the explosion. Confirmed by post-accident measurements, the nitrogen bubble output only partially fulfilled its role and did not prevent oxygen from entering the reactor when the manhole was opened.

The last reaction that took place in the reactor was a hydrogenation reaction involving a Palladium catalyst, which is a substance that spontaneously ignites in contact with the oxygen in the air when it is dry. The presence of traces of this catalyst in the reactor is suspected, particularly around the reactor seal.

The combination of these 3 elements (Combustible – Oxidant - Energy) lead to the explosion.



## ACTION TAKEN

Prior to the re-start of the unit, the Registered Installations Inspection requested the following:

- ✓ Identification of the accident's exact causes and circumstances,
- ✓ The determination of the measures to be taken to prevent such an event from happening again,
- ✓ The verification of the integrity of the installations by repeating a reactor hydraulic test.

## LESSONS LEARNED

Locally, the operator took the following measures to prevent an accident of this type from reoccurring:

- ✓ Implementation of a specific washdown procedure of the gasket specific to reactor R404,
- ✓ Modification of the nitrogen system, with increased output for the manhole opening and a nitrogen presence indicator,
- ✓ New written instructions and procedures displayed at the workstation,
- ✓ End of sequence by use of distilled water to clean the reactors following a reaction implementing a pyrophoric catalyser,
- ✓ A new awareness campaign among the personnel concerning the importance of the inerting operation and the strict respect for strict adherence to instructions (completion of operating logs and reactor drying procedures),
- ✓ New explosive atmosphere training for all operators.

The modifications proposed by the operator, and in particular the change of the procedure for cleaning the R404, as well as the new gasket cleaning and inerting procedures, must ensure that operations take place in improved safety conditions.

In relation to this and with the same concern for safety, the operator also installed loading hoppers operating by nitrogen thrust on several reactors. A new drier operating under the nitrogen inerting principle was also purchased.