

## Reaction getting out of control

3 September 1994

Saint Vulbas – [Ain]

France

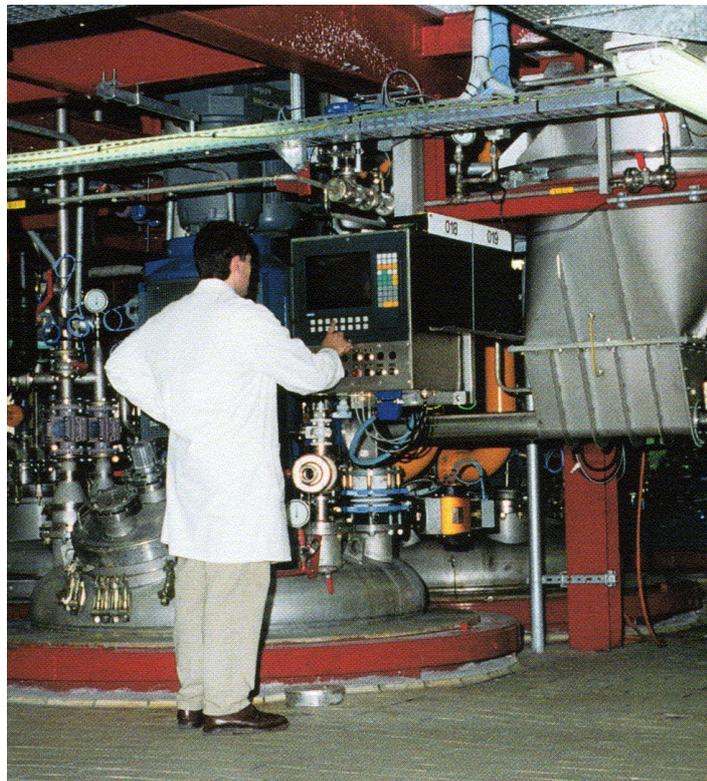
Fine chemistry  
Out of control reaction  
Design/Ergonomics  
Organisation/Operating mode  
Human factor  
Agitator

### THE FACILITY CONCERNED

In a fine chemistry unit specialised in manufacturing active principles for the pharmaceutical industry, a reaction got out of control at 11.16 a.m. in one of the two reactors of a production cell for 3, 4-methylenedioxyphenol (sesamol).

The facility was issued the operating license and commissioned in February 1994 and is regulated by the SEVESO directive. It comprises 43 employees. The products manufactured mainly include new molecules and active principles for the pharmaceutical sector. These may comprise both end products and intermediates. The facility produces 16-18 tonnes of 12-16 different substances per month. The facility does not have a R&D laboratory; a special unit is dedicated to the production of new molecules and drafting of new operating procedures.

The workshop includes 12 enamelled or stainless steel reactors with a volume ranging from 2,500 to 6,000 litres. The damaged reactor with a capacity of 2,500 litres is used to prepare the reagent by adding 233 kg of an aldehyde-phenol mixture to a mixture of hydrogen peroxide (324 kg), organic anhydride (304 kg), chlorinated solvent (1,100 kg) and dimethylformamide (62 kg) that acts as the catalyst. Hydrolysis is then performed in 2<sup>nd</sup> reactor that is not affected by the accident. A single technician is responsible for all the operations.



## ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

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### The accident

After having added about 150 kg of aldehyde into the reactor, the technician observed an abnormal increase in temperature of the mixture. He stopped adding the aldehyde, unplugged the metering pump and shut the drain valve of the aldehyde tank. Half an hour later, the reaction got violently out of control before the technical could neutralise the reaction with water. The glassworks of the unit exploded due to excess pressure in the facility.

### Consequences

No casualty was reported and there was no environmental impact: The emergency services were not required. The facility was cleared soon after and the liquid waste recovered. Internal damage was restricted to the damage of a rupture disc and the glass column of the apparatus. The glass panes of the production cell were also shattered.

### 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"/>				
Human and social consequences		<input 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 available at the following address:  
<http://www.aria.ecologie.gouv.fr>

Level 1 is attributed to the dangerous materials released (Q1 parameter,  $Q1 < 0.1\%$ ) as the amount of rejected substance (324 kg of hydrogen peroxide) represent less than 0.1% of the Seveso threshold (200 t).

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The technician, who wanted to turn off the high temperature alarm that was functional when the aldehyde was being added, unknowingly shut down an agitator, causing the separation of the reactive mixture in two phases. The temperature reading in the lower part of the reactor is no longer corresponds to the mixture. The local rise in temperature at the interface of the two phases until the temperature where the reaction gets completely out of control was thus not detected.

The control system of the reactor comprises two components:

- in a control room, two independent automatons display the various views of the facility: an overall view of the 12 reactors and related storage units, and a detailed view of each reactor with the various control parameters,
- a screen near each technician displays the reference values (temperatures, pressure, agitator speed, "the said safety" temperature and the actual values of the various parameters.

The alarm on the cabinet is both a light and sound alarm.

Temperature is not automatically regulated; the technician sets the reaction temperature that is specified in the instruction manual. The safety temperature is set by the team leader either in the reactive mixture or in the double jacket of the reactor. Besides the light and sound alarm, no other device controls this parameter. The inside temperature of the reactor is measured by two identical sensors at the bottom of the reactor.

There is no agitator control when the product is added and the alarms can be turned off without stopping the reaction.

When the reaction got out of control, the high pressure and temperature safety alarms ought to have warned the technician so that the reaction could be neutralised. This could not be carried out either due to lack of time (the alarms went off few seconds after the incident), or more likely due to the unclear reading of the situation by the alarms.

It is to be noted that the operating mode and the devices were not compliant with the provisions described in the danger studies.

## ACTION TAKEN

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Upon the recommendations of the inspection authorities of classified facilities, the operator must perform an internal audit on the parameters and equipment vital to the safety of all reactors and ensure compliance of operating modes with the danger studies conducted on the facility.

Several technical and organisational measures were taken subsequent to this accident:

- A dual control system to start and stop the agitator was installed (two buttons must be pushed at the same time),
- A sensor to monitor the rotation of the agitator with a light and sound alarm was installed in case the agitator failed to start or suddenly stopped operating,
- The agitator must be started (at least 30 rotations per minute) the moment the reactor contains a chemical substance,
- Instructions were drafted to ensure the mandatory presence of the operator near the reactor while adding the reagents.

## LESSONS LEARNT

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This accident illustrates several flaws in the design of the facility along with inadequate ergonomic study (Human Machine Interface):

- o The closeness of two totally different switches making it possible to stop the agitator instead of turning off the high-temperature sound alarm by the technician.
- o Badly positioned, and inadequate light and sound alarms that were not properly interpreted by the technician who failed to detect the moment when the reaction spun out of control
- o Badly positioned temperature sensors at the bottom of the tank where as the temperature started to rise in the upper part of the reactor. The situation was worsened when the agitator was stopped, thus preventing the ingredients from mixing and heat from spreading

A similar accident occurred in Calais on 25/04/1997: the adding of reagent/agitation control that was initially provided for in the blueprint did not actually exist, the technician turned off an alarm (agitation) at the beginning of the reaction (ARIA 11181\*).

The undetected stop of the agitator is the reason behind numerous accidents, reaffirming the important role of the agitator (sensor on the agitator axis, constant measurement of torque, etc.) Measuring the intensity of the motor may be inadequate as the motor may function without causing the agitator to rotate (ARIA 24723\*).

While drafting operating instructions and modes, the transitory phases must be taken into account. Training on these procedures and modes is also mandatory for technicians.

\* Accident summary available on [www.aria.ecologie.gouv.fr](http://www.aria.ecologie.gouv.fr)