# Explosion of a formulation reactor at a chemical plant
## January 11th, 2011
## Bourgoin-Jallieu (Isère) France

Chemical plant
Reactor
Explosion
Inerting
Toluene
Sodium methoxide
Glass equipment
Human factor

## THE FACILITIES INVOLVED

### The site:

This factory, classified as *Seveso*, produces high value-added organic molecules for a wide array of industries (chemical, pharmaceutical, cosmetic, photochemistry and glass treatment). It is located within the city limits of Bourgoin-Jallieu, 50 km south-east of Lyon, and its site covers roughly 10 hectares. This facility was employing about 100 personnel, and its 4 workshops were running three 8-hour shifts with a total floor area of 2,000 m². The formulation reactors were designed at a capacity of 100 m³, and the plant was operating with 26 distillation columns.

The site was located at the periphery of a developed zone within the municipal boundary adjacent to: a commercial district, three residential dwellings, and a transport infrastructure node.

***Figure 1: Aerial view of the site (source: http://www.pprtrhonealpes.com)***

### The specific unit involved:

The factory was laid out around different production workshops (see Fig. 2), one of which was dedicated to organic syntheses. The reaction responsible for this accident introduced both an aldehyde and camphorsulfonic acid in an anhydrous medium. Several phases were necessary, including a drying step for the camphorsulfonic acid suspended in toluene; azeotrope water / toluene was being distilled at approx. 85°C under atmospheric pressure.

***Figure 2: View of the damaged unit (source: Site operator)***

## THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

### The accident:

On Tuesday 11th January, 2011 around 1:40 am, an explosion occurred inside the formulation reactor (Fig. 3) once all the camphorsulfonic acid had been loaded into the toluene for dehydration via azeotropic distillation. No chemical reaction ensued, and the mix temperature held constant at 15℃. This operation was conducted under atmospheric pressure with an atmosphere rendered inert by means of nitrogen sweeping.

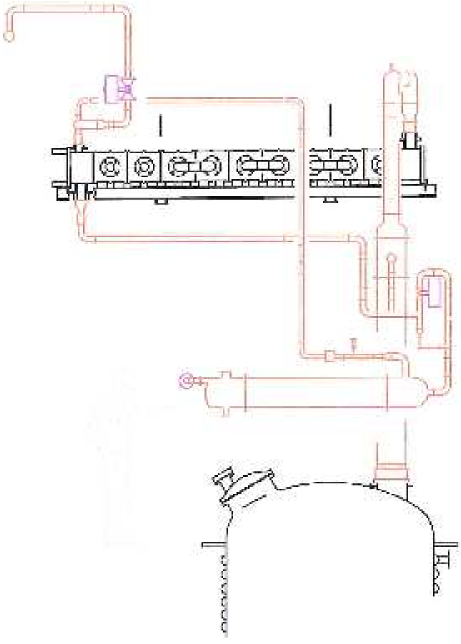


***Figure 3: Diagram of the damaged reactor, with glassworks shown in red and the reactor's enamelled steel housing or exchanger graphite shown in black (source: Site operator)***

### Consequences of this accident:

The explosion caused one injury as a result of the direct (blast) effect. It also broke the upper part of the distillation column, damaged the roof (ripping off asbestos-cement plates) and projected debris (mainly pieces of glass) 20 m to 30 m from the production building, while remaining inside the site boundary (Fig. 4).

***Figure 4: View of damage sustained by the workshop where the accident occurred (source: Site operator)***

The upper part of the column (DN 300, designed for a max pressure of 1 bar) burst into many small pieces of glass. At the column top, the temperature transmitter was stripped from the power supply cable and eventually found lying on the building roof. A flange (weighing 0.5 - 1 kg) was recovered outside, approx. 20 m from the production building facade, yet still within the site boundary (Fig. 5).

***Figure 5: Flange ejected outside the building (source: Site operator)***

A large quantity of soot was observed on the reactor walls, as well as inside the dome, on the manhole surface and along the agitator shaft (Fig. 6). Traces of soot were also visible in both the glass pipes and the (Florentine type) decanter, thus indicating that the circuits had been open when the explosion was triggered. The valve at the outlet of the Florentine decanter had remained in the closed position.

***Figure 6: Traces of soot inside the reactor (Source: Site operator)***

The manhole did not open, but the flat Teflon joint was deformed by retracting towards the centre. The reactor's rupture disc wound up bursting.

## 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:

| | | | | | | |
|---|---|---|---|---|---|---|
| **Dangerous materials released** | ■ | □ | □ | □ | □ | □ |
| **Human and social consequences** | ■ | □ | □ | □ | □ | □ |
| **Environmental consequences** | □ | □ | □ | □ | □ | □ |
| **Economic consequences** | ■ | □ | □ | □ | □ | □ |

The parameters composing these indices and their corresponding rating protocol are available from the following Website: http://www.aria.developpement-durable.gouv.fr.

The "dangerous material released" index was scored a level "1" as a result of toluene vapour release.

The "human and social consequences" index was rated a level "1" owing to the slight injuries sustained by one employee, requiring fewer than 24 hours of hospitalisation.

The "environmental consequences" index could not be scored since no environmental degradation was observed.

The "economic consequences" index received a level "1" due to property damage incurred by the unit, coupled with operating losses estimated at €120,000.

# THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THIS ACCIDENT

The site operator's investigation revealed that the column broke subsequent to an internal pressure surge; the glass tubes of this diameter (i.e. DN 300) were not designed to resist static pressure in excess of 1 bar. Both the splitting of the column into many small fragments and the damage recorded (essentially over the upper part of the building) attest to a fast-acting pressure rise phenomenon.

The large quantity of soot in the reactor reflects incomplete toluene combustion due to an insufficient oxygen concentration (i.e. partial reactor inerting) at the time of ignition. A lack of oxygen might also explain why the flame died and why a secondary fire never broke out (toluene is inflammable at room temperature).

In an agitated reactor, an inflammable vapour / air mix is capable of forming once oxygen concentration exceeds 9.6% (i.e. the minimum oxygen concentration with nitrogen as the inerting agent). A nitrogen sweeping instruction after loading was posted onsite, but it should be pointed out that simple sweeping at a rate of 1 or 2 $Nm^3/h$ would not have been sufficient to guarantee an oxygen concentration rate less than the prescribed limit for the medium in the presence of toluene.

**Ignition source:**

Sliding surface electrostatic discharges typically leave characteristic impacts on the reactor enamel. An enamel test was conducted following reactor cleaning: no defect was observed at the level of the reactor surface, except in the direction of a clamping collar joint positioned on the connecting flange at the reactor dome of the distillation column's first glass element (i.e. where the joint surface had been damaged).

Between two identical product manufacturing runs, the reactor was neither descaled nor rinsed. The end of the reaction was controlled by the change in methanol content stemming from the transformation of sodium methoxide (see reaction diagram in Fig. 7).

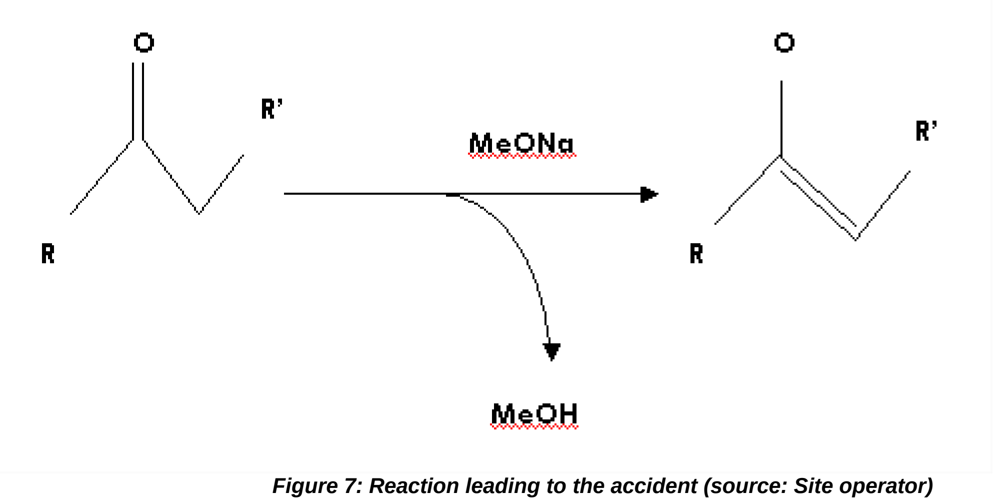
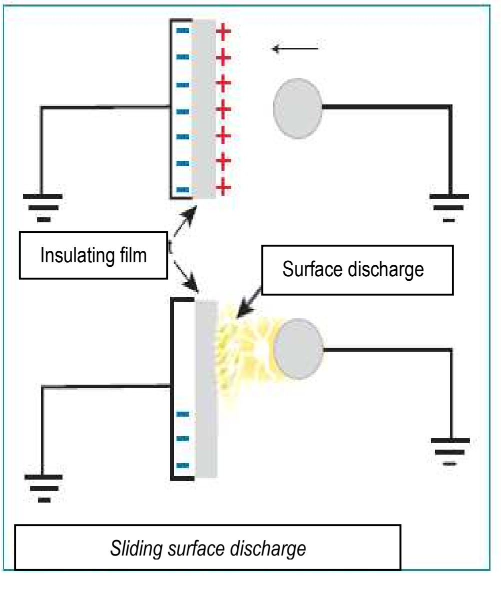



***Figure 7: Reaction leading to the accident (source: Site operator)***

***Definition of a sliding surface discharge:***

A sliding surface discharge occurs along the surface of a thin insulating layer and is generated on both sides; moreover, it features very strong charges of equal magnitude and opposite signs. This insulating layer may either be a thin, yet plated, independent layer on a conductor or else a metal surface lining.




Dilution with water constitutes an exothermic process. Final reactor rinsing between two operations was being performed using cold methanol. Formation of a sodium methoxide deposit (via methanol evaporation) either at the reactor dome surface or inside the distillation column must not be excluded. Cleaning with toluene reflux might have proven an insufficient step.

An infrared analysis conducted on a sample by an external laboratory revealed the presence of camphorsulfonic acid (Fig. 8).

***Figure 8: Camphorsulfonic acid at the reactor surface (source: Site operator)***

This risk of sliding surface discharge may be higher inside an enamelled reactor, not necessarily due to the liquid agitation phase but instead during the phase of toluene introduction. With respect to the search herein for ignition sources, a sliding discharge can be rejected since the enamel "comb" test yielded negative results, thus indicating that the enamel had remained intact: over its thickness, the material breakdown voltage had not been exceeded.

<u>Incident causes:</u>

- **Presence of an explosive mix within the free volume of both the reactor and distillation column subsequent to an inerting malfunction caused by the technician;**
- **The ignition source had not been clearly identified (product self-heating, electrostatic discharge?).**

## ACTIONS TAKEN

Following this accident, the operator adopted a number of measures, namely:

- Additional investigations into the causes of sodium methoxide deposit formation, which eventually led to self-heating of the product.
- Analysis of the feasibility of an electrostatic ignition source by means of a series of reduced-scale *in situ* measurements (mass density of charges for toluene alone, and for toluene + powder, both with and without agitation). The conclusion of this analysis demonstrated that even though camphorsulfonic acid is immiscible in toluene, this reason alone can still not explain a strong charge generation mechanism leading to a sliding surface discharge.
- Revision to all process guidelines posted in the production workshops, so as to include the systematic recording of reactor pressure on operations monitoring sheets as well as the requirement to obtain an oxygen value of ≤ 8% for a pressure of ≤ 150 mm Hg (or 200 mbar) during the inerting phase.
- Drafting of specific instructions relative to the inerting of formulation reactors, entitled "Atmospheric measurements inside closed capacities".
- For the targeted process, drafting of an operating procedure specifying continuous oxygen content measurements inside the reactor, along with replacement of the glass column by an enamelled column.
- Reminder of the importance of compliance with inerting instructions and procedures intended for technicians at the end of a phase introducing an insulating liquid into a reaction medium: training on inerting techniques was once again offered to all personnel working in the synthesis workshops.
- The reactor involved in the accident was equipped with a fixed oxygen probe. All reactors in the plant could gradually be fitted with this type of probe in order to streamline technicians' tasks.