Atmospheric discharge of the reaction mix from a polymerisation reactor

26 July 1995

Ribecourt-Dreslincourt (Oise)

France

Chemical engineering manufacture
Break
Rupture disc
Exothermic reaction
Thermal runaway

THE FACILITIES INVOLVED

The site:

The plant, located on the outskirts of the urban area, occupied a 40-ha parcel, 15 ha of which contained buildings. The facility, employing a workforce of 280 at the time, comprised 3 manufacturing sectors (resins - adhesives, glues and polymers - soaps) and an R&D Centre. When the accident struck, this plant was in non-compliance with regulations issued by Classified Facilities authorities and, as such, was required to submit a rectification request for all its activities.

Aerial photo of the site in 2010

The specific unit involved in the accident:

The workshop giving rise to the discharge had not been granted Prefectural authorisation on behalf of the Classified Facilities Inspectorate. In this workshop (devoted to resins), some ten reactors served to produce a formo-phenolic resin used in glues for agglomerated materials. The damaged reactor contained a volume of 15.2 m³.

The synthesis of a formo-phenolic resin, catalysed by soda, lasted some 10 hours. The reagents, namely formaldehyde and phenol, were loaded into the reactor; the mix was heated and the soda then gradually introduced into the reactor, which had been maintained in a vacuum. The highly exothermic reaction was controlled by the reactor's cooling systems, including 2 double shells, as well as by a return of the released steam condensates.

One of the plant's buildings

THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident:

On the day of the accident, after introducing the 3 reagents, a runaway reaction occurred accompanied by an increase in both reactor temperature and pressure. The rupture disc, set at 1.5 bar in order to protect the installation, broke. The reaction medium, ejected via the roof, fell back into the plant and vicinity over a radius of approx. 400 m.

Informed by the plant operator, Classified Facilities inspectors relayed notice to the Prefecture and Deputy Prosecutor before visiting the scene.

Consequences of this accident:

The quantity of products and reagents ejected was on the order of 6 tonnes (0.6% free phenol and 11.5% formaldehyde). Fallout could be detected in vegetable gardens and on the bodies of several cars.

Subsequent to site cleaning by the operator, 1,000 m³ of washing water were stored in the plant's retention basin.

The analysis conducted of soil and plants yielded phenol concentrations lying between 0.02 and 0.87 mg/kg for soil samples and between 0.17 and 4.08 mg/kg for the plants.

Lacking baseline reference values, the operator collected some of the vegetables from the garden, ordered the mowing of a wheat field adversely affected by product fallout and reimbursed third parties for any damages incurred.

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 available information, this accident can be characterised by the four following indices:

The substances ejected (namely formaldehyde and phenol) were both on the Seveso list, with the threshold for formaldehyde set at 50 tonnes and for phenol at 200 tonnes. The quantity of substances released equalled 690 kg of formaldehyde (or 1.38% of its threshold) and 36 kg of phenol (0.018%). In the event of an accident involving several listed substances, the highest level attained is to be selected. The index relative to the quantity of hazardous substances released was therefore scored a "3" (see parameter Q1).

No human or social consequences were observed, thus resulting in a "0" index value.

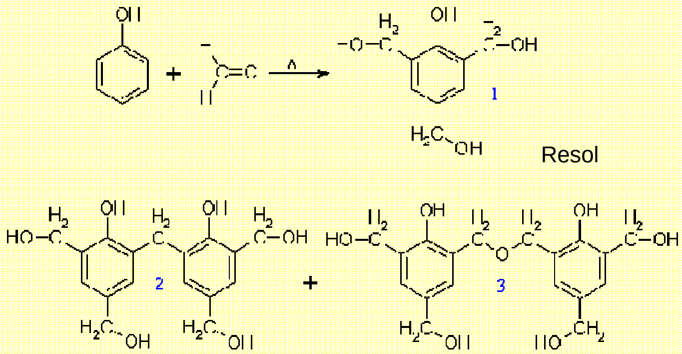
Since the polluted ground surface area needing to be cleaned was around 50 ha, the index relative to environmental consequences received a "5" rating (parameter Env13).

Given the total cost of cleaning the various fouled zones, which amounted to 7.135 million francs (i.e. €1,445,000, parameter €18), an index of "4" was ascribed to economic consequences.

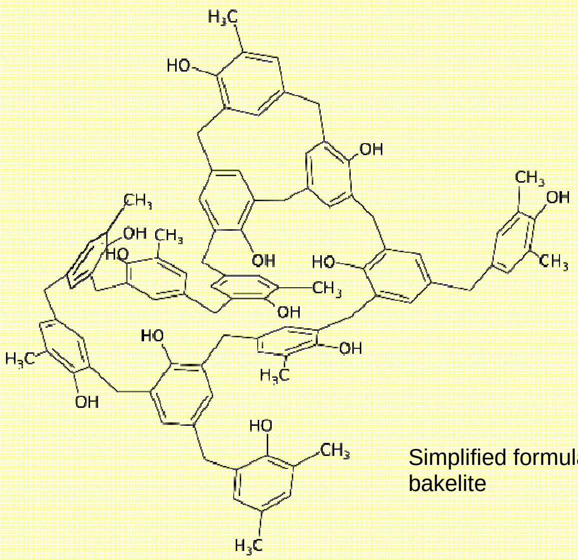
The parameters composing these indices and their rating methodology are available on the Web page: http://www.aria.developpement-durable.gouv.fr.

Formo-phenolic resins: 2 distinct steps

These are the oldest forms of thermosetting resins, initially discovered in 1909 by Baekeland. They are obtained by a reaction of phenol with formaldehyde in the presence of a basic catalyst, in this case soda. The reaction is highly exothermic. Obtained first is a liquid, alcohol-soluble and slightly polymerised resin, called resol. By means of heating at 190°C and under low pressure (14 MPa), the solvent evaporates and the polycondensation reaction then continues until a complex three-dimensional network forming bakelite is produced.



Resol



Simplified formulation of bakelite

THE ORIGIN, CAUSES AND CIRCUMSTANCES OF THIS ACCIDENT

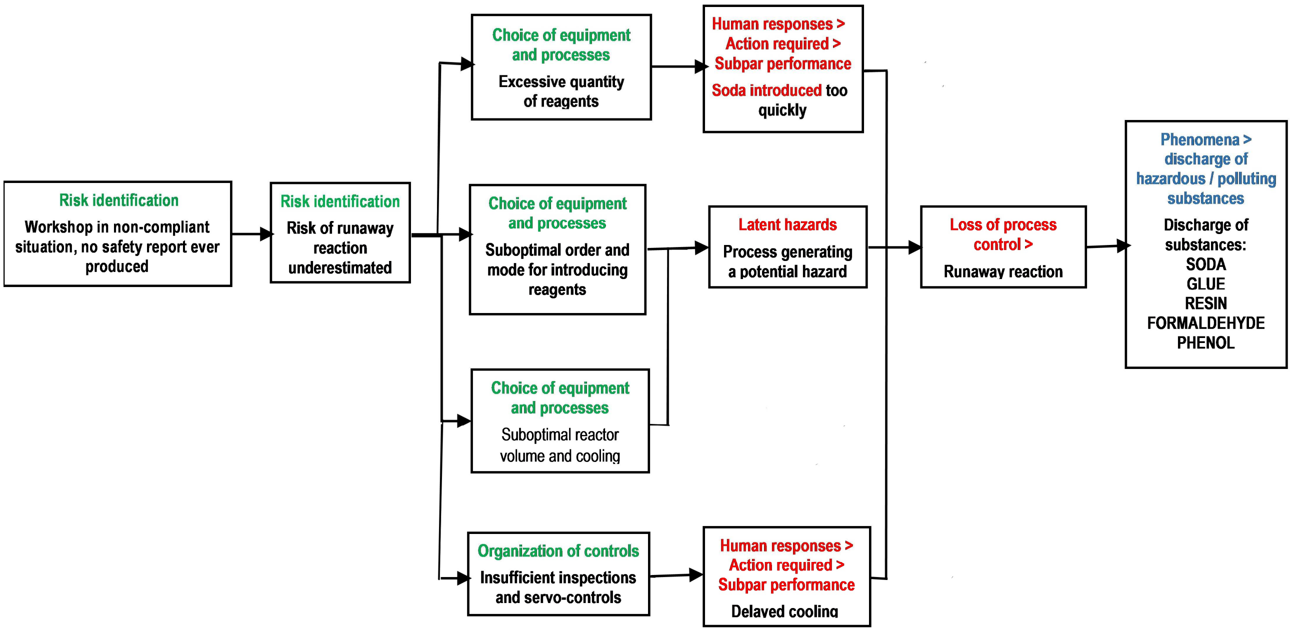
The runaway reaction was due to a combination of the following 3 causes:

- an excessively fast pouring of soda into the reactor, which already contained all of the primary reagents. This loading as of the beginning of the cycle constituted a factor causing drift in the reaction;
- a late start initiating the cooling system. Recordings of the main reaction parameters revealed that despite the quick temperature rise to 127°C, cooling did not take place until 12 min had elapsed after the temperature bump. This delay jeopardised reactor temperature controls, as did the lack of a temperature-cooling servo-control system and/or alarm to trigger the cooling mechanism;
- an overall process that generated a potential hazard for the following reasons:
  - excessive quantities of reagents,
  - a reactor volume not matched to its mode of cooling. In the case of double-shell cooling, reactor size must be reduced so that the shell surface area / reactor volume ratio allows for efficient cooling.

The risk of a runaway reactor had been underestimated, as a safety report would have detected. But such a report had not been produced, thus placing the workshop in a state of non-compliance.

In sum, the excessive quantities of reagents, injected as of the beginning of the cycle, combined with the soda being poured too quickly, insufficient availability of cooling capacities and inappropriate temperature settings, served to create the conditions necessary for the reaction process to drift until generating a violent and uncontrollable reaction.

The modelling diagram shown below summarises the set of disturbances and causes resulting in this accident.



ACTIONS TAKEN

In the aim of restarting production, the plant operator conducted a study and proposed the following measures:

- A new manufacturing process was to be launched, to improve control over the reaction heat release and thus limit the risk of a runaway reaction. This so-called "continuous formaldehyde pouring" process would make it possible, should reaction parameters begin to drift, to resume control by suspending the addition of formaldehyde.
- The reduction in quantities involved would also help to gain better control over the reaction.
- The monitoring of reactor operating parameters and chemical reaction steps were both slated for improvement.

For its part, Classified Facilities Inspection Authorities noted that no safety report had ever been produced regarding this new resin manufacturing procedure. Since the unit had not been granted any authorisations, a summons was proposed to file a rectification request with a 6-month deadline. A series of protective measures intended to avoid recurrence of a similar accident were implemented under the scenario of suspending facility production until reaching a decision relative to the authorisation request.

LESSONS LEARNT

Known since the beginning of the 20th century, formaldehyde/phenol reactions often cause incidents. Due to the extensive heat release of this polycondensation, thermal runaway reactions become primarily responsible for either forcing open the reactor's protective relief valve or breaking its safety disc[1,2]. Such a violent ejection makes it impossible to channel the discharged substances.

Efforts must thus be aimed at preventing such a runaway reaction. Attention must therefore be paid to ensure:

- supervision of initial loads inside the reactor and control over the soda flow rate, which triggers polymerisation;
- the reactor's sufficient cooling capacity, more specifically the size of the reactor must be optimised to enhance cooling via the double shell (for a better surface area : volume ratio). This point excludes large reactor volumes;
- effective reactor cooling as of the start of reaction (servo-controlled pouring or alarm system to initiate cooling).

Modification of the process proposed by the operator (introducing formaldehyde during the reaction) offered a significant improvement aimed at preventing runaway reactions.

Specific recommendations

It is recommended herein to tie hazardous reaction launch phases to key safety-related parameters. For example, the pouring of soda must be made dependent on effective reactor cooling.

To verify the quantities being introduced into the reactor, the installation of a backup system is recommended, i.e.:

- Multiple preliminary dosing upstream of the reactor: placement of a fixed-volume dosing jar, whose number of unit loads to be introduced into the reactor requires monitoring (dual controls on the number of jar inlet valve cycles as well as the number of racking cycles).
- Preliminary dosing upstream of the reactor (intrinsic safety):
    - addition of a metered quantity into a tank placed on a weight scale,
    - verification of this pre-load by means of weight measurements,
    - validation of the load to be introduced into the reactor provided the loads measured using the 2 techniques show little difference,
    - placement of the pre-load into the reactor.
- In the reactor itself (delayed safety shutoff: time slightly longer than the average insertion time):
    - load inserted controlled by meter 1 (e.g. mass) and, for safety reasons, shutoff if allotted time has been exceeded,
    - charge verified by meter 2 (e.g. volume) or by level in the racking tank or else inside the reactor,
    - validation of the load by comparison of indications and if the time delay has not been activated.

Each time the process allows, it is recommended to introduce the compounds "driving" the reaction while the reaction is underway. An accurate control of their insertion flow rate during the reaction thus guarantees complete process control. A set of key safety parameters may be used to trigger the introduction of these reagents, e.g.: reactor pressure and temperature, double shell pump.

General recommendations

Generally speaking, in the event of reactions with high energy potential, it is recommended to reduce the reactor size in order to raise the double shell surface area-to-volume ratio. On an existing reactor, it is recommended to install an inhibition system, either blow down or flooding, to serve as the ultimate safety backup.

To assist the technician assigned to this process, it would be worthwhile to set up alarms to first notify the technician and then motivate his response upon detection of a hazardous drift. These alarms would be activated by 2 thresholds that could be combined into one:

- The *monitoring threshold* may be defined as the point at which the technician must prioritise monitoring of the targeted parameter and then verify that the installation returns to a safe state, even if it means taking action;
- The *response threshold* may be defined as the point at which the technician or programmable controller (active safety) must act upon the targeted parameter and reset it within the safe interval.

In order to familiarise technicians with appropriate intervention techniques should parameters drift, drills must be held, in replicating the most likely incident scenarios. Active safety features (automatic intervention) must be periodically verified.

(1) J.C. Leung, H.K. Fauske, H.G. Fisher, *Thermochimica Acta* 104, pp. 13-19, 1986.

(2) R. Andurand, *Les matières plastiques : leurs précurseurs chimiques, les agents additifs ; les grands accidents connus* ("*Plastics: Their chemical precursors, additives; most prominent accidents*") 142 p., 1992.