Fire in a synthetic rubber production plant

27th November, 1996

Notre Dame-de-Gravenchon (Seine-Maritime) France

Chemistry
Ethylene Propylene Diene Monomer (EPDM)
Level probe
Sedimentation tank
Cooling tower
Clogging / malfunction
Fire
Physical defect
Organisation / control

THE FACILITIES INVOLVED

The site:

In operation since 1958, the Notre Dame-de-Gravenchon plant comprised 3 production units:

- EPDM (Ethylene Propylene Diene Monomer) rubber
- Isobutene used inside the butyl unit
- Elastomer (butyl rubber).

This facility, whose site had been zoned for a public utility easement, was classified as Upper Tier Seveso and employed a workforce of 360.

Photo: Risk Directorate

The specific unit involved:

The accident occurred in the EPDM rubber production unit, whose capacity had reached 80,000 tons/year; plant operations had been authorised by Prefecture order issued on 1st August, 1991.

The EPDM production process:

EPDM products resulted from the co-polymerisation of ethylene, propylene and a diene. This reaction took place in a hexane solvent medium in the presence of a catalyst. The output, denoted "CEMENT", was a synthetic rubber solution in the hexane whose contents included unreacted monomers and a catalyst residue; the monomers and residue were to be eliminated.

The CEMENT was then suspended in water and directed to a sedimentation tank to separate out the "water + catalyst" fraction. Transferred to a cooling tower (ST1300S), this aqueous fraction made its way, by overflowing and through a pit (D1321), to a treatment plant designed for liquid effluent.

In order to avoid CEMENT migration from the sedimentation tank to the tower, the CEMENT / Water + catalyst interface level was adjusted by a servo-controlled valve in accordance with the interface level variation. This valve was positioned in the lower part of the site's sedimentation tank on the water + catalyst outlet. On the day of the accident, this level meter was backed up by a 2nd device, composed of a test phase membrane level also positioned in the lower part of the sedimentation tank. These measurement instruments were complemented by a 2nd interface level control, operated using an independent device located on the appendix of the sedimentation tank to control valve closure. The interface level was thus being monitored by means of 2 separate devices featuring the same technology yet performing measurements at 2 distinct points within the installation, while a 3rd device based on a different technology and designed to repeat measurements at the lower part of the sedimentation tank was still undergoing testing. The 2 basic level controls were both equipped with a "flushing" apparatus, i.e. a water injection device to allow cleaning the level pipes and preventing them from clogging. For optimal cleaning, these flushing levels required at least a minimum water flow rate.

The EPDM (Ethylene Propylene Diene Monomer) compounds:

These compounds are obtained by means of the co-polymerisation in equal proportions (close to 50/50) of ethylene and propylene. The addition of a small proportion of diene brings the double bonds allowing a conventional vulcanisation.

EPDM present characteristics close to those of natural rubber, with in particular, excellent resistance to bad weather, ozone, light, air and cold, as well as very good resistance to acids. They are black in colour.

THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident:

A sudden pressure surge in the de-mineralised water network disturbed controls of CEMENT / water + catalyst interface height, causing 10 to 15 tons of CEMENT to be transferred from the sedimentation tank to cooling tower ST1300S. One hour after completion of this transfer, the tower as well as the pit (D1321) ignited at the surface.

Accident chronology:

- 3:30 pm: variations in the de-mineralised water pressure interfered with the interface level measurement.
- 3:40 pm: a disturbance was detected on the flushing level recording at the lower part of the installation, with the reading found at 60% of the setting. The membrane level, positioned at 62%, detected a decrease.
- 6:30 pm: though still disturbed, the flushing level continued to display a 60% sedimentation tank filling rate; in contrast, the membrane level now posted a 48% reading.
- 7:10 pm: the flushing level drifted towards 97%, while the membrane level dropped to 3%.
- 7:30 pm: while making his round, an operator detected a hexane odour along with the presence of CEMENT. It was noticed on the unit that the flushing flow rates were zero and that the cement/water interface level measurement was erroneous (at 97%), as CEMENT was flowing at the bottom of the sedimentation tank towards the ST1300S tower. The outlet valve of the D137 fat flask towards the ST1300S tower was closed from the control terminal. The migration of CEMENT to the ST1300S tower and D1321 pit occurred between 7:10 and 7:28 pm, with 10 to 15 tonnes of product being channelled in the wrong direction. Once identified, the incident could be brought under control.
- 8:30 pm: one hour after CEMENT stopped being channelled with a return to normal operations for the flushing levels and after 45 minutes of displacement action with de-mineralised water (coming from the D137 fat flask) in the connecting pipes between the sedimentation tank and ST1300S tower, the ST1300S tower and D1321 pit ignited at the surface. The "C" threshold of the internal emergency plan was activated.
- The fire was brought under control at 8:50 pm and then completely extinguished at 9:20 pm.

The consequences of this accident:

Only property damage was recorded: cooling tower ST1300S taken offline, and damage to the pumps at pit D1321. The unit had to be shut down. According to the site operator, the atmospheric pollution related to CEMENT combustion was only minimal and moreover none of the liquid effluent discharge limits announced in the standards had been exceeded.

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:

The lost reaction mix contained cement and hexane. The SEVESO threshold for hexane had been set at 500 tonnes. In the absence of data yielding an exact quantification of substances actually released, the index relative to the quantity of dangerous materials released was scored a "1" as a default setting (see Parameter Q1). No human, social or environmental consequence could be observed, thus leading the corresponding index values associated with these consequences to receive a "0" score. Given that property damage costs were not known, the index relative to economic consequences was not rated.

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

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THIS ACCIDENT

The site operator submitted a fault tree analysis to the Classified Facilities Inspectorate on December 23rd, 1996.

Presence of hydrocarbons:

This incident revealed a lack of reliability in the flushing level technology, which became even more acute as the occurrence of flushing reached the end of the de-mineralised water network.

The clogging due to flushing malfunction exerted the same impact on both level controls, i.e. one on the sedimentation tank the other installed on the appendix. The appendix level control was functioning correctly at the time of the test conducted 3 days prior and then again the day after the incident.

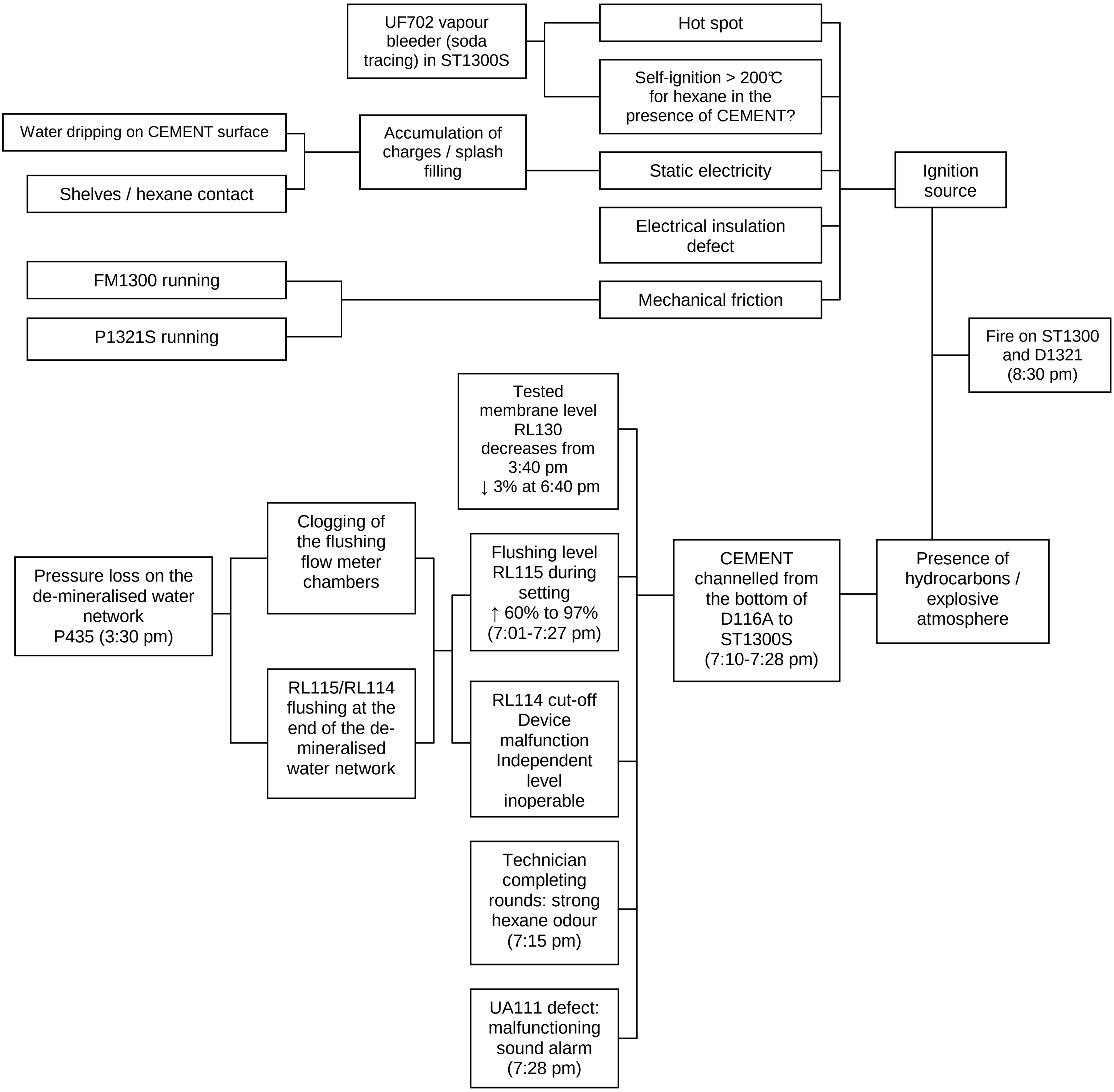
The explosimeter installed on the ST1300S tower did not reveal any abnormality nor did the sound alarm trigger even though a strong hexane odour could be detected nearby. A more efficient means of detection would undoubtedly have reduced technician response time.

Ignition at the surface of the cooling tower (ST1300S) and pit (D1321)

The onsite electrical equipment was evaluated: an insulation defect was a priori eliminated (annual controls tested positive, external masses controlled and found to be compliant, presence of ADF motors, etc.). This ignition was most likely related to static electricity along with a phenomenon of "splash filling" or accumulation of electrical charges generated by contact with water dripping onto the cement/hexane mix at the ST1300S surface. The contact with propylene/hexane shelves was a priori rejected since by 8:30 pm water had already been arriving at the shelves surface for 45 minutes. Two other hypotheses were also forwarded:

- A hot spot caused by the accumulation of condensed vapours at the level of the bleeder on a flow rate measurement device placed on the tracing path of the soda line associated with the pit (D1321), though temperatures were significantly lower than the hexane self-ignition threshold (perhaps the CEMENT effect?);
- Temperature rise due to mechanical friction (FM 1300 fan motors running in the ST1300S tower or P1321 accelerator pumps motors in the D1321 pit moved towards the heavy metals basins).

Fault tree analysis for the accident



ACTIONS TAKEN

Having demonstrated control over the causes leading to this type of accident, as well as ensuring the efficient treatment of unit effluents, installation start-up was ordered on December 2nd. Several modifications had been performed or taken into account, namely:

- verification and eventual renovation of the atmospheric refrigerant chamber on the northern ST1300 tower (including the fan), applicable as well to the D1321 sump basin (including pumps and level controls);
- removal from service of the southern ST1300 tower chamber due to fire damage;
- assignment of the northern SR1300 tower chamber (previously used exclusively during the summer in order to cool basin S1321 effluent) to the current stemming from the de-mineralisation circuit via a pipeline installed between the northern and southern chambers;
- personnel attention focused on the existence of a 3rd sedimentation tank level (membrane level), whose reliability seemed better than that of the other levels. The indications provided on this 3rd level, on a test basis, had not until then been taken into account by the technician;
- medium-term research programme launched to transition from the sedimentation tank level control to the membrane level as well as from the lower sedimentation tank level safety to a radioactive probe level.

Remedial actions undertaken by the site operator:

- *Membrane level:* The effective introduction of the membrane level was accelerated and ultimately took place on December 12th, 1996. The associated flushing level was retained. Any divergence between the 2 indicators was recorded by the process computer and potentially used to anticipate a problem on the flushing line that was also capable of affecting the level control on the tank appendix. The 2 flushing levels would be eliminated when the action item outlined in the following point was carried out.
- *Densitometer with radioactive sources:* At the end of the 1st quarter 1997, the flushing level on the sedimentation tank appendix that had been activating closure of the sedimentation tank bottom valve was replaced by a cobalt probe, considered as a more reliable technology for interface measurements. A formal training course was specially organised for technicians prior to start-up focusing on use of this technology and the operating procedures to be implemented during sedimentation tank cleaning. An emergency drill was scheduled during the next year based on a scenario involving risks to the radioactive sources.
- *Automatic valve at the sedimentation tank bottom:* The valve located on the automatic valve bypass placed in the output line of the sedimentation tank D116A (volume: 48 m³) has been padlocked shut since December 1996.
- *Other unit equipment displaying conditions similar to those of the sedimentation tank indicated above:* This set of equipment was inspected on a case-by-case basis so as to undergo, if deemed necessary, the same remedial actions or other dedicated measurements.
- *Densitometer on the D137 fat flask output line:* In the event of defect / safety device bypass to avoid channelling CEMENT to the ST1300S tower, one compensatory measure might, according to the site operator, involve the use of a densitometer on the D137 fat flask output line, downstream of both the de-mineralisation current intake of the pilot and currents originating from sedimentation tanks D116A and D116B. An alarm on this conventional technology instrument would save reaction time before hydrocarbons reached the ST1300S tower. This configuration was studied during 1997.
- *Improvement of the gas detection system adjacent to the ST1300S tower:* The 1st threshold activates the sound alarm (at 25% of the lower flammability limit). On November 27th, the alarm was not triggered, as the 1st default state was only activated 15 minutes after the detection of hexane odours within the zone. The operator proceeded by scheduling the following (prior to the end of the 1st quarter 1997):
    - An assessment of potential improvements to system reliability through use of a single threshold in conjunction with a sound alarm;
    - Installation of an explosimeter on the ST1300N and ST1300S adjoining towers at the chamber output heading towards pit D1321;
    - Search for a technology compatible with water vapour in order to equip a 3rd explosimeter on top of the ST1300S tower, where hexane vapours were more likely to be detected rather than trapped in the CEMENT at the pit surface.
- *Tracing water bleeder:* The bleeder on the vapour tracing circuit of the soda feed line for the ST1300S tower was capable of generating a hot spot and, for this reason, was placed in an underground pipe.
- *Relocation of controls:* During the November 27th, 1996 incident, fans on the ST1300 tower were turned off by the technician a few minutes after the fire outbreak. To avoid exposing plant personnel in the event of accident, both pump and fan controls were moved.

- *Emergency procedure:* Beginning with the initial condition of "CEMENT found in the ST1300 tower and D1321 pit, presence of ignition risk", an emergency procedure was drafted and inserted into the mandatory training modules (shutdown of the polymerisation process, drainage of D116 sedimentation tank contents into the sewer, instruction to keep fans running and refrain from climbing onto the ST1300 tower's upper platform, precautions to be taken before starting pumping, sprinkling procedure to be implemented to prevent the ignition risk, etc.).

LESSONS LEARNT

Organisation and controls / training:

This accident has illustrated the necessity of an in-depth assessment on the level measurement technology to be employed in processes that involve sedimentation with interface monitoring between 2 immiscible liquid phases. The choice of the technology to implement includes as parameters the zone to be monitored and the series of products to be introduced into the process. In the present case, level controls equipped with a "flushing" feature to allow cleaning the level pipes and preventing against their clogging require a sufficient water flow rate in order to operate effectively, yet this condition had not been fulfilled due to their positions at the end of the de-mineralised water network and ensuing pressure variations. The selected technology did not therefore offer adequate reliability. The membrane level indicated the appropriate value, though this test phase level had not been taken into account by the technician. The control of all levels introduced would have accelerated the intervention and demonstrated the importance of training personnel in the technologies implemented and operating procedures required.

Identification and evaluation of accident risks, supervision of modifications:

The CEMENT / water + catalyst sedimentation depends entirely on an accurate localisation of the interface. The repetition of this level measurement constitutes a helpful barrier to avoid routing the CEMENT to the sedimentation tank, with any divergence between the 2 measurements alerting the technician and facilitating the introduction of measures to avert such an incident.

Since CEMENT is an EPDM / monomer / hexane solution, the fire risk cannot be excluded, and the installation of a reliable alarm at the level of the cooling tower is essential. One or more carefully positioned explosimeters make it possible to detect hexane vapours.

Lastly, the relay of controls outside of sensitive zones capable of containing hexane vapours provides an effective means for protecting technicians during the outbreak of an accident.

Feedback management:

A detailed analysis of the causes and circumstances surrounding this accident enabled the operator to modify onsite installations by improving the detection of eventual anomalies relative to level measurements while at the same time enhancing the detection of secondary effects, such as ignition of the organic solvent introduced into the process.

These modifications, performed in order to avoid the recurrence of such an accident or at least limit its consequences, were backed by a specific training sequence offered to technicians on the new technology being applied. The drafting of an emergency procedure to be followed in case of sedimentation tank malfunction and the insertion of this procedure into the mandatory training modules also serves to ensure better protection of unit personnel, installations and the environment.

Other inventoried cases:

ARIA 18 339. Thermal runaway of a styrene/acrylonitrile co-polymerisation reactor - Villers-Saint-Sépulcre (France) - IMPEL 2001.

ARIA 31 227. Overflow of a semi-buried jet fuel tank - Sainte-Marie [Reunion Island] (France) - IMPEL 2007.