# Extended release of mercaptan at a chemical plant

## 21 January 2013

## Rouen (Haute Normandie)

## France

**Chemical plant**
**Additives**
**Mercaptan**
**Automatism**
**Management of change**
**Decomposition**

## THE FACILITIES INVOLVED

### The site:

Since 1954, this plant has been producing additives for motor oils and other transport-related fluids, industrial lubricants, and fuels for automobiles (running on either gasoline or diesel engines). The site employs a workforce of over 300 and occupies 14 hectares at an industrial park located on the left bank of the Seine in the city of Rouen. A technological risk prevention plan had been drawn up specifically for this facility, given its assigned upper-tier Seveso rating.

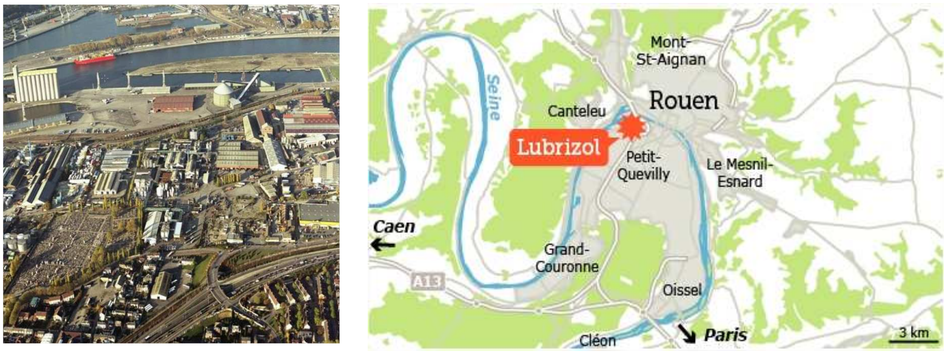



*Fig. 1: Location and view of the plant within its surrounding industrial park (Google Maps / Le Figaro)*

The site comprises a number of production units (Fig. 2):

- antioxidant additives: phosphorus pentasulfide (384 tonnes in storage) and zinc dialkyl dithiophosphates (50,000 tonnes/year);
- detergent additives (20,000 tonnes/year) and dispersants (25,500 tonnes/year);
- calcium (3,000 tonnes/year);

along with additive packaging, storage and delivery units, as well as ancillary installations set up to treat the aqueous or gaseous effluent and cool production equipment.

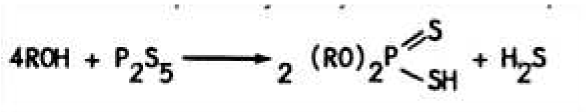

*Fig. 2: Main plant installations (site operator)*

## The specific unit involved in this accident:

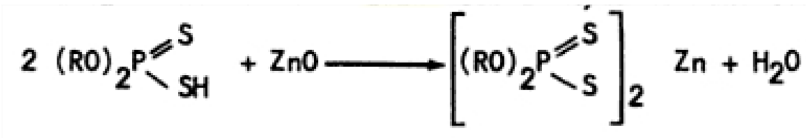
The unit involved in this accident was dedicated to the batch synthesis of zinc dialkyl dithiophosphates (ZDDP) using dithiophosphoric acid fed from an adjacent unit. Part of the metal dithiophosphate family, discovered in 1936 and available on the market since the 1940's, ZDDP has enjoyed considerable commercial success by virtue of combining several highly desirable properties in lubricating mechanical parts: antioxidant, anti-corrosion, detergent, wear-resistant, and seizure prevention. This zinc salt has thus become one of the primary additives, with a content of between 3% and 12%, in lubricating mineral oils for engines.

ZDDP is synthesised by means of a double decomposition reaction:

1. Synthesis of the dithiophosphoric acid by introducing phosphorus pentasulphide and a hydroxylated compound (secondary alcohol) in an inert atmosphere at a 100℃ temperature:



2. Reaction of dithiophosphoric acid on zinc oxide:



The complex compound obtained is then dissolved in a hydrocarbon (oil on the diagram), separated from the aqueous phase by stripping (neutralisation on the diagram) and filtered before altering its composition by adding hydrocarbons. This adjustment step is carried out in the 30-$m^3$ capacity T76 tank equipped with a product recirculation line that contains a manual pump and sampling device. Reaction stability of the sample is controlled on-site by the technician responsible for extraction. The product's commercial compliance is then verified in the plant's laboratory. In case of noncompliant specifications, the product is once again pumped into the filtration process for a repeat filtration. The compliant product is fed to a unit storage tank (T35) prior to commercial distribution (Fig. 3).

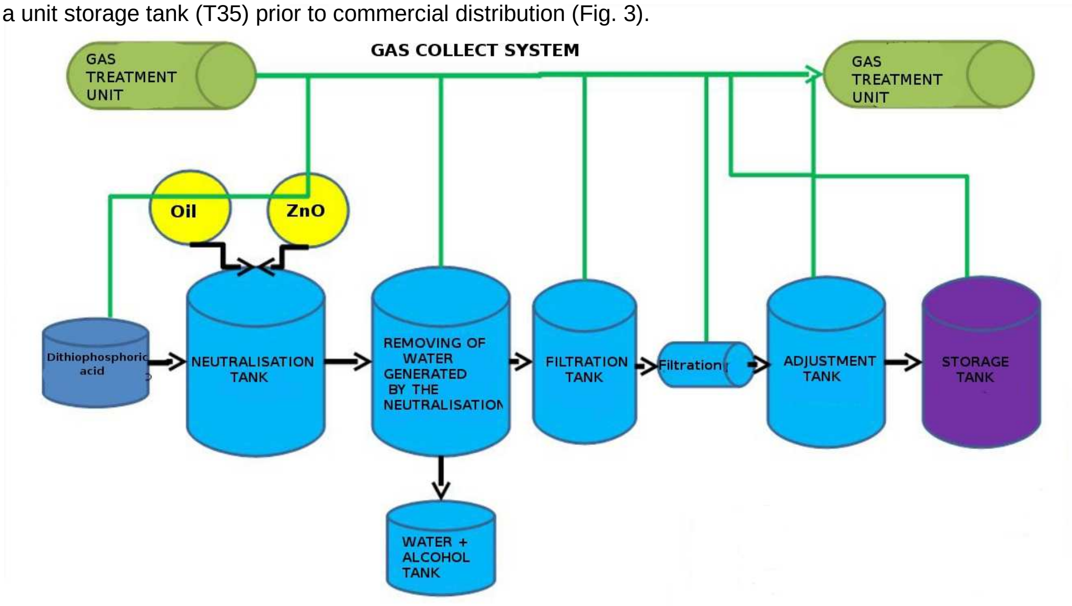



*Fig. 3: Final part of the ZDDP synthesis process (DREAL Agency, Haute-Normandie)*

*Fig. 4: Gas treatment unit (Paris Normandie)*

All storage and mixing equipment vents are connected to a gas collect system (extraction flow rate: 500 $m^3/h$), which channels gases to the gaseous effluent treatment unit (Fig. 4), where 3 columns wash the gases with soda water either on its own or mixed with liquid bleach. One of these columns also served to inject chlorine dioxide ($ClO_2$) in order to neutralise, by means of oxidation-reduction, the traces of mercaptan released in the event of decomposition at the time of the synthesis step. The unit is fitted with an exhaust stack connected to a continuous analyser (gaseous phase chromatograph along with a sulphur compound detector) used to measure traces of hydrogen sulphide ($H_2S$, a highly toxic and foul-smelling gas) and mercaptan (a foul-smelling and toxic gas when present in high concentrations) at the release point in addition to detecting any eventual excess of authorised contents for these compounds. Occasional measurements using colorimetric (Draeger type) tubes may be conducted.

So-called "olfactory" employees trained to identify odours are asked to patrol the vicinity so as to evaluate with greater precision the olfactory nuisance. Stationary $H_2S$ detectors installed around the production units trigger an alarm in the event certain airborne concentration thresholds are exceeded (5 and 10 ppm). Moreover, portable detectors are available in the control room to complete the deployed protection system.

## THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

### Chronology of this accident:

Friday 18 January: While the T76 adjustment tank was being filled with a batch of product after completing a filtration step, the unit's automated control system detected a very high level inside one of the ZDDP storage tanks and shut down the recirculation pump around 2 pm. Activating this instrumented safety feature served to avoid any accidental overfilling of storage tanks, given that the transfer circuit between these tanks and the adjustment tank had only been equipped with a set of manual valves, thus preventing the use of remote controls. The recirculation pump could no longer be activated from the control room, but solely in manual mode via a control board housed inside one of the unit's utility rooms. In seeking to restart the pump at 4:44 pm to filter the solution once again, a technician mistakenly started up the stirrer on tank T76. Upon returning to the control room, he observed that the pump was still off and went back to turn it on locally. Declared compliant around 10:30 pm, the newly-filtered batch was ultimately transferred into a storage tank using this same pump, while the stirrer continued to operate in the empty tank.

The weekend of 19 and 20 January: Tank T76 was filled by another 33-tonne batch of product at 1:53 am. The pump was turned on twice for the sampling operation; the product was stable and compliant, though market demand was weak and the batch remained in the heat-insulated adjustment tank. Visual inspections during rounds conducted within the unit did not detect any anomaly.

Monday 21 January: During the night, the treatment unit's analyser recorded a gradual rise in $H_2S$ emissions and mercaptan[1] at the stack outlet (less than 4.5 ppm). Around 8 am, odours inside the unit building were noticed by a technician performing a sampling at the time of pump start-up. The high temperature alarm in the tank was triggered shortly thereafter in the control room: the pump was turned off and the temperature once again dropped. Analysis of the sample showed a undergoing decomposition in tank T76, leading the technician to give the alarm.

An initial inerting procedure was undertaken by means of adding an aqueous zinc oxide solution in the tank; furthermore, chlorine dioxide was injected into a washing column on the gaseous effluent treatment system. An electric short-circuit, followed by difficulties encountered when hooking up the device for mixing neutralising solution, wound up slowing the operation. Zinc oxide was injected a second time as this inerting procedure was ongoing, yet the tank temperature still exceeded 100℃. Around 11:15 am, the temperature be gan to drop, although the analyser at the stack outlet posted an error reading, indicating incomplete removal of the mercaptan. As of 10 am, strong smells had begun permeating the plant. Around 11:30 am, the operator activated the Internal Emergency Plan and notified the Environmental Agency. During the afternoon, a test intended to lower temperature by adding 5 tonnes of oil failed, as did a neutralisation test calling for the gradual introduction of 3 tonnes of calcium sulphonate into the tank.

Tuesday 22 and Wednesday 23 January: The local government (Rouen Prefecture) activated the External Emergency Plan at 10:35 am on Tuesday the 22. A revised product treatment protocol was designed and then validated by the Prefect. On Wednesday the 23 around 6 am, another neutralisation operation was launched with a low injection rate in order to better control the exothermic reaction, while limiting the risks of a runaway reaction and release of toxic gases above 75℃. The tank used for this purpose needed t o be constantly cooled. The contents of tank T76 were injected in small quantities into a neutralising solution (composed of soda water and bleach) prepared in one of the unit's storage tanks (T35). A 30-min interval was respected between each transfer step in order to: homogenise the mix, limit heating (exothermic reaction), and monitor the reaction (Fig. 5). All vapour released during transfers was still being routed into gas washing columns (the plant's stationary installations for tanks T76 and T35, mobile installations for the vents on road tankers handling the neutralised product).

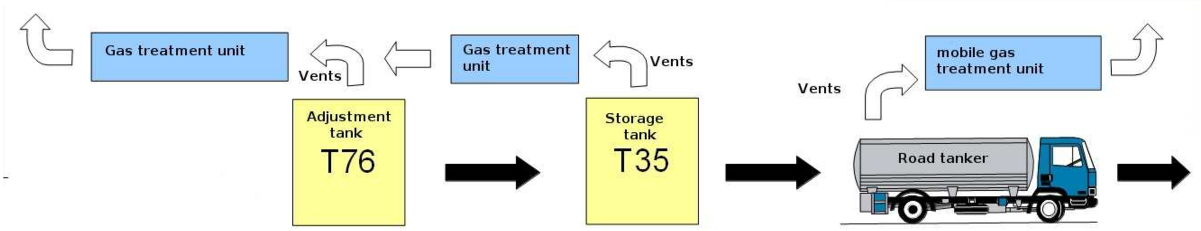



*Fig. 5: Neutralisation and treatment of gases released during the accident (DREAL Agency)*

Thursday 24 and Friday 25 January: Early in the morning, 12 tonnes of the mix were treated and dispatched by truck to a hazardous waste disposal centre. Two subsequent neutralisation operations on 12-tonne mix batches had been completed by Friday evening after draining tank T35 and hauling its contents offsite.

[1] Aromatic organic compounds, also called "thiol", display a sulfhydryl group (-SH), e.g. methanethiol, used to odorise natural gas due to its strong olfactory effect at very low concentrations. The isopropanethiol (or isopropyl mercaptan) involved in this accident possesses an olfactory detection threshold of less than 1 part per billion (ppb).

Friday 25 to Saturday 26 January: During the night, 5 tonnes of oil were poured into tank T76 in order to dissolve the unstable products remaining on the bottom. Tank contents were then drained into tank T35, which contained a new batch of neutralising solution, prior to a road transfer scheduled around 6 am. Once the drainage step had been completed, a pasty residue[2] could be observed on both the tank walls and stirrer shaft.

Saturday 26 to Sunday 27 January: Since this pasty residue was still causing considerable gaseous emissions in tank T76, the tank was filled with 25 tonnes of oil while the stirrer was kept running so as to gradually dissolve the remaining residue. At the same time, the Prefect authorised a resumption of packaging / shipment activities for finished products rolling off the lines in other units.

Monday 28 and Tuesday 29 January: Another solvent (ethylhexanol) was introduced to better dissolve the solid residue left in tank T76 and on the stirrer. Several instances of a clogged recirculation filter attested to solvent efficiency.

Wednesday 30 January to Sunday 3 February: The residue dissolution protocol continued, in conjunction with drainage immediately upon saturation of the cleaning mix.

Monday 4 through Wednesday 6 February: Tank T76 was emptied of the cleaning mix. An endoscopic inspection of its bottom revealed a chunk that had not been removed from a recess. Pure solvent was once again injected. Another endoscopic control performed at 11 pm on Monday confirmed product dissolution following drainage of the mix using a soda water/bleach solution. The final cleaning phase with soda water was completed Wednesday morning around 9. The tank was opened at noon, deodorised and rinsed with water. At 12:30 pm, the Prefecture's crisis management unit was disbanded and the External Emergency Plan lifted. The Prefect authorised all site activity to resume, except for the specific workshop concerned, where operations remained suspended in compliance with an emergency order enacted on 21 January.

## Consequences of this accident:

The ZDDP decomposition generated several toxic or flammable by-products in the adjustment tank. Since this tank's vents were connected to the gas treatment system, all or some of these by-products wound up being treated by the washing columns integrated into the plant's treatment system (see Table 1).

| By-products stemming from ZDDP decomposition | Estimated quantity produced in the tank (kg) | Maximum quantity discharged to the stack (kg) | Average concentration at the chimney / night of $21^{st}$-$22^{nd}$ Jan. (ppm) conservative estimate[3] | Max. concentration in the environment[4] (ppm) | Primary hazards |
|---|---|---|---|---|---|
| **Mercaptan** | | | | | - Toxic through inhalation at high concentration, threshold set at 20 ppm for 8 hrs of accidental exposure and 0.5 ppm for professional exposure.<br>- Strong foul smell at low concentration: olfactory threshold < 1 ppb. |
| Isopropanethiol | 430 | 214 | 2036 | 10 | |
| Methyl penthane thiol | 115 | 58 | 356 | 1.8 | |
| **Hydrogen sulphide** | | | | | - Toxic through inhalation, thresholds at 372 ppm (lethal effects) and 80 ppm (irreversible effects) for 1-hr exposure.<br>- Foul smelling at low concentration: olfactory threshold at 20 to 100 ppb. |
| | 95 | N/A | < 0.34[5] | / | |
| **Olefins (alkenes)** | | | | | - Easily flammable.<br>- Irritating for the eyes, skin and respiratory tracts.<br>- Toxic through inhalation at very high concentration (> 5,000 ppm), threshold of 500 ppm for professional exposure. |
| Propylene | 2,492 | N/A[6] | N/A | N/A | |
| Methyl-pentenes | 554 | N/A | N/A | N/A | |
| **Sulphide compounds** | | | | | Foul smelling at low concentration: olfactory threshold at 20-100 ppb, vegetable smell during decomposition. |
| | 17 | < 10 | < 10 | N/A | |

*Table 1: Evaluated quantities and concentrations of the main ZDDP decomposition by-products during the accident, under the most conservative hypothesis (site operator / Ineris / DREAL)*

The performance of this system was not adequate to eliminate the mercaptan. These compounds, with an extremely low olfactory detection threshold (due to an organic decomposition type smell) and toxic at high concentrations, are capable of causing temporary bouts of nausea, digestive disorders, headaches, eye and throat irritations even at low doses.

The mercaptan released was of the $C_3RSH$ and $C_6RSH$ varieties (mainly isopropanethiol and 4-methyl-2-penthanethiol). Their oxidation in the presence of olefins[7] resulting from decomposition also gave rise to the formation of sulphide compounds (sulphides and disulphides). These mercaptans were dispersed into the atmosphere at a rate depending on the wind force and intensity, both of which changed several times on the day of the accident and the day after. The

[2] A "peanut butter" type of bulk grease, estimated at 3,300 kg per site operator, contains 61% sulphur-rich solids.
[3] In adopting the conservative hypothesis of a maximum discharge over a minimum duration: approx. 12 hours, 30 min.
[4] Using the lowest coefficient of dilution observed during the accident (200).
[5] Excluding the 4-ppm peak recorded on 21 January between 10:30 am and 11 am.
[6] In considering the plant's gas treatment system efficiency to be negligible on the olefins and according to the same set of hypotheses as those applied for sulphur compounds, the maximum concentration reached in the environment would not have exceeded some 100 ppm (with a maximum measured during the subsequent days of less than 50 ppm).
[7] Mainly propene and methyl-pentenes.

plume covered a wide geographic zone extending from the south of England to the Paris Metropolitan Area (Fig. 6), adversely affecting tens of thousands of individuals and, in some instances, responsible for headaches, nausea and temporary vomiting. The InVS Institute's health monitoring of population living near the plant indicated that the accident only had minor repercussions on the activity of health emergency services in the city of Rouen: fewer than 20 medical visits on 21 and 22 January, including two house calls (one of which was an asthma attack requiring hospital treatment).

The neutralisation phases generated 270 tonnes of liquid effluent with a basic pH, containing 2.5% sulphur for the neutralised solution and more limited rinsing solution contents (this ZDDP batch initially contained 15%); the corresponding transport to a disposal centre and incineration required 17 road tanker trips and produced emissions equivalent to 192 tonnes of $CO_2$. No other environmental impact was recorded.


*Fig. 6: Synopsis of the plume's path over the period 21st to 23rd January 2013 (La Croix newspaper)*

The chronology of external effects and related media repercussions from this accident is summarised below:

Monday 21 January: The operator received the initial complaints from neighbours around 10 am, at which point it activated the site's Internal Emergency Plan and informed municipalities in the vicinity, the Prefecture and the DREAL Environmental Agency. The Prefecture issued two press releases around 1 pm and 2:30 pm and gave statements to the local media (France Bleu, France 3 stations). At the same time, the GALA[8] system notified the 33 town halls of municipalities potentially lying downwind of the plant (Fig. 7).

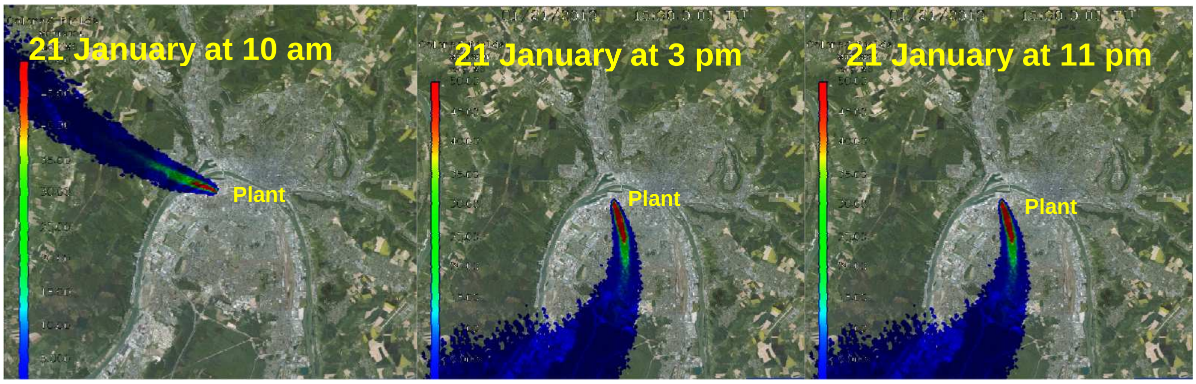



*Fig. 7: Modelling of the foul-smelling plume in the vicinity of the plant on 21st January (Ineris)*

Around 3 pm, the wind direction changed and the odour spread in and around the city of Rouen; information began to circulate on social media as well (Fig. 8).


*Fig. 8: Tweets shared on social media, during the afternoon of Monday 21 and morning of Tuesday 22 January (Twitter)*

From 5 pm until midnight, calls from concerned individuals began to flood switchboards of the fire department, police and Rouen main hospital. The fire department switchboard, which received over 2,900 incoming calls, reported being temporarily saturated. A Prefecture press release was issued at 7 pm. The plant received 70 direct calls from nearby residents.

Tuesday 22 January: During the night, the wind changed directions several times. The smell of mercaptan first reached the Paris metropolitan area, then southern England (Figs. 6 and 9). The switchboard of Paris' fire department received over 10,000 calls during the morning hours. The French Ministry of the Interior disseminated an initial press release

[8] Local remote alarm system automatically warning the town halls of municipalities threatened by a major hazard (natural, technological, etc.).

around 5 am. At the Rouen Prefecture, the county operations centre was up and running at 7 am and the population information unit by 10 am. As a preventive measure, the Prefect also activated the External Emergency Plan at 10:35 am. The Prefecture released an announcement to the press at 11:30 in the morning.

The crisis became a national event and the crisis management units of the Ministries of the Interior, Sustainable Development and Health were alerted as of 2 pm. A national football match scheduled during the evening had to be postponed. The Prefecture held a press conference at 3:30 pm. At 4:40 pm, the Ministries' first press releases were uploaded to the Internet, as was the plant operator's. The Prefecture held another press conference at 5 pm. The Minister of Ecology, Sustainable Development and Energy conducted a site inspection at 7 pm.


*Fig. 9: Modelling of the foul-smelling plume (shown in red) between 21st and 22nd January (Ineris)*

Wednesday 23 January: Employees at neighbouring industrial sites were authorised to return to work. The Prefect held two press conferences at 7 am and 5 pm (Fig. 10). The plant updated its press releases on the company website.

*Fig. 10: Succession of press conferences at the Prefecture, along with interviews of authorities during the first few days of the accident event (Paris Normandie / France 3)*

Thursday 24 January: The Prefect reviewed the situation during two press conferences at 11 am and 5:30 pm.

From Friday 25 through Wednesday 30 January: A daily press bulletin published by the Prefecture indicated the state of progress in cleaning the neutralisation tank and disposing of the residue.

Wednesday 6 February: A press release announced the completion of neutralisation operations and lifting of the External Emergency Plan.

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

The "hazardous substances released" index is rated a "2" due to the absence of airborne discharge of $H_2S$ and only the 272 kg of mercaptan are to be taken into consideration for a "Seveso" (toxic) threshold of 200 tonnes.

The "human and social consequences" index is scored a "3" since fewer than 20 medical consultations attributable to the accident were required by the Rouen Metropolitan emergency services for individuals displaying symptoms of nausea, headaches and irritations of their upper respiratory tracts.

The "environmental consequences" index could not be rated given the absence of environmental impacts.

The "economic consequences" index received a temporary score of "2" as a result of costs associated with the neutralisation / elimination operations and production losses caused by shutting down the ZDDP manufacturing line for several months, with these costs still ongoing at the time this accident report was filed.

## THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THIS ACCIDENT

The starting point of the sequence that led to this accident consisted of human error. On Friday 18 January, the technician on duty mistakenly turned on the adjustment tank stirrer instead of the recirculation pump on the control board, despite a different labelling and triggering mode (pushbutton for the stirrer and a handle for the pump, see Fig. 11). He then failed to turn off the stirrer when returning to the unit to start up the pump after noticing its idle status on the control room display. This stirrer did not draw any special attention from technical staff due to the fact it had, in theory, been decommissioned for several years.

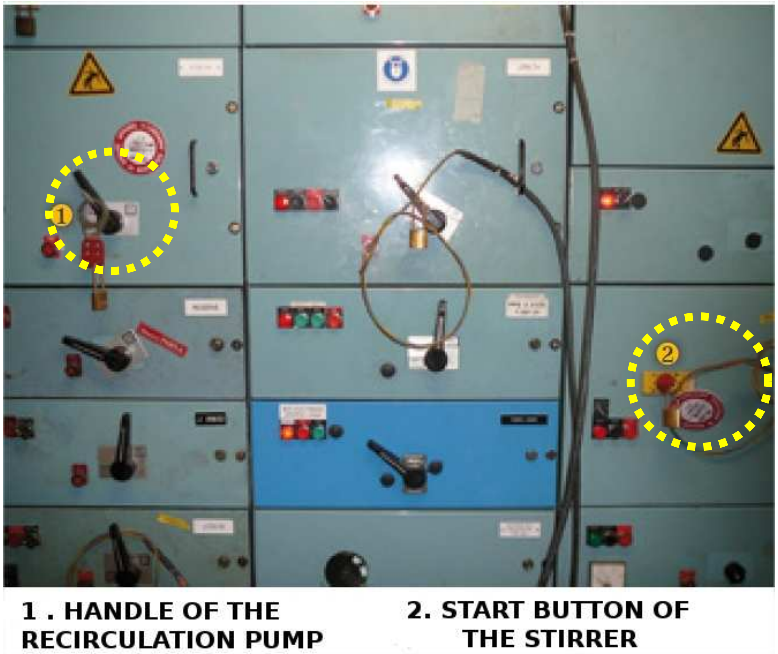



*Fig. 11: View of the control board for the process implicated in the accident (Preventique Group)*

Subsequently, a "collective error" stemming from the failure to detect the temperature rise in time to prevent the accident from occurring can definitely be cited. During the ensuing weekend, the technicians assigned to monitor the installation failed to notice that the stirrer was operational, despite the indicator light being lit on the control board and the visibility they had of the stirrer shaft rotating at the top of the tank (Fig. 12). On Sunday 20 January, the technicians on duty in the control room also showed a lack of concern for an eventual gradual temperature rise in the tank. Since Friday, the tank's recirculation pump had been shut down and temperature detection in the recirculation loop was no longer indicating the actual temperature existing inside the tank.

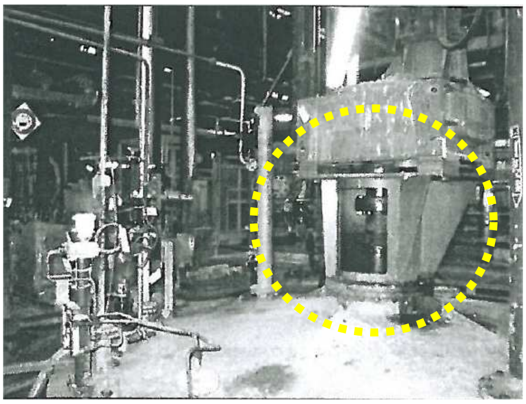


*Fig. 12: Stirrer motor and shaft visible on the upper part of adjustment tank T76 (plant operator)*

This sequence, as part of the production context (with the product remaining in the adjustment tank due to reduced market demand and arriving at a normal temperature of 94℃) and unit configuration (heat-insulated tank, continuous operation of the stirrer, causing the product to heat by 1℃/hr [9] as of Saturday night), initiated a slow ZDDP decomposition reaction, with temperature in the tank surpassing 110℃ by 8 am Monday morning.

Moreover, two elements contributed to exacerbate this accident:

- a delay in preparing the 1st neutralising solution on Monday morning subsequent to difficulties encountered in starting up the mobile mixer (due to a missing drive), logically resulting in a poorly mixed solution;
- performance of the gas treatment system which, despite being well designed to treat the $H_2S$ released quickly became saturated once mercaptan emissions rose to high levels.[10]

Beyond these direct causes, the accident analysis exposed several deep-rooted organisational type causes:

- **An insufficient process risk analysis:** The risk of ZDDP decomposition when stored for several days around 100℃ had not been identified, even though the site's safety report had anticipated such a risk for shorter exposures at temperatures of around 120° to 130℃. A greater recognition of the significance of measuring temperature for process safety would have led the plant operator to set up several temperature measurement points instead of just a single one on the tank recirculation line (solely available during pump operations). Given the absence of such features, technicians were only able to notice a temperature rise in the tank on Monday morning at 7:50 am, when the pump was turned on after detecting suspicious odours in the unit, and a mere 3 minutes before the high temperature alarm on the adjustment tank was tripped. Moreover, taking account of the heating risk inside the adjustment tank, especially given the presence of a stirrer, would have resulted in the removal of its heat insulation which was useless for the process.

  Focused on the risk of toxic $H_2S$ emissions, the unit's analysis also paid insufficient attention to the risk of a massive mercaptan release. The gas treatment system had only been designed for low mercaptan emissions, and the emission measurement chain at the stack outlet had only been calibrated to measure trace amounts of mercaptan.

- **Poor management of change:** Unlike the pump, the stirrer had not use in the process and furthermore its operating status was not relayed to the control room. The unit's technical staff had not been given specific instructions on the stirrer's condition or its manual activation. The adjustment tank, used previously in another process, had been transferred to the ZDDP unit in 1997 without any prior "management of change" type of analysis that could have revealed the need to eliminate the stirrer or, at the very least,[11] allowed technicians to learn of its operating status. In addition, technicians had not been made aware of the potential consequences of a rotating stirrer for process safety. During their rounds, technicians were thus concentrating on a visual inspection of other indicators and equipment inside the building, even though the indicator was lit and the stirrer shaft was visibly rotating at the top of the tank.

- **A debatable technical choice** regarding the safety barrier selected to avoid storage tank overflows. Since the unit was being controlled remotely from the control room, the technician on duty was not accustomed to manually activating the adjustment tank recirculation pump from the control board, given that the programmable operations and safety controller normally handled this task, but the very high level of one storage tank had, for safety reasons, disabled the remote start-up function on the pump at 2 pm on Friday. As a risk of ZDDP storage tank overflow existed, given that the transfer line leading from the adjustment tank could not be closed remotely, an indirect "software" safety barrier (obstructing the recirculation / transfer pump) was the chosen option for mitigating this risk rather than a direct "physical" safety barrier involving installation of automatic shutoff valves instead of manual valves.

- **Inadequate control over maintenance operations:** Even though the stirrer start-up switch on the control board had been decommissioned in 2006 (it had become apparent that the stirrer was adversely affecting the quality of finished products by virtue of generating particles), poor supervision of maintenance operations conducted on the adjustment tank later led to the accidental commissioning of the stirrer.

- **A lack of practice in performing neutralisation operations:** During preparation of the zinc oxide mix, an excessive quantity of powder inserted into the mixer caused a short-circuit on the mixer's electrical supply line. By hastily disconnecting the plug from its socket, the plug was stripped due to a lack of familiarity with its specifications, an action that prevented subsequent use. The mix was produced "by hand", which not only delayed its implementation, but also led to lower homogeneity and efficiency.

[9] According to the results of thermodynamic modelling conducted by the site operator after the accident.
[10] The operator evaluated its output at a maximum of 50% of the mercaptan released.
[11] Accident response steps revealed that the stirrer might, on the other hand, have facilitated the neutralisation of ZDDP decomposing in the tank.

## ACTIONS TAKEN

The DREAL Environmental Agency , alerted midday on 21 January, visited the site the same day and proposed an order consisting of emergency measures prescribing shutdown of the ZDDP manufacturing facility, in imposing that it only be restarted upon implementation of a series of remedial actions derived from the analysis of event causes and identification of equipment on which a similar event could recur.

Given the operator's inability to resolve this problem according to the outlined set of procedures, causing among other things pre-emptive activation of the External Emergency Plan on the morning of Tuesday 22 January, six inspectors worked in shifts on-site around the clock (in addition to a continuous presence for 10 straight days in the Prefecture's crisis management unit and a permanent correspondent at the DREAL office for the first two days) until completion of the response on 6 February. Each step of these neutralisation operations was formalised by the operator into protocols, evaluated with assistance from the INERIS Institute and validated by the Prefect (compliance was controlled on-site by the Inspectorate). The DREAL Agency also assigned INERIS agents to oversee emissions measurements taken in the field as of the evening of 22$^{nd}$ January following saturation of the continuous measurement devices set up on-site.

Subsequent to this crisis, actions adopted by the competent authorities were primarily intended to:

- consolidate the environmental impact, mainly with the aim of validating the emission evaluation hypotheses through conducting a dispersion study in corroboration with the location distribution of all complaints recorded during the crisis;
- provide exhaustive information, as known by administrative authorities, to all pertinent local actors and joint feedback, in collaboration with the various institutional players (at the national level, spearheaded by air quality monitoring associations, INERIS and the Ministry of Sustainable Development) so as to improve response steps specific to such events, as well as with the local level (namely Prefecture offices, DREAL Environmental Agency, Health and Air Quality monitoring agencies to streamline communication procedures during accidental situations).

## LESSONS LEARNT

The plant operator learned a number of technical and organisational lessons:

**Technical lessons leading primarily to:**

- removing the adjustment tank heat insulation and procuring cooling systems for 15-minute availability on those unit tanks and exchangers not equipped with such cooling devices;
- maintaining the adjustment tank stirrer for the purpose of homogenising the product mix with a neutralising solution in the event of decomposition. Stirrer activation either locally or remotely will only be possible via an automated system activated by authorised personnel and solely in the event of ZDDP decomposition;
- after the feasibility study, modernising the control system and separating it from the automated system dedicated to safety, by means of creating displays and hierarchical alarms dedicated to preventing the decomposition risk, with continuous monitoring of $H_2S$ and mercaptan concentrations at the level of production equipment and at the stack outlet;
- enhancing reliability of the mobile mixer's electrical supply and improving the devices used to feed the neutralising mix;
- redesigning the unit's gas treatment system based on a conservative scenario of accidental emissions, to be capable of treating 100% of the mercaptans and alkenes released according to this scenario, while raising online analyser performance: extended measurement range, measurement of total sulphur content, etc.

**Lessons of an organisational nature primarily intended to:**

- modify the unit's operational procedures on the basis of feedback drawn from the accident, especially for process monitoring should manufacturing be interrupted, as well as for degraded operating modes and emergency procedures;
- adapt the neutralisation procedure to suit decomposition characteristics;
- strengthen personnel training and raise awareness of both the risks associated with ZDDP decomposition and emergency procedures, with a recycling component held every three years;
- improve the evaluation of ZDDP decomposition risks present in the management of change process and analyse the decomposition-related risks on equipments reallocated to the ZDDP unit in 1997: filter press, plus filtration and adjustment tanks;
- bolster the reliability of safety systems by means of upgrading control and test procedures and supervising alarm bypass and shunt conditions tied to the set of instrumented devices.

In conjunction with remedial actions implemented by the plant operator, the Ministry of Sustainable Development sought to draw lessons regarding the way in which this accident response was managed. In April 2013, the Ministry announced the enactment of some 20 measures intended to strengthen safety around Seveso-rated industrial sites within the scope of a "mobilisation plan for preventing technological risks". This plan stipulates the creation of a rapid intervention force capable of both quickly deploying experts along with resources from other industrial sites and engaging independent laboratories and associations to measure without delay the level of accidental releases. The plan also specifies an accelerated implementation of Technological Risk Prevention Plans, plus additional financial assistance for the protective works imposed by these plans on local authorities and neighbouring communities.


*Fig. 13: Media feedback from this accident in the international press*