

Fire wash tank explosion in a hydrazine derivative manufacturing facility

July 11th, 1999

**Lannemezan (Hautes Pyrénées)
France**

Thermal decomposition
Human error
Organisation / deficient process controls
Procedures / instructions
Modification management / SMS
Risk analysis
Equipment malfunction

THE FACILITIES INVOLVED

The site:

The chemical facility in Lannemezan employs 180 persons and synthesizes hydrate from hydrazine and some of its derivatives. The establishment is SEVESO classified for its chlorine (100 tons) and ammonia (500 tons) storage facilities.

The involved unit:

The unit produces Azobis 2 methylbutyronitrile (AIVN), a hydrazine hydrate. This was the 4th production series of this product, each series lasting 2 to 3 weeks.

After reaction, the AIVN is recovered using a centrifuge, and then dried. The wash-water from the centrifuge is collected in a tank, then drained into the "acid juice" pit.

THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident:

At the end of the batch, as the centrifuge was damaged, the AIVN content in the wash-water was too high. The technician, anticipating that draining the tank would be difficult using the tank's pump, introduced a hose into the tank via the inspection hatch and heated the mixture with steam (128°C) for 15 minutes.

The instructions call for washing with water at 40°C; because the AIVN decomposes at 50°C. The decomposition of the mixture began to accelerate and after 70 minutes of latency, the tank exploded at 11:53 am. The cover, secured by 50 bolts, was ripped off and thrown away by the blast. The decomposition gases spread through the workshop and caught fire, with flashback to the tank. The fire then attained the combustible parts of the unit.

The POI ("Plan d'Organisation Interne", internal contingency plan) was put into action. Combustion of the AIVN stopped 5 minutes later. Total extinction of the areas where the fire started by hot points in the workshop occurred after 35 minutes thanks to the plant's internal fire prevention means.

Consequences of the accident:

No one was injured; the 2 individuals normally present during the operation had left due to a shift change between 11:45 am and 12:00 pm.

The accident had no environmental consequences.

The workshop was 50% destroyed and all derivative manufacturing operations were suspended. The damage (10 MF) concerns primarily the equipment in question (tank, centrifuge, belt filter...) and combustible materials (electric wiring, PVC piping...).

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 II' directive on handling hazardous substances, and in light of the information available, this accident can be characterised by the four following indices:

Dangerous materials released			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input 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"/>

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

The overall level of the "hazardous materials released" index scored a "default value" of 1, since the TNT equivalent of the explosion is unknown (parameter Q2).

Given that no human or environmental consequences were reported, both the corresponding indices ("human and social consequences" and "environmental consequences") posted a 0.

Lastly, the "economic consequences" index is valued at 2, given that damages amounted to between €0.5 and €2 million.

THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THE ACCIDENT

There was abnormal accumulation of AIVN in the tank considering the wear of the centrifuge fabric (sheet ripped). The accident occurred on a new fabrication using an existing production line. The safety manual had been compiled by analogy with the product previously manufactured (AZDN), although the latter was less tacky and less abrasive than the AIVN.

Having anticipated pumping difficulties, the technician replaced the hot water washing operation by heating the solution with steam, causing the temperature of the tank to rise to a temperature greater than the AIVN's self-accelerated decomposition temperature. The self-accelerated decomposition temperature is 85°C for AIVN in powder form and 50°C in this case (AIVN in blocks).

The rinsing water formed a "thermal buffer" until depletion by boiling; the rise in tank pressure thus caused the cover to rupture and be projected into the air. The combustion of the AIVN was incomplete as it was very avid for oxygen, causing a significant black carbon deposit inside the tank. The lack of deposit on the internal surface of the cover shows that the AIVN decomposition gases exploded then caught fire with flashback to the tank.

This accident thus results in 3 simultaneous causes:

- √ Accumulation of the product in the tank due to the deterioration of the centrifuge caused by the abrasive character of the AIVN.
- √ Poor design of the tank, designed for AZDN and not suitable for the production of AIVN, which is a more tacky substance. The preliminary hazard analysis should have identified the differences between the 2 products. The safety mechanisms existing for the AZDN could have been completed.
- √ Excessive heating of the tank as a result of the initiative of the technician, ignoring the hazards involved with this manufacturing operation.

The absence of an alarm and temperature measurement should also be noted.

ACTIONS TAKEN

A prefectural order conditioned the restart of the derivatives facility upon the presentation of a safety study and manual for AIVN.

The study must include an analysis of the accident's circumstances and causes, the measures to be taken to ensure that an accident of this type does not happen again and to ensure production in safe conditions (to avoid product accumulation), a reliability study on the operation of the AIVN fabrication activity with the establishment of recommended safety measures. Prior to 11/01/99, the operator must conduct a study of the decomposition hazards and establish measures to be taken relative to all the derivatives produced at the site. General awareness-raising actions must be

taken with the personnel relative to safety (strict respect for procedures and instructions). The activity will only be allowed to resume after regulated facility inspectorate has issued its report relative to the study on the AIVN process.

A complete analysis of process safety led to

- √ the reduction of the sticky characteristic of the AIVN. This property is a result of the impurities produced during the process. The manufacturer plans to optimise chlorine consumption, to improve the purity of the Cyanhydric MEK by changing the supplier, and to increase its introduction speed in order to improve the reaction yield.
- √ The search and elimination of accumulation zones (examination of all product lines, vent and effluent). The design of the wash-water recovery tank was reworked: addition of an agitator, temperature and pressure control, explosion vent and the workshop roof with conical bottom. A new vent recovery line was installed: removal of high points, hot-water cleaning is replaced by cleaning with pressurized water.
- √ a temperature monitoring resulting in modifications on the safety devices to be installed.
- √ new instructions and training for the personnel about the specific hazards related to the decomposition of unstable products.

LESSONS LEARNT

The procedure for shutting down the AIVN manufacturing operation was not adequately precise, particularly concerning the tank drainage operations. This procedure was still undergoing tests for a production cycle that had just begun (4th series). This was the second accident in less than one year on the site, due to the unfortunate initiative of an operator associated with a weakness in the safety organization.

This accident was caused by breakdown in supervision for a process that had been launched, due first and foremost to adapting current operating procedures without conducting an assessment of safety conditions relative to a new process, which differed from the previous one. The existing production line was being used without any modification, even though the products manufactured displayed different characteristics (AIVN being stickier and more abrasive than AZDN; the presence of an accelerated decomposition temperature for AIVN). All new production operations conducted on existing lines must be thoroughly examined to verify equipment suitability, safety features and operating protocols.

The lack of compliance with current procedures and instructions as well as an improvised response when confronted with an unexpected situation are what triggered this accident. Such observations underscore the importance of appropriate training for operating personnel in order to manage the risks inherent in a controlled production setting and ensure instructions are being properly followed.