

## Silane leak and fire in a gas conditioning facility

30th march 1999

**Chalon-sur-Saône (Saône et Loire)  
France**

Compressed gas  
Organisation /  
Management of  
modifications  
Procedures  
Risk analysis  
Pressurised equipment  
Design flaws  
Fittings  
Access constraints

### THE FACILITIES INVOLVED

#### The site:

The site is a storage, conditioning and unloading centre of gases primarily used in the high-technology electronics industry (the manufacture of semi-conductors). The gases used at the site are grouped into four main categories:

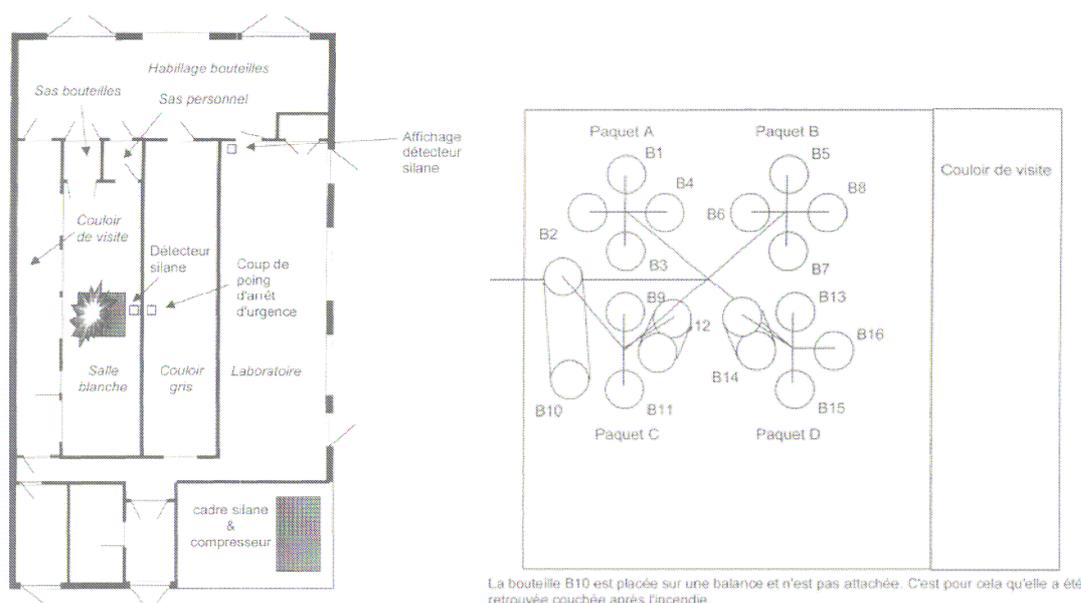
- √ hydrides (silane, arsine, phosphine, diborane,...),
- √ corrosives (chlorine, hydrogen chloride,...),
- √ fluorinated gases (hexafluoroethane, tetrafluoromethane,...)
- √ organometallic gases (trimethylgallium, trimethylaluminium,...) which are only stored.

A fifth category is stored in greater quantities: oxide gases (nitric oxide, carbon monoxide...).

The establishment is located approximately 1,500 m from the town centre and employs 48 persons. The plant operates under the SEVESO directive for its arsine and phosphine storage facilities.

#### The involved unit:

The workshop in question was built in 1993 and formed the subject of a specific authorization request file which resulted in the prefectorial authorization order of July 22nd, 1993. The request concerned a white room to avoid pollution during cylinder connection and disconnection operations. The gases concerned by the authorization were silane, phosphine and the CF4 type fluorocarbon compounds. The workshop was used only for conditioning silane and, in light of the quantities used, it was not subjected to a section in the nomenclature.



*Scheme of the building and bottle organisation within the white chamber (source operator)*

## THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

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### The accident:

At about 9 am, a fire was reported in the white room of the silane workshop. The fire started during the filling operation of 16 silane cylinders from a bank of high-pressure cylinders located outside. An alarm was then sounded following the detection of a silane leak. The operator activated the emergency shutdown which closed all of the automatic valves. No fire was observed.

The operator then closed the two manual supply valves on the bank of cylinders. A second operator who was observing the white room via the observation hall observed two small symmetrical flames develop after approximately 1 minute (typical of a VCR connection) on one of the cylinders. These two flames grew then set the interior of the laminar flow hood on fire without explosion. After fifteen minutes, thick smoke filled the white room.

The electricity was cut to spray down the latter which caused the ventilation to shut down. The fire brigade arrived at the site 20 minutes later, broke the observation hall window and opened the doors to gain access. The natural ventilation of the air revived the fire. The fire was brought under control after a half hour, except for the silane fire as some of the cylinders had ignited leaking silane gas at the neck.

The intervention lasted more than 8 days, until April 7th at approximately 4 pm. At this time, all of the silane in 16 cylinders located in the white room had been released and the entire installation inside the workshop was secure.

### Consequences of the accident:

The accident had no consequence on the environment nor on the population or the personnel. Equipment damage was significant: the direct losses associated with the refurbishing operations were estimated at 11 MF, and production losses at 15 MF.

### 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"/>	<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 checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<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 score of the "Hazardous materials released" index was assigned a "0", given that silane is not listed as a SEVESO Directive substance.

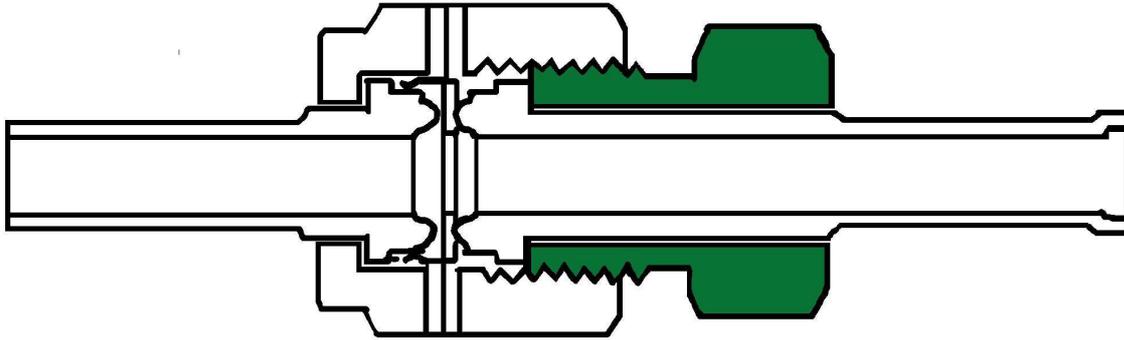
With no human or environmental impact to report, both the "Human and social consequences" and "Environmental consequences" indices were rated a "0" as well.

Lastly, the "Economic consequences" index reached a "2" level, as property damage was announced at between €0.5 and €2 million.

## THE ORIGIN, CAUSES AND CIRCUMSTANCES SURROUNDING THE ACCIDENT

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The origin of the accident was due to a defect in the design of the VCR connectors between the gooseneck and the valve on the cylinders. These components consist of parts supplied by different suppliers which lead to guide length differences of the fitting nuts. In some cases, this could lead to a cross threading which may be gas-tight at the time of leak testing but are rather precarious. In certain cases (hammering or humming transmitted by the gooseneck, shocks, vibrations...), the connection may shift slightly and develop a leak.



*Schematic diagram of a VCR fitting*

The cylinders were filled from a bank consisting of two independent half-banks: while the pressure in the system was stabilized at 17 bar, the operator switched from one half-bank to another and set the pressure of the system at the latter's pressure, or 60 bar. The overpressure probably caused the seal on the VCR connector to suddenly burst.

The installation itself is also at issue as it was designed to load phosphine type toxic gases: workshop confinement, dual ventilation and treatment with active carbon gas in case gas is detected. In this case, the silane caught flame spontaneously in contact with the air creating silica which quickly saturated the filters. Due to the confinement of the facility and the interconnection of the cylinders, the fire spread, strengthened by the presence of the hood and its combustible curtain. The temperature was so hot that the false ceiling collapsed. When the water sprinkler system was activated, the electricity was cut causing the ventilation system to shut down and the re-ignition of the fire when the firemen opened the doors. Also, the fire caused the Teflon seal on the cylinder valves to be damaged, resulting in silane leaks on the other cylinders.

## ACTIONS TAKEN

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It should be noted that the activity actually performed in the workshop (silane conditioning) is not covered by the French nomenclature of classified installations. However, due to the elements which demonstrated insufficiencies regarding the workshop's design, the study of the intervention in the case of accident, and the actions to be taken following the leak test, the inspectorate proposed that the restart of the installation be subject to a new authorization.

## LESSONS LEARNT

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The main causes of the accident are :

- √ Poor installation design (VCR connector poorly designed, poor work station ergonomics).
- √ Lack of precise and strict organization in terms of the analysis of test results: the day before the accident, during the leak test, a leak was detected on a VCR connector. Leaking during tests occurred frequently and no follow-up was initiated.

The VCR connectors must be reviewed (parts of the same origin, connector locking...), and leak tests should be given more importance. All of the cylinders must be able to be closed independently and be isolated by a fire protection, response in case of accident must be better studied, and finally, the design of the facility must be reviewed (hood made of non-combustible materials, heat-resistant false ceiling support structure, smoke ventilation triggered automatically upon detection of smoke, and the room must be insulated by a fire-stop door ...).

The consequences of the accident were limited due to the absence of toxic products in the workshop. Even though incorporated in the design of the facility, the operator's choice not to mix toxic and flammable products in the white rooms appears to have been a wise one.

Tree diagram of causes (Source: Site operator)

