

## Explosion of a railroad tank car containing toxic gas

July 14; 2001

Riverview - [Michigan]

United States

Chemistry  
BLEVE  
Loading / unloading  
Methyl mercaptan  
Chlorine  
Rupture  
Erosion  
Corrosion  
Organisation  
Maintenance  
Inspection  
Procedures  
Safety valve  
Regulations

### THE INSTALLATIONS IN QUESTION

#### Geographic location

The chemical group, headquartered in Philadelphia, has 4,000 employees in 20 plants in the United States and 16 others worldwide.



*Figure 1 - Michigan state*

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In operation since 1898, the Riverview [Michigan] plant employs 212 people. It produces alkylamines, alkylalkanolamines, organic sulphur compounds, hydroxylamines, amyphenol disulfides, hydroxylamines and endothall derivatives, used in multiple sectors and manufacturing operations: main pharmaceutical active substances, electronic components (computer, television, CD player...), cosmetic products, tyres, paints, agricultural products, water treatment and photography... Methyl mercaptan is used in the synthesis of pharmaceutical substances and for poultry feed.

The "Process 46" unit produces methanesulfonyl chloride ( $\text{CH}_3\text{SO}_2\text{Cl}$ ) and methanesulfonic acid ( $\text{CH}_3\text{SO}_3\text{H}$ ) via several synthesis stages implementing methyl mercaptan and chloride. The accident took place in the railway tank car unloading zone. Tank cars are used to supply unit 46.

The substitution of the  $\text{CH}_3\text{SO}_2$ - group of methanesulfonyl chloride in certain reactions produces intermediate chemical products for photography, agrochemical and pharmaceutical substances, as well as stabilisers, catalysers and chlorination agents.

### THE ACCIDENT, ITS BEHAVIOUR, EFFECTS AND CONSEQUENCES

#### The accident

**July 14, 2001.** In order to supply the plant, 3 empty tank cars parked on the unloading siding of the Process 46 building were replaced by 3 full tank cars: 1 containing methyl mercaptan and 2 containing chlorine. In all, 5 tank cars were now on the sidings: 2 containing methyl mercaptan, 2 containing chlorine and one anchor car also for the chlorine. The methyl mercaptan tank cars are connected directly by pipes that supply unit 46 according to production requirements. The chlorine

tank cars were unloaded into an anchor car, which was itself connected to the process building. According to an employee, two operators were in charge of securing and testing the unloading arm connecting the tank cars to the plant's pipework. At 3 am, both chlorine tank cars were connected. An experienced worker then connected the methyl mercaptan tank car.

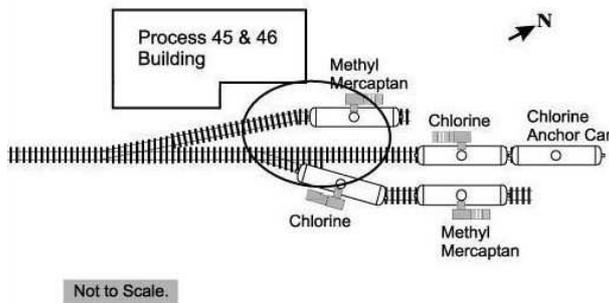


Figure 2 – Location of the methyl mercaptan and chlorine rail cars[1]

At 3.45 am, 2 employees were unloading a methyl mercaptan tank car when the connecting pipe secured on the unloading line ripped free from a faulty valve. Depending on the source, 67 [1] to 74 t of gaseous methyl mercaptan were released into the atmosphere.

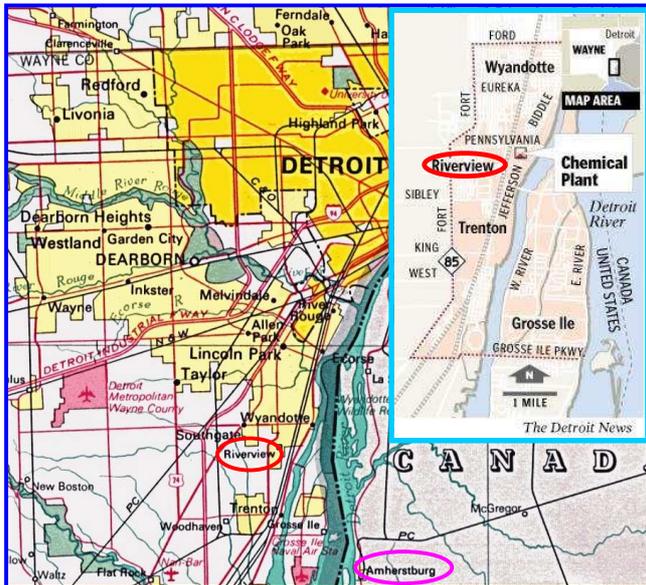


Figure 3 – Riverview localisation

<http://www.baldauf-stefanie.de/images/Detroit/detroit.jpg>  
<http://www.detroitnews.com/2005/metro/0502/04/A01-79779.htm>

An operator pulled the fire alarm and the production foreman alerted the employees and requested that the fire department be called. At 3.47 am, the methyl mercaptan detectors recorded a high concentration of gas on level 2 of the process 46 building. An operator exited the building and discovered the production foreman lying on the ground near the manually tripped fire alarm, roughly 15 m from the unloading zone. The employees working in the other production shops donned self-contained breathing apparatus, made their way to the site of the alarm and discovered the bodies of one of the two operators and the production foreman. They were taken to Riverside Osteopathic Hospital, located 4.3 km from the plant, where they were declared dead.

The firemen decided to spray down the methyl mercaptan tank car after smoke was noticed rising from it. At 3.52 am, the external firemen headed toward the plant and at 3.58 am, 2 units and the police were on the scene.

At 4.09 am, nearly 25 minutes after the start of the accident, a leak was noticed followed by a rumbling noise: the toxic gas ignited, engulfing the tank car in flames, and sending a 15 m-wide fireball 61 m into the air. The tank car exploded (BLEVE) releasing methyl mercaptan and its decomposition products into the atmosphere. The highly

volatile compound can cause skin and eye irritations, as well as respiratory troubles. The Fire Department Chief called for reinforcements from other fire stations. The tank car on fire and those parked nearby were cooled down with sprayed water. Fortunately, the fire did not spread to the rail car containing methyl mercaptan and the 3 rail cars containing chlorine.

The climatic conditions were favourable at the time of the accident: a northwesterly breeze pushed the smoke far from the city. The toxic cloud moved to the southeast in the direction of Grosse Ile, an island in the middle of the Detroit River and connected by 2 bridges to the mainland. A mist cloud was noticed cross the north end of Grosse Ile at around 5 am, and the local police reported that strong odours had been detected. Initially, the order to stay indoors was initially given. After evaluating the situation further, a decision was made to inform residents systematically by telephone to evacuate Grosse Ile by the southern bridge, the only bridge open to traffic to the continent. As a safety measure, 400 residents within a radius of 1 km were initially evacuated. In all, 2,000 people were evacuated for 10 hours in a perimeter encompassing several communities (Riverview, Grosse Ile, Trenton and Wyandotte). Due to the fumes released, at 6.30 am, the American authorities, followed by the Canadian authorities, decided to close part of the Detroit River to navigation until 4.45 pm.

Fire departments from 5 cities came to assist. The fire, which had spread to the chemical plant, was finally surrounded between 8.30 and 9.30 am.



*Figure 4 – Firefighting operations [1]*

Once the fire was put out, employees wearing respiratory equipment discovered the body of the second operator laying on the railway tracks. They then reported the rupture of a 1" steel pipe carrying methyl mercaptan, secured to a 2"-1" adapter, itself screwed on to an open drain valve. The valve was then closed. The 2 valves, connected to the hose that connects the unloading device to the Process 46 workshop, were closed and the hose was burned.

The hose connecting the chlorine rail car to the plant was also destroyed. All of the chlorine system's valves were open when the crews arrived at the unloading zone; 12 of the 81 tons of chlorine in the rail car were released from the time the hose ruptured to when the valves were closed by the rescue personnel.

The leak was stopped at 12.47 pm.

Starting Saturday, July 14th, at around 1 pm, analyses performed by the Environmental Protection Agency's (EPA) mobile laboratory, alerted at 8 am, showed that the air quality was correct.

At 2.48 pm, it was confirmed that all the plant's valves and storage tanks were closed and the evacuation order was lifted. The residents were able to return to their homes as of 3 pm.

The firemen left the scene of the accident at 1.30 am on July 15th. One unit remained on site until July 17th to ensure that the site was secure.

### Consequences

**Significant property damage** was observed; the methyl mercaptan rail care was 90% destroyed (shell, wheels, brakes...). The damage visible on the chlorine railcar were located on the left-hand side facing the methyl mercaptan rail car. The hoses connected to each of the rail cars melted during the fire. The railway under the methyl mercaptan rail car had become twisted due to the intense heat of the fire... The explosion and fire also destroyed the local air analysers.

This accident resulted in the **death of 3 employees: 2 by inhalation of methyl mercaptan, and the 3<sup>rd</sup> by inhalation and burns**. The accident also resulted in **several injuries: 9 workers, 3 firemen and 40 residents**. One of the employees fell and broke 3 ribs after having breathed in methyl mercaptan. 5 others were slightly injured: intoxication... Three members of the rescue crew were slightly burned, including nasal irritations. People living around the plant complained of sore throats, headaches and/or dizziness were quarantined...

Type of injury	Employees	Rescue crew	Other	Total
<b>Deadly</b>	3	0	0	3
<b>Serious</b>	1	0	0	1
<b>Slight</b>	5	3	40	48
<b>Total</b>	9	3	40	52

**METHYL MERCAPTAN** 

This extremely flammable gas is heavier than air and may travel along the ground. Its vapours or gases may ignite at distant ignition sources and flash back. The substance decomposes on burning, producing toxic fumes including sulphur oxides and hydrogen sulfide. Methyl mercaptan reacts violently with strong oxidants, water, steam or acids to form flammable and toxic gas (dimethylsulfide...).

Air/gas mixtures are explosive; closed system, ventilation, explosion-proof electrical equipment and lighting may be used...

<http://www.cdc.gov/niosh/ipcsnfrn/nfrn0299.html>

**European scale of industrial accidents**

By applying the rating rules of the 18 parameters of the scale made official in February 1994 by the Committee of Competent Authorities of the Member States that oversees the application of the 'SEVESO' directive, the accident can be characterised by the following 4 indices.



The parameters that comprise these indices and the corresponding rating method are indicated in the appendix hereto and are available at the following address: <http://www.aria.ecologie.gouv.fr>

The 67 or 74 tons of methyl mercaptan released represent 33 to 37% of the corresponding Seveso threshold (200 t – highly flammable liquefied gas), which equals level 4 of the "dangerous materials released" index according to parameter Q1 (Q1 between 10 and 100%).

The 12 tons of chlorine released represents 48% of the corresponding Seveso threshold (25 tons - chlorine), which equals level 4 of the "quantities of dangerous materials" index according to parameter Q1 (Q1 between 10% and 100%).

As the effects of the explosion had not been characterised and windows were broken at distances less than 300 m, parameter Q2 was given a rating of 1.

The overall "dangerous materials released" rating is thus 4.

Three parameters are involved in determining the level of the "Human and social consequences" rating: H3, H4, H5 and H7.

- The parameter H3 reaches level 3: 3 deaths.
- The parameter H4 reaches level 1: 1 employee seriously injured.
- The parameter H5 is 3: 48 slightly injured.
- The parameter H7 is 4: 2,000 people evacuated for 10 hours (N = 2,000 x 10 hours, 5,000 ≤ N < 50,000).

As a result, the overall "Human and social consequences" rating is 4.

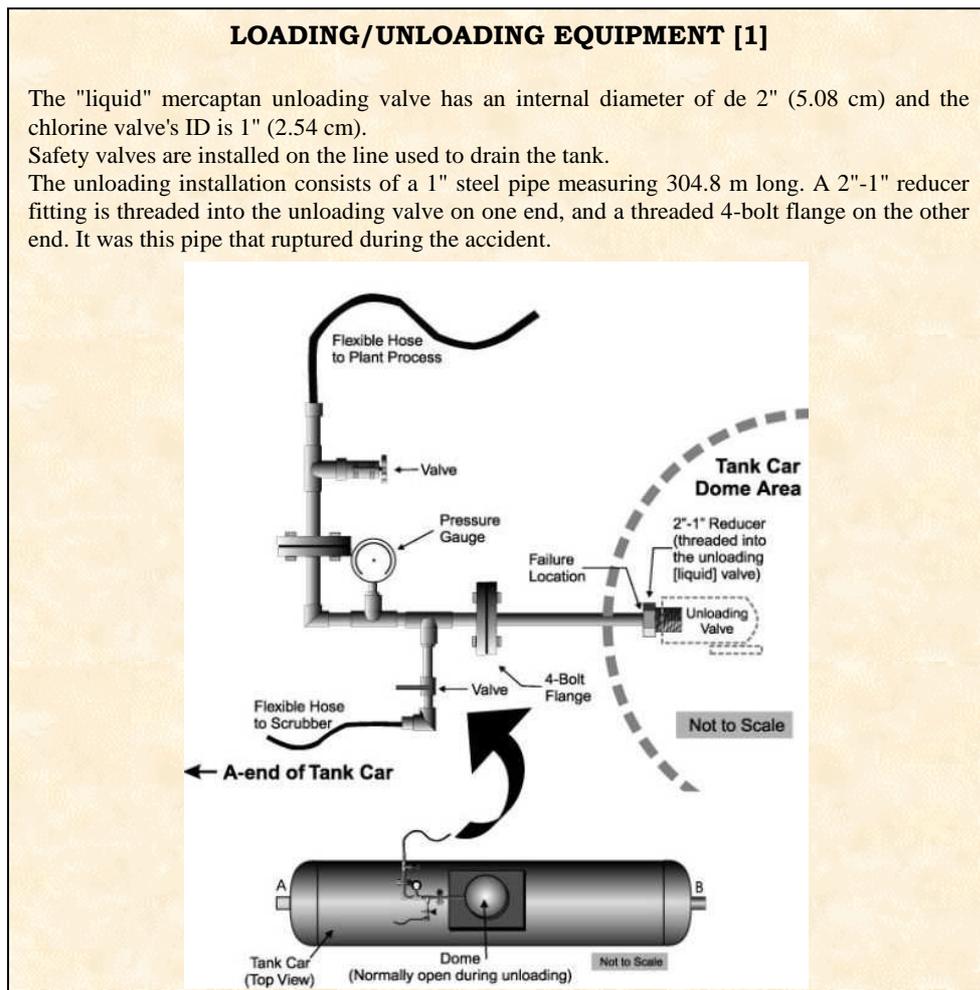
## ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

According to the National Transportation Safety Board (NTSB) [1], the primary cause of the accident was the disregard for safety rules. The NTSB's report stipulated that the transfer line was eroded and corroded; traces of rust and pitting are visible inside and outside the pipe. Routine visual inspections conducted during each unloading operation had nevertheless not detected the deterioration of the 1" (2.54 cm) steel pipe. The measurements show that the thickness of the pipe's internal wall at the fracture had decreased 23% in relation to a new pipe. The accident was the result of insufficient maintenance and inspection of the transfer equipment, as well as inappropriate monitoring of the unloading of dangerous substances by the Federal organisation. The manufacturer stated that no inspection or replacement had been made on the ruptured pipe in 5 years.

The manufacturer had included methyl mercaptan unloading instructions in its "Standard Practice Instructions Manual". This document describes the operations required to connect the transfer lines to a methyl mercaptan rail car and to test for leaks prior to unloading. On the other hand, the instructions do not stipulate that operators must wear self-contained breathing apparatus, or the use of hood-masks equipped with an air cylinder (5-10 min) allowing operators to quickly exit the toxic zone. The employees thus do not wear the appropriate equipment (self-contained breathing apparatus...) and must detect methyl mercaptan leaks.

The chlorine unloading procedures stipulate the following: operators must wear self-contained breathing apparatus, ammonia is used to detect chlorine leaks by forming a white cloud.... The only way to stop the release of gas in leak of this kind is to close a manual valve at the top of the rail car, as a remote operating device is not installed.

It appears that the plant did not have an internal contingency plan. According to a local association, chlorine was also released during the accident; two other chemical substances were also involved in the explosion: sodium hypochlorite and TefZel, a modified ethylene and tetrafluoroethylene (ETFE) fluopolymer [15, 16]. According to some inspectors, TefZel would have reacted with the methyl mercaptan releasing the heat that ignited the toxic gas. Other sources indicate that the reaction between the sodium hypochlorite, a strong oxidizing agent, and the methyl mercaptan generated the flash [11].

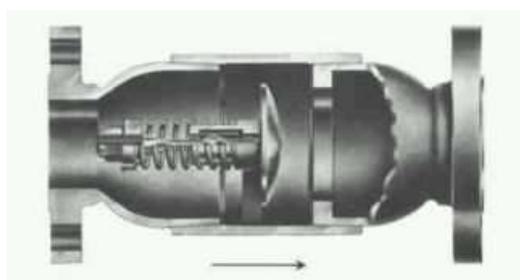
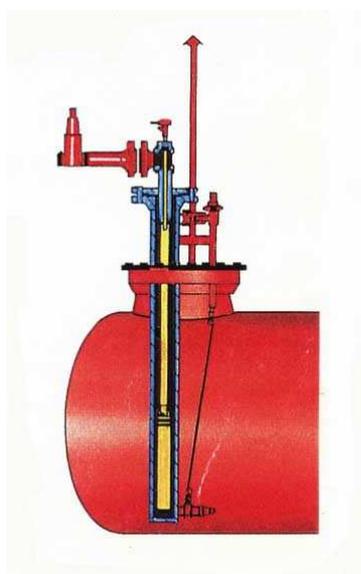


Six methyl mercaptan detectors with an analysis range between 0 and 30 ppm were installed in the Process 46 zone. The sensor's recorder located on the damaged methyl mercaptan rail car indicated "0" or had been out of service for 24 hours.

In the United States, manufacturing facilities are inspected by various administrations such as the "Federal Railroad Administration" (FRA), the "Environmental Protection Agency" (EPA) and the "Occupational Safety and Health Administration" (OSHA).

FRA inspectors had inspected the site 7 times between 1996 and June 2001. These inspections or audits highlight insufficiencies concerning dangerous equipment regulations: insufficient marking....

The EPA considers that transport tankers connected to installations as part of the process equipment. The Agency had received the plant's risk management document on July 3, 2000. At the time, 14 manufacturing process, including that of Process 46, were subject to EPA regulations. The thresholds from which a "risk management" program must be implemented are 4.5 t (10,000 pounds) for methyl mercaptan and 1.1 t (2,500 pounds) for chlorine. Toxic substance release scenarios are established based on the failure of a connecting hose between the unloading arm and the plant's fixed installations. Each scenario includes the safety valve as means to reduce the risk. This risk management program identifies the need to conduct frequent inspections of the unloading lines and to include gas detectors as leak prevention systems. Between June 1996 and July 2001, the EPA performed on-site inspections at 3 of the 2,800 installations subject to the risk management program. Since the accident, the regional EPA has conducted several inspections in this plant.



**Figure 5 – Safety valve**

[http://www.vanaz.com/images/lpgdispenser\\_dig.jpg](http://www.vanaz.com/images/lpgdispenser_dig.jpg)

<http://www.lineflow.com/gen.htm>

OSHA regulations are stipulated in 29 CFR (Code of Federal Regulations). OSHA considers the transport tanks connected to the fixed installation as being part of the process. The thresholds are not the same as those of the EPA: 2.3 tons (5,000 pounds) for methyl mercaptan and 0.7 t (1,500 pounds) for chlorine. From September 8 to November 2, 1994, the members of the MIOSHA (Michigan OSHA) thoroughly inspected both processes, although Process 46 was not included in their operations. The inspectors noted that a safety management program did in fact exist, although it had major shortcomings: 31 serious insufficiencies and 1 deliberate violation of the rules. 18 of the 31 deviations corresponded to process safety management standards, 1 to the lack of inspections and tank, reactor and piping tests... Following these findings, the manufacturer agreed to implement the written procedures regarding the inspection of the installations and the tests aimed at checking the mechanical integrity of the equipment prior to November 26, 1997. The MIOSAH does not ensure that these improvement measures are actually carried out. The procedures do not establish the frequency of inspection cycles: often if the deterioration is extreme, rare if it is minimum... They emphasise the detection of equipment deformations and the rupture of pipe supports. In a post-accident inspection, the MIOSHA identified 22 probable violations of OSHA regulations. The company paid a \$500,000 fine and spent more than \$5 million to improve employee safety.

The Department of Consumer Industry Services sited 22 rules of the safety code that were not respected by the manufacturer.

## **ACTION TAKEN**

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In March 2000, the manufacturer presented a general emergency program for the installations, including procedures specific to Process 46. This document aims to reduce the consequences of explosions, fires or toxic releases on the public health and the environment. A copy was sent to the Riverview emergency services and the surrounding cities. Periodic training programs are scheduled with the Riverview and Wyandotte fire departments.

As causes of the accident were known, the company modified numerous procedures and certain pieces of equipment. The unloading installation, with all the associated piping, must be dismantled every 2 years and tested to check the integrity. In addition, the unloading equipment was redesigned. The operators must now wear self-contained breathing apparatus when they work on the mercaptan tanks and protective masks equipped with an emergency air supply when working in the rail car unloading zone. Since the accident, before opening the rail car valve, the employees conduct leak tests on the unloading installation.

The NTSB feels that the federal regulations insufficient with regard to unloading/loading operations; the FRA regulations concern only the tank car brakes and chocking of the wheels... and foresee neither the inspection, maintenance and servicing of unloading installations, nor the procedures for checking for leaks on the installations or the use of protective equipment by the employees.

The company decided to improve its safety management:

- the installation of a new sprinkling system,
- the installation of supports on the piping in the unloading zone,
- the installation of new underground high-pressure fire hydrant supply lines and 11 additional fire hydrants,
- the redevelopment of the unloading zone in order to move the methyl mercaptan rail cars away from the chlorine rail cars,
- the installation of a more efficient loading area confinement system,
- the construction of firewalls, installation of an additional alarm system and radio on the maintenance workshop.

It requested that a specialised firm conduct a safety audit (\$800,000).

Federal laws require that plants, such as the Riverview plant, to set up contingency plans with both public and emergency response authorities. The company had such a plan, although no information was available to determine if it included monitoring the air.

Local residents regret the inappropriate evacuation, particularly those living on the northern side of Grosse Ile who felt the evacuation was excessively long. The Fire Department Chief stated that he would examine the procedures for possible improvement.

The local residents brought charges against the industrial group for negligence. The State of Michigan negotiated with the industrial group for \$6.2 million in damages, including \$500,000 in penalties and \$5.7 M for improving safety, training and the compensation of residents.

The Ontario emergency services authorities stated that they were not informed of the accident in a reasonable period of time. The authorities in Amherstburg, Canada were only informed several hours after the toxic cloud had passed which effected some of its residents. The Amherstburg Fire Chief requested that a chemical product leak alert protocol be established between the authorities on both sides of the river. The City of Amherstburg, which has several hydrochloric acid and sodium chloride manufacturing plants, operates a siren alert system to warn its population, although Riverview, Grosse Ile and Trenton do not have such a system [11].

The director of the Riverview plant initiated a meeting between the authorities of the 5 cities and 3 manufacturers to define and coordinate an emergency alert system [9].

In 2002, the company accepted to pay \$6.2 M in damages. This agreement includes, among others:

- a fine (\$500,000),
- compensation paid to those evacuated (\$550/person) [8],
- a payment of \$100,000 to Riverview, \$50,000 to Grosse Ile, and \$25,000 to Trenton and Wyandotte,
- the development and implementation of programs designed to monitor, evaluate and improve the safety management procedures and the analysis of dangers (\$800,000),
- the organisation of an emergency training program (\$250,000),
- the creation of a fund in memory of those who perished in the accident (\$80,000),
- the creation of a safety training centre in memory of those who perished in the accident (\$250,000)...

## LESSONS LEARNED

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The NTSB report recommends new regulations regarding the loading/unloading of tank cars / portable tanks. It recommends that the following actions be taken by the agencies concerned:

❖ **US Department of Transportation:**

- Develop, in conjunction with the EPA and OSHA, safety instructions which integrate the inspection and maintenance of unloading equipment, emergency shutdown procedures and individual protection,
- The implementation of a program to monitor these recommendations.

❖ **FRA:**

- Dissemination of a bulletin pertaining to danger equipment to inform the manufacturers concerned by unloading/loading operations and particularly the safety valves installed on the dip pipe which do not allow the systematic shutdown of a leak and which can be considered a safety device in this case.

❖ **OSHA:**

- Develop, in conjunction with the US Department of Transportation, safety recommendations that integrate the inspection and maintenance of unloading equipment, emergency shutdown procedures and individual protection.

❖ **EPA:**

- Develop, in conjunction with the US Department of Transportation, safety recommendations that integrate the inspection and maintenance of unloading equipment, emergency shutdown procedures and individual protection.
- Notify the EPA of all installations governed by the risk management system (identical to the FRA recommendation above). Manufacturers who have based their safety management program on this type of equipment must identify them and implement other systems able to detect a leak on a chemical substance transfer line during a loading/unloading operation.

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