

## Mindre explosion och brand på en kemikaliefabrik.

870430 MARS 1987\_05

Olyckan inträffade på en kemikaliefabrik i en reaktor (reaktor 6) där ett hydrogeneringssteg ägde rum. Ungefär vid midnatt hördes en högljudd explosion från processutrymmet. Då nattarbetarna utrymde byggnaden såg de flammor kring reaktor 6. Det automatiska sprinklersystemet släckte branden. En andra explosion inträffade efter ett par minuter. Denna resulterade i en brand med kraftig svart rök, karakteristiskt för förbränning av lösningsmedel. Sprinklersystemet släckte även denna brand. Räddningstjänsten som anlände kort därefter ägnade sig åt eftersläckningsarbete. Explosionen ansågs ha orsakats av en bristfällig omrörare i reaktorn. Vätgas som läckt ut i lokalen antändes. Den andra branden uppstod då aceton i lokalen antändes.

### Inblandade ämnen och mängder

	CAS Nr.	Mängd
väte	1333-74-0	1-3 m3
aceton	67-64-1	634 kg

### Skador:

Människor:	Inga.
Materiella:	Inga.
Miljö/ekologi:	Inga effekter rapporterade.
Infrastruktur:	Inga.

### Erfarenheter redovisade (Ja/Nej): Ja

Kortfattat anges förebyggande åtgärder.

## Report Profile

### Identification of Report:

country: FA ident key: 1987\_005\_01

reported under Seveso I directive as major accident reports: SHORT+FULL

### Date of Major Occurrence: Time of Major Occurrence

start: 1987-04-30 start:

finish: finish:

### Establishment:

name:

address:

industry: 2001 general chemicals manufacture

Organic Chemical (Chemical Syntheses and Production of Bulk Pharmaceuticals)

Seveso II status: not applicable: Yes art. 6 (notification): No

art. 7 (MAPP): No

art. 9 (safety report): No

### Date of Report:

short: full:

### Authority Reporting:

name:

**address:**

**Authority Contact:**

**rep\_cont\_name:**

**rep\_cont\_phone:**

**rep\_cont\_fax:**

**Additional Comments:**

a) - not applicable -

b) - not applicable -

c) - not applicable -

d) - not applicable -

e) - not applicable -

## Short Report

**country:** FA **ident key:** 1987\_005\_01

**Accident Types:**

**release:** Yes **explosion:** Yes

**water contamination:** No **other:** No

**fire:** Yes

**description:**

ACCIDENT CASE HISTORY DESCRIPTION:... see Appendix Short Report / description of accident types

**Substance(s) Directly Involved:**

**toxic:** No **explosive:** Yes

**ecotoxic:** No **other:** No

**flammable:** Yes

**description:**

- Hydrogen (C.A.S. CODE: 1333-74-0, E.E.C. CODE: 001-001-00-9): amount involved = 0.09 kg (equivalent to 1 m3,

the approximate volume in vapour space above liquid level in reactor)... see Appendix Short Report /

description of substances involved

**Immediate Sources of Accident:**

**storage:** No **transfer:** No

**process:** Yes **other:** No

**description:**

The accident occurred in the Reactor 6 used to carry out the hydrogenation of a pharmaceutical intermediate.

The Company carried out a wide range of chemical syntheses, producing finished bulk pharmaceuticals for

different customers. All th... see Appendix Short Report / description of immediate sources

**Suspected Causes:**

**plant or equipment:** Yes **environmental:** No

**human:** No **other:** No

**description:**

CAUSES:... see Appendix Short Report / description of suspected causes

### **Immediate Effects:**

**material loss:** Yes

**human deaths:** No

**human injuries:** No **community disruption:** No

**other:** No

**ecological harm:** No

**national heritage loss:** No

**description:**

MATERIAL LOSS:... see Appendix Short Report / description of immediate effects

### **Emergency Measures taken:**

**on-site systems:** Yes **decontamination:** No

**external services:** Yes **restoration:** No

**sheltering:** No **other:** No

**evacuation:** No

**description:**

INTERNAL TO THE ESTABLISHMENT:... see Appendix Short Report / description of emergency measures taken

### **Immediate Lessons Learned:**

**prevention:** Yes **other:** No

**mitigation:** No

**description:**

MEASURES TO PREVENT ANY RECURRENCE OF SIMILAR ACCIDENTS:... see Appendix Short Report / description of immediate lessons learned

## **A Occurrence Full Report**

**country:** FA **ident key:** 1987\_005\_01

### **1 Type of Accident**

**remarks:** During an hydrogenation reaction carried out in a reactor of an organic chemical industry, an hydrogen leak occurred (code 1101). As the reactor was located in a general process area with plants operating nearby, the hydrogen easily found a... see Appendix Full Report A / type of accident

### **2 Dangerous Substances**

**remarks:** The total establishment and the potential directly involved inventories of acetone refer to the whole contents of the Reactor 6 (about 1200 litres). The total establishment and the potential directly involved inventories of hydrogen refer t... see Appendix Full Report A / dangerous substances

### **3 Source of Accident**

**illustration:** - not applicable -

**remarks:** The accident occurred in a pressurized batch reactor (codes 3101 and 4002)

used to carry out the hydrogenation of a pharmaceutical intermediate in an organic chemical industry (code 2001). The Company carried out a wide range of chemical sy... see Appendix Full Report A / source of accident - remarks

#### 4 Meteorological Conditions

**precipitation none: fog: rain: hail: snow:**

No No No No No

**wind speed (m/s):**

**direction (from):**

**stability (Pasquill):**

**ambient temperature (°C):**

**remarks:** - not applicable -

#### 5 Causes of Major Occurrence

**main causes**

**technical / physical** 5102 operation: component/machinery failure/malfunction

- not applicable -

- not applicable -

- not applicable -

- not applicable -

**human / organizational** 5302 organization: management attitude problem

5303 organization: organized procedures (none, inadequate, inappropriate, unclear)

5307 organization: process analysis (inadequate, incorrect)

5308 organization: design of plant/equipment/system (inadequate, inappropriate)

5313 organization: maintenance/repair (none, inadequate, inappropriate)

**remarks:** The most probable cause of the accident was a defective agitator (code 5102) that malfunctioned allowing a hydrogen leak. As the reactor was located in a general process area with plants (not suitable for use with hydrogen) operating nearby... see Appendix Full Report A / causes of major occurrence

#### 6 Discussion about the Occurrence

- not applicable -

**Type of Accident** country: FA ident key: 1987\_005\_01

**event:**

**major occurrence** 1307 explosion: VCE (vapour cloud explosion; supersonic wave front)

**initiating event** - not applicable -

**associated event** - not applicable -

**event:**

**major occurrence** 1202 fire: pool fire (burning pool of liquid, contained or uncontained)

**initiating event** 1101 release: gas/vapour/mist/etc release to air

**associated event** - not applicable -

## Dangerous substances

country: FA ident key: 1987\_005\_01

### a) total establishment inventory

CAS number: 1333-74-0 identity: Hydrogen

name from Seveso I Directive: - not applicable -

name from Seveso II Directive: - not applicable -

category from Seveso II: - not applicable -

other hazards (1): - not applicable -

other hazards (2): - not applicable -

maximum quantity (tonnes): 0,001

use of substance as: STARTING MATERIAL

### b) substance belongs to relevant inventory directly involved: Yes

actual quantity: 0,001 potential quantity: 0,001

### c) substance belongs to relevant inventory indirectly involved: No

actual quantity: -1 indir\_pot\_quant: -1

### a) total establishment inventory

CAS number: 67-64-1 identity: Acetone

name from Seveso I Directive: - not applicable -

name from Seveso II Directive: - not applicable -

category from Seveso II: - not applicable -

other hazards (1): - not applicable -

other hazards (2): - not applicable -

maximum quantity (tonnes): 0,634

use of substance as: STARTING MATERIAL

### b) substance belongs to relevant inventory directly involved: Yes

actual quantity: 0,634 potential quantity: 0,951

### c) substance belongs to relevant inventory indirectly involved: No

actual quantity: -1 indir\_pot\_quant: -1

## Source of Accident - Situation country: FA ident key: 1987\_005\_01

### situation

#### industry

initiating event 2001 general chemicals manufacture

associated event - not applicable -

#### activity/unit

major occurrence 3101 process: chemical batch reaction

initiating event 3101 process: chemical batch reaction

associated event - not applicable -

**component**

**major occurrence** 4002 reaction vessel; pressurised

**initiating event** 4002 reaction vessel; pressurised

**associated event** - not applicable -

## **B Consequences Full Report**

**country:** FA **ident key:** 1987\_005\_01

### **1 Area concerned**

**affected**

**extent of effects installation:** Yes

**establishment:** Yes

**off-site; local:** No

**off-site; regional:** No

**off-site; transboundary:** No

**illustration of effects** - not applicable -

**remarks** In the Original Report there is no evidence of significant effects outside the e... see Appendix

Full Report B / area concerned - remarks

### **2 People**

**establishment popul. emergency personnel off-site population**

**total at risk** 1

**immediate fatalities**

**subsequent fatalities**

**hospitalizing injuries**

**other serious injuries**

**health monitoring**

**remarks** No people were injured by the explosion because, when the accident occurred, the... see Appendix

Full Report B / people

### **3 Ecological Harm**

**pollution/contamination/damage of:**

- residential area (covered by toxic cloud) not applicable

- common wild flora/fauna (death or elimination) not applicable

- rare or protected flora/fauna (death or elimination) not applicable

- water catchment areas and supplies for consumption or recreation not applicable

- land (with known potential for long term ecological harm or not applicable

preventing human access or activities)

- marine or fresh water habitat not applicable

- areas of high conservation value or given special protection not applicable

**remarks** In the Original Report there is no evidence of significant ecological harms.... see Appendix

Full Report B / ecological harm

## 4 National Heritage Loss

effects on:

- **historical sites** not applicable - **historic monuments** not applicable

- **historic buildings** not applicable - **art treasures** not applicable

remarks No data available.

## 5 Material Loss

establishment losses off site losses

costs (direct costs to operator) (social costs)

in ECU Irish Pounds ECU Irish Pounds

material losses 300000

response, clean up, restoration

remarks The extent of damages was: the reactor was badly distorted; the valve on the und... see Appendix

Full Report B / material loss

## 6 Disruption of Community Life

establishment/plant evacuated disabled/unoccupiable destroyed

- **nearby residences/hotels** No No No

- **nearby factories/offices/small shops** No No No

- **schools, hospitals, institutions** No No No

- **other places of public assembly** No No No

interruption of utilities etc. no / yes duration

- **gas** No

- **electricity** No

- **water** No

- **sewage treatment works** No

- **telecommunications** No

- **main roads** No

- **railways** No

- **waterways** No

- **air transport** No

significant public concern none local level national level

- **off site populations** Yes No No

- **media interest** No No No

- **political interest** No No No

remarks In the Original Report there is no evidence of significant effects outside the e... see Appendix

## 7 Discussion of Consequences

# C Response Full Report

country: FA ident key: 1987\_005\_01

## 1 Emergency Measures

**taken - on site** - not applicable - - not applicable -

- not applicable - - not applicable -

- not applicable - - not applicable -

- **off site** - not applicable - - not applicable -

- not applicable - - not applicable -

- not applicable - - not applicable -

**still - on site** - not applicable - - not applicable -

**required**

- not applicable - - not applicable -

- not applicable - - not applicable -

- **off site** - not applicable - - not applicable -

- not applicable - - not applicable -

- not applicable - - not applicable -

**continuing contamination or danger**

-**on site** not applicable

-**off site** not applicable

**remarks** - not applicable -

## 2 Seveso II Duties

**pre-accident evaluation**

**Article item not due yet not done done/submitted evaluated**

**6 notification** No No No No

**7 policy (MAPP)** No No No No

**9 safety report** No No No No

**9, 10, 11 update** No No No No

**11 internal plan** No No No No

**11 external plan** No No No No

**13 informing public** No No No No

**9, 12 siting policy** No No No No

**post-accident evaluation**

**Seveso II duty was actual were actual compared with actual**

**contingency consequences consequences, the**

**addressed? addressed? predicted extent was?**

**Article item**

**7 policy (MAPP)** not applicable not applicable not applicable

**9 current safety report** not applicable not applicable not applicable

**11 internal plan** not applicable not applicable not applicable

**11 external plan** not applicable not applicable not applicable



**13 informing public** not applicable not applicable not applicable

**9, 12 siting policy** not applicable not applicable not applicable

**evaluation of safety organisation**

**organisational element** element existed did element relate to actual circumstances of

yes / no no / partly / yes adequate?

- written policy objectives No

- specified management No

structure

- specified responsibilities No

- specified working procedures No

- specified procedures for No

assessment/auditing of

management system

- specified procedures for No

review and update of

management policy

- specified general training No

procedures

- specified emergency No

training procedures

evaluation of ecological impact control

**organisational element** element existed did element relate to actual circumstances of

yes / no no / partly / yes adequate?

- ecological status review No

before incident

- potential ecological No

consequences assessment

- ecological impact review No

after incident

- ecological restoration No

procedures

- subsequent review of No

restoration success

remarks - not applicable -

### **3 Official Action Taken**

legal action

- not applicable -

other official action

- not applicable -

### **4 Lessons Learned**

measures to prevent recurrence

After this accident, the follo... see Appendix Full Report C / lesson learned - prevent

**measures to mitigate consequences:**

- not applicable -

**useful references:**

- not applicable -

**5 Discussion about Response**

- not applicable -

## **Appendices for the FA / 1987\_005\_01 report**

**Appendix Short Report / description of accident types:**

**ACCIDENT CASE HISTORY DESCRIPTION:**

The operation of the plant was organized in two shifts. Since the hydrogenation at Reactor 6 would have taken at least 30 hours, it was not possible to complete the reaction during a single shift. The reaction was commenced at 8:00 a.m. on the day of the accident and, at 11:50 p.m., the shift chemical operator closed down the system as follows:

- he shut off the hydrogen addition at the reactor and closed the valve at the hydrogen cylinder bank;
- the reactor's agitator was turned off and the reactor was left isolated with an hydrogen atmosphere over the liquid.

No nitrogen inerting was used. The operator checked the reactor's control panel which showed normal operating temperature and pressure. The operator was also in control of Reactor 5 which he shut down in a similar manner. At approximately midnight, as the chemical operators were changing in their locker room, they heard a loud explosion coming from the process area. As they evacuated the building, they observed a fire around Reactor 6. The area sprinkler system was automatically activated and quenched the fire. It was noticed that one operator was missing. He came to the assembly point a few minutes later and said that when the explosion occurred he was trapped in the mill room weighing finished product. He could not exit by the process area and had to exit through a hatch on the floor, jump onto a rotary dryer below and climb down to the ground floor. A second explosion occurred a few minutes later. A fire with a characteristic black smoke resulted, indicative of a solvent fire. The sprinkler system extinguished this fire. A short while later, the fire services arrived and put out small localized fires on the ground floor around Reactor 6. The building was left vacant for the rest of the night.

**Appendix Short Report / description of substances involved:**

- Hydrogen (C.A.S. CODE: 1333-74-0, E.E.C. CODE: 001-001-00-9): amount involved = 0.09 kg (equivalent to 1 m<sup>3</sup>, the approximate volume in vapour space above liquid level in reactor).
- Acetone (C.A.S. CODE: 67-64-1, E.E.C. CODE: 606-001-02-8): amount involved = 634 kg (about 800 litres).

**Appendix Short Report / description of immediate sources:**

The accident occurred in the Reactor 6 used to carry out the hydrogenation of a pharmaceutical intermediate. The Company carried out a wide range of chemical syntheses, producing finished bulk pharmaceuticals for different customers. All the processes were carried out in one common production building. The hydrogenation was carried out by bubbling hydrogen into a well stirred mixture of the intermediate in acetone, the solvent, with a palladium catalyst at 35°C. The hydrogen was fed into the reactor through a 1 cm diameter pipeline from a cylinder bank of hydrogen stored outside at ground floor level.

**Appendix Short Report / description of suspected causes:**

**CAUSES:**

An analysis of the Reactor 6 contents showed that approximately 400 litres of the total contents (about 1200 litres) remained inside the vessel. A quality control analysis of this material showed that the reaction was progressing satisfactorily before the incident. Examinations have shown that combustion should be supported inside the reactor as nitrous oxide was generated in the process. An electrostatic discharge could have caused the first explosion but this was considered unlikely on investigation. The most probable cause of the incident was a defective agitator. The maintenance record on the agitator showed that it malfunctioned on numerous occasions. It was felt that the agitator possibly malfunctioned again allowing a hydrogen leak. As the reactor was located in a general process area with plants operating nearby, the released hydrogen could easily have found an ignition source as some of the electrical plants operating nearby were not suitable for use with hydrogen. The investigation showed that the reactor's pressure relief line did not operate as the bursting disc was found to be intact.

**Appendix Short Report / description of immediate effects:**

**MATERIAL LOSS:**

The extent of the damages caused by the explosion and the following fires was as follows: the reactor was badly distorted; the valve on the underside of Reactor 6 was also distorted and leaked; the sightglass in the manlid was shattered; the agitator was blown from its seating and deposited a few metres away; the glass fittings on Reactors 5 and 7 were shattered; electric cable insulation was charred and paintwork on the walls, ceilings and nearby millroom doors was scorched as far as 15 metres away; the glass in the windows on the first floor was shattered and the window frames distorted next to Reactors 5 and 7; windows up to 30 metres were blown out.

The cost of these damages has been estimated in about 300,000 Irish Pounds (about 0.39 MECU).

**Appendix Short Report / description of emergency measures taken:**

**INTERNAL TO THE ESTABLISHMENT:**

The fires were extinguished by the automatically activated sprinkler system. The Fire services (15 fire fighters) arrived a short while later and put out small localized fires on the ground floor around Reactor 6.

**EXTERNAL TO THE ESTABLISHMENT:**

No off-site emergency measures were necessary.

## **Appendix Short Report / description of immediate lessons learned:**

### MEASURES TO PREVENT ANY RECURRENCE OF SIMILAR ACCIDENTS:

After this accident, the following measures were established:

- 1- to carry out hydrogenation in a separate dedicated process area with electrical equipment suitable for use with hydrogen;
- 2- to provide adequate alarms to warn when a hydrogen leak could occur.

The Company was also required to:

- 3- implement a more extensive preventive maintenance system;
- 4- install appropriate pressure relief devices to ensure that emissions do not vent into the process area;
- 5- review procedures to ensure that processes which have to be left unattended overnight are left in a safe state;
- 6- provide nitrogen inerting in any reactor containing highly flammable solvents which have to be left unattended overnight.

## **Appendix Full Report A / type of accident:**

During an hydrogenation reaction carried out in a reactor of an organic chemical industry, an hydrogen leak occurred (code 1101). As the reactor was located in a general process area with plants operating nearby, the hydrogen easily found an ignition source, exploding (code 1307). The explosion of the unconfined vapour cloud was then followed by a fire of an acetone pool (code 1202).

## **Appendix Full Report A / dangerous substances:**

The total establishment and the potential directly involved inventories of acetone refer to the whole contents of the Reactor 6 (about 1200 litres). The total establishment and the potential directly involved inventories of hydrogen refer to the approximate volume in vapour space above liquid level in Reactor 6 (about 1 m<sup>3</sup>).

## **Appendix Full Report A / source of accident - remarks:**

The accident occurred in a pressurized batch reactor (codes 3101 and 4002) used to carry out the hydrogenation of a pharmaceutical intermediate in an organic chemical industry (code 2001). The Company carried out a wide range of chemical syntheses, producing finished bulk pharmaceuticals for different customers. All the processes were carried out in one common production building. The lay-out of the factory is shown on a map attached to the Original Report.

## **Appendix Full Report A / causes of major occurrence:**

The most probable cause of the accident was a defective agitator (code 5102) that malfunctioned allowing a hydrogen leak. As the reactor was located in a general process area with plants (not suitable for use with hydrogen) operating nearby, the released hydrogen could easily have found an ignition source (codes 5307 and 5308). The maintenance record on the agitator showed that it malfunctioned on numerous situations but the maintenance was not sufficient (codes 5302 and 5313).

## **Appendix Full Report B / area concerned - remarks:**

In the Original Report there is no evidence of significant effects outside the establishment. The extent of the effects is shown on a map attached to the Original report.

## **Appendix Full Report B / people:**

No people were injured by the explosion because, when the accident occurred, the operators were changing in their locker room except for an operator that was trapped in the mill room weighing finished product. He could not exit by the process area and had to exit through a hatch on the floor, jump onto a rotary dryer below and climb down to the ground floor.

## **Appendix Full Report B / ecological harm:**

In the Original Report there is no evidence of significant ecological harms.

## **Appendix Full Report B / material loss:**

The extent of damages was: the reactor was badly distorted; the valve on the underside of Reactor 6 was also distorted and leaked; the sightglass in the manlid was shattered; the agitator was blown from its seating and deposited a few metres away; the glass fittings on Reactor 5 and 7 were shattered; electric cable insulation was charred and paintwork on the walls, ceilings and nearby millroom doors was scorched as far as 15 m away; the glass in the windows on the first floor was shattered.

## **Appendix Full Report B / disruption of community life:**

In the Original Report there is no evidence of significant effects outside the establishment.

## **Appendix Full Report C / lesson learned - prevent:**

After this accident, the following measures were established:

- 1- to carry out hydrogenation in a separate dedicated process area with electrical equipment suitable for use with hydrogen;
- 2- to provide adequate alarms to warn when a hydrogen leak could occur.

The Company was also required to:

- 3- implement a more extensive preventive maintenance system;
- 4- install appropriate pressure relief devices to ensure that emissions do not vent into the process area;
- 5- review procedures to ensure that processes which have to be left unattended overnight are left in a safe state;
- 6- provide nitrogen purging in any reactor containing highly flammable solvents which have to be left unattended overnight.