

# Eldflamma på en fabrik för produktion för farmaceutika.

850630 MARS 1985\_08

I samband med rengöring av en reaktor antändes en mindre mängd etanol. Reaktorn som skulle rengöras var en tank på 4000 liter. Etanolen skulle tappas över från en annan tan som innehöll den dubbla mängden etanol. När den mindre reaktorn fyllts med etanol förseglades tanken och reaktorn värmdes upp till 70°C. Efter en stund upptäcktes att temperaturkontrollen fallerat och att temperaturen var närmare 90°C. Kort därefter slog en eldflamma ut ur manluckan på reaktorn. Flamman släcktes av det automatiska sprinklersystemet. Man fann att manluckan inte varit helt tillsluten. Man fann att den mest sannolika källan till en tändande gnista var närvaron av den pyrofora nickelkatalysatorn.

## Inblandade ämnen och mängder

	CAS Nr.	Mängd
Raney nickel (katalysator)	7440-02-0	spårmängder
etanol	64-17-5	10 kg

## Skador:

Människor:

Materiella:

Miljö/ekologi: Inga effekter rapporterade.

Infrastruktur:

## Erfarenheter redovisade (Ja/Nej): Ja

Kortfattat anges förebyggande åtgärder.

## Report Profile

### Identification of Report:

country: FA ident key: 1985\_008\_01

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

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

start: 1985-06-30 start:

finish: finish:

### Establishment:

name:

address:

industry: 2004 pesticides, pharmaceuticals, other fine chemicals

Pharmaceutical (Process Plant)

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:** 1985\_008\_01

**Accident Types:**

**release:** Yes **explosion:** No

**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:**

- Raney Nickel (C.A.S. CODE: 7440-02-0); amount involved = traces on the side of the 4,000 litres 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 a 4,000 litres reactor (where a process using Raney Nickel as a catalyst was carried out) of a pharmaceutical industry.

**Suspected Causes:**

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

**human:** Yes **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:** No **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:** 1985\_008\_01

### **1 Type of Accident**

**remarks:** During the heating of the contents of a reactor containing ethanol and Raney

nickel the failure of the temperature control loop led to the emission of

ethanol vapours and pyrophoric nickel material through the partially closed

reactor man-h... see Appendix Full Report A / type of accident

### **2 Dangerous Substances**

**remarks:** No data are available about the amount of pyrophoric nickel material

involved in the accident. In any case, this amount was negligible (only

traces on the side of the 4,000 litres reactor). The total establishment and

the potential directly... see Appendix Full Report A / dangerous substances

### **3 Source of Accident**

**illustration:** - not applicable -

**remarks:** The accident occurred in a 4,000 litres reactor (code 4002) of a

pharmaceutical industry (code 2004). In the reactor was carried out a batch

process which used Raney nickel as a catalyst (code 3101) and, at the end of

the process, the react... 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** 5105 operation: instrument/control/monitoring-device failure

- not applicable -

- not applicable -

- not applicable -

- not applicable -

**human / organizational** 5303 organization: organized procedures (none, inadequate, inappropriate, unclear)

5304 organization: training/instruction (none, inadequate, inappropriate)

5401 person: operator error

- not applicable -

- not applicable -

**remarks:** Post-accident investigations carried out by the company showed that temperature control

loop failed (code 5105) allowing the temperature rise to 87°C instead of required 70°C.

The reactor's man-hole clamps were not fully tightened and ethan... see Appendix Full

Report A / causes of major occurrence

#### 6 Discussion about the Occurrence

- not applicable -

**Type of Accident** country: FA ident key: 1985\_008\_01

**event:**

**major occurrence** 1204 fire: flash fire (burning vapour cloud, subsonic flame front)

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

**associated event** - not applicable -

#### Dangerous substances

country: FA ident key: 1985\_008\_01

##### a) total establishment inventory

**CAS number:** 7440-02-0 **identity:** Raney Nickel

**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):** -1

**use of substance as:** NORMAL FINISHED PRODUCT

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

**actual quantity:** -1 **potential quantity:** -1

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

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

**a) total establishment inventory**

**CAS number:** 64-17-5 **identity:** Ethanol

**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):** 6,314

**use of substance as:** STARTING MATERIAL

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

**actual quantity:** 0,01 **potential quantity:** 3,157

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

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

**Source of Accident - Situation** country: FA **ident key:** 1985\_008\_01

**situation**

**industry**

**initiating event** 2004 pesticides, pharmaceuticals, other fine chemicals

**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: 1985\_008\_01

## 1 Area concerned

**affected**

**extent of effects installation:** Yes

**establishment:** No

**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 i... see Appendix

Full Report B / area concerned - remarks

## 2 People

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

**total at risk**

**immediate fatalities**

**subsequent fatalities**

**hospitalizing injuries**

**other serious injuries**

**health monitoring**

**remarks** When the accident occurred no one was in the area and so no one was injured by t... see Appendix

Full Report B / people

## 3 Ecological Harm

**pollution/contamination/damage of:**

- residential area (covered by toxic cloud) Suspected

- common wild flora/fauna (death or elimination) Suspected

- rare or protected flora/fauna (death or elimination) Suspected

- water catchment areas and supplies for consumption or recreation Suspected

- land (with known potential for long term ecological harm or Suspected

preventing human access or activities)

- marine or fresh water habitat Suspected

- areas of high conservation value or given special protection Suspected

**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 1000**

**response, clean up, restoration**

**remarks** The cost of the damages caused by the flash fire to the electrical cables around... 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 i... see Appendix

## **7 Discussion of Consequences**

# **C Response Full Report**

**country:** FA **ident key:** 1985\_008\_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 the accident, the Indust... 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 / 1985\_008\_01 report

## Appendix Short Report / description of accident types:

### ACCIDENT CASE HISTORY DESCRIPTION:

A reaction (which used Raney Nickel as a catalyst) was carried out in a 4,000 litres reactor. After the reaction had been completed, the vessel (which was located on a lower floor) was to be flushed out using ethanol decanted from a 8,000 litres reactor. The control room operator, aware that the contents of the larger vessel would not fit into the 4,000 litres vessel, instructed the local operator to check the decanting operation into the lower vessel. The operator manually checked the level in the 4,000 litres reactor a number of times. During the last inspection, he observed that the smaller reactor was full. He closed the man-hole and the heating started. After a certain period of time, the control room operator discovered that the temperature of the reactor's contents was 87°C, well above the pre-set level of 70°C. He shut off the reactor's jacket steam but shortly afterwards the fire alarm in the area and the sprinkler system was activated. An investigation of the scene showed that the sprinkler system was activated and an area around the reactor's man-hole was blackened as a result of a flash fire. The flash fire was extinguished by the sprinkler system. As no one was in the area when the accident occurred, no one was injured.

## Appendix Short Report / description of substances involved:

- Raney Nickel (C.A.S. CODE: 7440-02-0): amount involved = traces on the side of the 4,000 litres reactor.
- Ethanol (C.A.S. CODE: 64-17-5): amount involved = 10 kg.

## Appendix Short Report / description of suspected causes:

### CAUSES:

Post-accident investigations carried out by the company showed that the temperature control loop failed allowing the temperature rise to 87°C instead of 70°C required (the output of the automatic control failed to update the control valve position even though it was correctly set). The reactor's man-hole clamps were not fully tightened and ethanol vapours must have been emitted from an overfull reactor. An examination of the contents of the 8,000 litres reactor after the accident showed that the smaller reactor was slightly overfilled. The most probable source of ignition was the pyrophoric Nickel material forced out of the reactor by the boiling ethanol through the partially closed man-hole. The investigation revealed that all electrical equipments in the area were correctly functioning.

## Appendix Short Report / description of immediate effects:

### MATERIAL LOSS:

The cost of the damages caused by the flash fire to the electrical cables around the reactor has been evaluated in about 1,000 Irish Pounds (about 0.0013 MECU).

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

### INTERNAL TO THE ESTABLISHMENT:

The fire at the reactor man-hole activated a sprinkler head located above the vessel. It resulted in the fire alarm and the activation of the sprinkler system. By the time the supervisor arrived on the scene (2 minutes later) the fire was extinguished by the sprinkler system. The company fire crew was activated but its intervention was not necessary.

### 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 the accident, the Industrial Inspectorate required the company to:

- 1- repair the faulty temperature control loop;
- 2- provide for the post-campaign flush-out batch sheet to give a warning of potential overfilling of the reactor;
- 3- introduce proper man-hole cover bolting practices;
- 4- ensure that control room attendants carefully review all non-standard operations with local operators;
- 5- update preventive maintenance plans to ensure that steam control valves and associated control loops are regularly checked.

## Appendix Full Report A / type of accident:

During the heating of the contents of a reactor containing ethanol and Raney nickel the failure of the temperature control loop led to the emission of ethanol vapours and pyrophoric nickel material through the partially closed reactor man-hole cover (code 1101). Ethanol vapours were then ignited by the pyrophoric nickel material resulting in a flash fire (code 1204).

## Appendix Full Report A / dangerous substances:

No data are available about the amount of pyrophoric nickel material involved in the accident. In any case, this amount was negligible (only traces on the side of the 4,000 litres reactor). The total establishment and the potential directly involved inventories of ethanol refer, respectively, to the volumetric capacity of the 8,000 litres reactor containing the decanted ethanol and to the volumetric capacity of the 4,000 litres vessel.

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

The accident occurred in a 4,000 litres reactor (code 4002) of a pharmaceutical industry (code 2004). In the reactor was carried out a batch process which used Raney nickel as a catalyst (code 3101) and, at the end of the process, the reactor had to be flushed out with ethanol decanted from a 8,000 litres capacity vessel at a temperature of 70°C to clean it by the pyrophoric nickel material. From the Original Report is not fully clear if the reactor was pressurized or not.

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

Post-accident investigations carried out by the company showed that temperature control loop failed (code 5105) allowing the temperature rise to 87°C instead of required 70°C. The reactor's man-hole clamps were not fully tightened and ethanol vapours must have been emitted from the reactor that was slightly overfilled (codes 5401, 5303 and 5304). The most probable source of ignition was the pyrophoric nickel forced out of the reactor by the boiling ethanol through the partially closed man-hole.

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

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

**Appendix Full Report B / people:**

When the accident occurred no one was in the area and so no one was injured by the flash fire.

**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 cost of the damages caused by the flash fire to the electrical cables around the reactor has been evaluated in about 1,000 Irish Pounds (about 0,0013 MECU).

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

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

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

After the accident, the Industrial Inspectorate required the company to:

- 1- repair the faulty temperature control loop;
- 2- provide for the post-campaign flush-out batch sheet to give a warning of potential overfilling of the reactor;
- 3- introduce proper man-hole cover bolting practices;
- 4- ensure that control room attendants carefully review all non-standard operations with local operators;
- 5- update preventive maintenance plans to ensure that steam control valves and associated control loops are regularly checked.