

Skenande reaktion och utsläpp på en kemikaliefabrik för produktion av hårvårdsprodukter.

851023 MARS 1985_09

Man förlorade kontrollen över en reaktion som är kraftigt värmeutvecklande. Reaktionen kontrollerades genom en noga avvägd tillsats av väteperoxid. Under morgonen observerade en operatör att temperaturen i reaktionskärlet steg plötsligt. Trots att man omedelbart släppte innehållet i en nödsläckningstank rakt ovanför ned i reaktionsblandningen inträffade en explosion några minuter senare. Det mesta av innehållet i tanken spreds över den omedelbara omgivningen i fabriken som en fin dimma. De tre personer som utsattes för dimman skölldes snabbt under nödduschar. Efter olyckan fann man att tillsatsen av väteperoxid hade varit närmare 10 gånger snabbare än normalt under en kort tid före olyckan. Man misstänkte att någon operatör av misstag undrlätit att stänga ett par ventiler, men kunde inte finna närmare bevis för att så varit fallet.

Inblandade ämnen och mängder

	CAS Nr.	Mängd
2-chloropyridine	109-09-1	900 kg
maleic anhydride	108-31-6	650 kg
väteperoxid	7722-84-1	170 kg
2-chloropyridine-N-oxide	2402-95-1	okänt

Skador:

Människor: Ingen skadades men tre arbetare utsattes för en dusch av den finfördelad dimma som spreds. De dränktes snabbt under nödduscharna och erfor inga efterverkningar.

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: 1985_009_01

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

Date of Major Occurrence: Time of Major Occurrence

start: 1985-10-23 start:

finish: finish:

Establishment:

name:

address:

industry: 2001 general chemicals manufacture

Organic Chemical (Omadine compounds manufacturing, basis of anti-dandruff shampoos)

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_009_01

Accident Types:

release: No explosion: Yes

water contamination: No other: No

fire: No

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:

- 2-Chloropyridine (C.A.S. CODE:109-09-1): amount involved = 900 kg... 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 an organic chemical industry and involved an oxidation reactor located in a process room. The process involved the oxidation of a pyridine compound with 70% hydrogen peroxide using a maleic anhydride catalyst to for... see Appendix Short Report / description of immediate sources

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: No

human deaths: No

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

other: Yes

ecological harm: No

national heritage loss: No

description:

OTHER:

The effects of the explosion were negligible (no plants were damaged by the accident).

Emergency Measures taken:

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

external services: No **restoration:** No

sheltering: No **other:** No

evacuation: No

description:

No emergency measures were necessary, neither on-site nor off-site.

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_009_01

1 Type of Accident

remarks: During the oxidising of a pyridine compound with hydrogen peroxide using a maleic anhydride catalyst, an accelerated rate of addition of hydrogen peroxide (estimated to be about one order of magnitude higher than the normal addition rate) l... see Appendix Full Report A / type of accident

2 Dangerous Substances

remarks: The total establishment and the potential directly involved inventories of 2-Chloropyridine, maleic anhydride and hydrogen peroxide refer to the amounts involved in the explosion. When the explosion occurred, a large

amount of the raw mate... see Appendix Full Report A / dangerous substances

3 Source of Accident

illustration: - not applicable -

remarks: The accident occurred in an organic chemical industry (code 2001) during the oxidation of a pyridine compound with hydrogen peroxide using a maleic anhydride catalyst to form a pyridine-N-oxide (code 3101). The component involved was the ox... 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 5106 operation: runaway reaction

- not applicable -

- not applicable -

- not applicable -

- not applicable -

human / organizational 5307 organization: process analysis (inadequate, incorrect)

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

inappropriate)

5401 person: operator error

- not applicable -

- not applicable -

remarks: The explosion was caused by a runaway reaction (code 5106) that occurred because of an addition rate of hydrogen peroxide higher than that expected. It was caused by an operator error (code 5401) in following the operating procedures. Besid... see Appendix Full Report A / causes of major occurrence

6 Discussion about the Occurrence

- not applicable -

Type of Accident country: FA ident key: 1985_009_01

event:

major occurrence 1304 explosion: runaway reaction explosion (usually exothermic)

initiating event - not applicable -

associated event - not applicable -

event:

major occurrence 1101 release: gas/vapour/mist/etc release to air

initiating event 1304 explosion: runaway reaction explosion (usually exothermic)

associated event - not applicable -

Dangerous substances

country: FA **ident key:** 1985_009_01

a) total establishment inventory

CAS number: 108-31-6 **identity:** Maleic Anhydride

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): 0,65

use of substance as: STARTING MATERIAL

b) substance belongs to relevant inventory directly involved: Yes

actual quantity: 0,65 **potential quantity:** 0,65

c) substance belongs to relevant inventory indirectly involved: No

actual quantity: -1 **indir_pot_quant:** -1

a) total establishment inventory

CAS number: 7722-84-1 **identity:** Hydrogen Peroxide

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): 0,17

use of substance as: STARTING MATERIAL

b) substance belongs to relevant inventory directly involved: Yes

actual quantity: 0,17 **potential quantity:** 0,17

c) substance belongs to relevant inventory indirectly involved: No

actual quantity: -1 **indir_pot_quant:** -1

a) total establishment inventory

CAS number: 2402-95-1 **identity:** 2-chloropyridine-n-oxide

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: ABNORMAL 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: 109-09-1 identity: 2-chloropyridine

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): 0,9

use of substance as: STARTING MATERIAL

b) substance belongs to relevant inventory directly involved: Yes

actual quantity: 0,9 potential quantity: 0,9

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_009_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: 1985_009_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 3

immediate fatalities

subsequent fatalities

hospitalizing injuries

other serious injuries

health monitoring

remarks As no operators were working in the process area when the accident occurred, no ... 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 ECU

material losses

response, clean up, restoration

remarks The effects of the explosion were negligible. No plants were damaged in the acci... 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_009_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_009_01 report

Appendix Short Report / description of accident types:

ACCIDENT CASE HISTORY DESCRIPTION:

The accident involved a reactor used to oxidize a pyridine compound with hydrogen peroxide using a maleic anhydride catalyst to form a pyridine-N-oxide. The reaction was recognised to be exothermic; therefore, hydrogen peroxide was added at controlled rates. On the morning of the accident, the chemical operator added the pyridine compound, the catalyst and a peroxide plug (12% of total to be added). The plug was added quickly to the reactor by opening valves 4 and 5 on the by-pass transfer line. For

further peroxide addition, valves 4 and 5 had to be closed and valves 1, 2 and 3 and flow meter F1 opened. The flow meter controlled the rate of peroxide addition at 4.5 kg per minute. A few minutes after the peroxide addition had commenced, the operator in the control room observed the reaction temperature to increase suddenly. Although the quench tank was automatically activated, an explosion occurred a short time later and the whole reactor contents was released. Most of the contents was emitted into the process area through the reactor man-hole cover, which was covered with an aluminium foil disc which would burst at 0.14 bar. The remaining contents was released to the atmosphere through the pressure relief line. As no operators were working in the process area when the accident occurred, no one was injured but 3 construction people working 30 metres away were showered by a fine spray mist. They were quickly drenched under an emergency shower and suffered no side-effects. No plants were damaged in the accident.

Appendix Short Report / description of substances involved:

- 2-Chloropyridine (C.A.S. CODE:109-09-1): amount involved = 900 kg.
- Maleic Anhydride (C.A.S. CODE:108-31-6): amount involved = 650 kg.
- Hydrogen Peroxide (C.A.S. CODE:7722-84-1): amount involved = 170 kg.
- 2-Chloropyridine-N-oxide (C.A.S. CODE:2402-95-1): amount involved = when the explosion occurred a large amount of the raw materials had been converted into this product but, as no material remained after the explosion, it was not possible to determine the yield of the conversion.

Appendix Short Report / description of immediate sources:

The accident occurred in an organic chemical industry and involved an oxidation reactor located in a process room. The process involved the oxidation of a pyridine compound with 70% hydrogen peroxide using a maleic anhydride catalyst to form a pyridine-n-oxide. The reaction was recognized to be exothermic. It was controlled by the rate of addition of the peroxide to a well stirred mixture of the catalyst in pyridine compound. The required peroxide for each batch was transferred from bulk storage to an intermediate holding tank. This tank was located on the ground floor process area and the peroxide was pumped into the reactor via a flow meter. The pyridine was pumped into the reactor from 200 litres drums. The catalyst was added from 50 kg bags through the man-hole. The safety features for this exothermic reaction included:

- circulation of the reactor contents through two heat exchangers during oxidation;
- a 200 cm pressure relief line to atmosphere with a 0.7 bar bursting disc;
- a water quench tank located 3 metres above the reactor, which would automatically dump its contents into the reactor should a sudden temperature increase ($> 3^{\circ}\text{C}$) occur.

The peroxide addition pump would not operate if:

- the quench tank was not full;
- the circulation pump was not operating;
- the reactor's vent was not open to the atmosphere.

Appendix Short Report / description of suspected causes:

CAUSES:

The investigations carried out by the company after the accident showed that approximately 115 kg of peroxide were added to the reactor over a 3 minutes period instead of the normal 4.5 kg/minute. The subsequent company investigations found valves 4 and 5 closed on the peroxide transfer line and valves 1, 2 and 3 opened just after the accident. For the above accelerated rate of peroxide addition, valves 4 and 5 must have been opened. It is thought that an operator failed to close valves 4 and 5 and opened valves 1, 2 and 3 following the operating instructions. Just after the accident, he must have realised his mistake and reset the valves in accordance with the correct instructions before the accident investigations. The accelerated rate of peroxide addition resulted in an exothermic runaway reaction. Besides, the process analysis and the design plant were not adequate.

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- close the reactor man-hole during oxidation;
- 2- remove the by-pass on the peroxide transfer line;
- 3- provide an emergency dump tank on the reactor 200 cm vent line.

Appendix Full Report A / type of accident:

During the oxidising of a pyridine compound with hydrogen peroxide using a maleic anhydride catalyst, an accelerated rate of addition of hydrogen peroxide (estimated to be about one order of magnitude higher than the normal addition rate) led to a sudden temperature increase that resulted in an exothermic runaway reaction (code 1304). Although the quench tank was automatically activated, an explosion occurred a short time later and the entire contents of the reactor was released (code 1101).

Appendix Full Report A / dangerous substances:

The total establishment and the potential directly involved inventories of 2-Chloropyridine, maleic anhydride and hydrogen peroxide refer to the amounts involved in the explosion. When the explosion occurred, a large amount of the raw materials had been converted into 2-Chloropyridine-N-oxide but, as no material remained after the explosion, no data are available about the yield of the conversion and, therefore, of the amount involved.

Appendix Full Report A / source of accident - remarks:

The accident occurred in an organic chemical industry (code 2001) during the oxidation of a pyridine compound with hydrogen peroxide using a maleic anhydride catalyst to form a pyridine-N-oxide (code 3101). The component involved was the oxidation reactor (code 4002) located in a process room dedicated to this synthesis.

Appendix Full Report A / causes of major occurrence:

The explosion was caused by a runaway reaction (code 5106) that occurred because of an addition rate of hydrogen peroxide higher than that expected. It was caused by an operator error (code 5401) in following the operating procedures. Besides, the process analysis and the design plant were not adequate (codes 5307 and 5308).

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:

As no operators were working in the process area when the accident occurred, no one was injured by the explosion but 3 construction people working 30 metres away were showered by a fine spray mist. They were quickly drenched under an emergency shower and suffered no side-effects.

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 effects of the explosion were negligible. No plants were damaged in the accident.

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- close the reactor man-hole during oxidation;
- 2- remove the by-pass on the peroxide transfer line;
- 3- provide an emergency dump tank on the reactor 200 cm vent line.