

Explosion och gasutsläpp i en fabrik för produktion av farmaceutika

860315 MARS 1986_11

Olyckan inträffade i en farmaceutisk industri där man använde väteperoxid för att avlägsna illaluktande svavelföreningar från det kemiska avfallet. Reaktionen ägde rum i en behållare av rostfritt stål med ett fastskruvat topplock. En kylig lördagsmorgon i mars inträffade en explosion där locket blåses av. En operatör i närheten dödades och en eld som producerade giftig rök spred sig snabbt i fabriken. Fabriken utrymdes och katastrofåtgärder trädde i kraft. Kylvatten sprutades på närliggande tankar. Allmänheten uppmanades att stanna inne och hålla fönster och dörrar stängda.

Behandlingsmetoden hade inte ägnats någon större uppmärksamhet på fabriken. Metoden består i att först tillsätta väteperoxid (35%) och sedan natriumhydroxid (25%) för att öka pH till ungefär 9. Vid några tillfällen uppstod skum men fenomenet hade inte undersökts närmare. Några operatörer hade observerat att om tillsatsen av natriumhydroxid skedde för tidigt uppstod en tryckökning. Vid högre pH inträffar en snabb exoterm nedbrytning av väteperoxid. Vid den resulterande högre temperaturen förångas olika alifatiska alkoholer i effluenter vilket ger upphov till en explosiv blandning. Det var inte känt om den tändande gnistan var en statisk urladdning eller om explosionen orsakats av en spontan antändning.

Inblandade ämnen och mängder

	CAS Nr.	Mängd
isopropanol	67-63-0	55 kg
metanol	67-56-1	27 kg
väteperoxid	7722-84-1	100 kg

Skador:

Människor:	En person avled.
Materiella:	Skadorna begränsades till byggnadens inre.
Miljö/ekologi:	Inga effekter rapporterade.
Infrastruktur:	En närliggande väg stängdes av och allmänheten uppmanades att stanna inne och hålla fönster och dörrar stängda.

Erfarenheter redovisade (Ja/Nej): Ja

Kortfattat anges förebyggande åtgärder.

Report Profile

Identification of Report:

country: FA ident key: 1986_011_01

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

Date of Major Occurrence: Time of Major Occurrence

start: 1986-03-15 start: 10:00:00

finish: finish:

Establishment:

name:

address:

industry: 2004 pesticides, pharmaceuticals, other fine chemicals

Pharmaceutical (Sulphur-based Intermediate Products for Pharmac. & Agricultural)

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: 1986_011_01

Accident Types:

release: Yes explosion: Yes

water contamination: No other: No

fire: Yes

description:

Hydrogen peroxide was used in a pharmaceutical industry to deodorize an aqueous chemical effluent containing various strong smelling sulphur compounds. The stainless steel treatment vessel was connected to a cast iron holding receiver by bo... see Appendix Short Report / description of accident types

Substance(s) Directly Involved:

toxic: Yes explosive: Yes

ecotoxic: No other: No

flammable: Yes

description:

- Isopropyl Alcohol (C.A.S. CODE: 67-63-0, E.E.C. CODE: 603-003-00-0): amount involved = 55 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 the deodorization unit of a pharmaceutical industry manufacturing intermediates for

pharmaceutical and agricultural chemicals based on sulphur industry. This unit was used to deodorize an aqueous chemical effluent ... see Appendix Short Report / description of immediate sources

Suspected Causes:

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

human: No **other:** No

description:

INITIATING EVENTS AND CONSEQUENCES:... see Appendix Short Report / description of suspected causes

Immediate Effects:

material loss: Yes

human deaths: Yes

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

other: No

ecological harm: No

national heritage loss: No

description:

EFFECTS ON PEOPLE:... see Appendix Short Report / description of immediate effects

Emergency Measures taken:

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

external services: Yes **restoration:** No

sheltering: Yes **other:** No

evacuation: Yes

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:** 1986_011_01

1 Type of Accident

remarks: The decomposition of hydrogen peroxide, catalyzed by sulphur compounds in the effluent, caused the vapourization of the aliphatic alcohols producing a foam potentially explosive. This mixture filled the head space in the treatment vessel an... see Appendix Full Report A / type of accident

2 Dangerous Substances

remarks: The total establishment and the potential directly involved inventories of

the substances involved in the accident (hydrogen peroxide [35%], methyl alcohol and isopropyl alcohol) refer to the amounts involved in the accident. The acidic smo... see Appendix Full Report A / dangerous substances

3 Source of Accident

illustration: - not applicable -

remarks: The accident occurred in the aqueous effluent treatment (deodorizing) facility (code 3104) of a pharmaceutical industry (code 2004) manufacturing intermediates for pharmaceutical and agricultural chemicals mainly based on sulphur chemistr... 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

5107 operation: unexpected reaction/phase-transition

5109 operation: electrostatic accumulation

- not applicable -

- not applicable -

human / organizational 5302 organization: management attitude problem

5307 organization: process analysis (inadequate, incorrect)

- not applicable -

- not applicable -

- not applicable -

remarks: The foaming was caused by the decomposition of hydrogen peroxide catalyzed by the sulphur compounds. This reaction was not identified during the process analysis of the deodorization of aqueous organic chemical effluent (code 5307). The sou... see Appendix Full Report A / causes of major occurrence

6 Discussion about the Occurrence

- not applicable -

Type of Accident country: FA ident key: 1986_011_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 1307 explosion: VCE (vapour cloud explosion; supersonic wave front)

associated event 1401 other: combustion products into air

Dangerous substances

country: FA **ident key:** 1986_011_01

a) total establishment inventory

CAS number: 67-56-1 **identity:** Methyl Alcohol

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): 0,027

use of substance as: STARTING MATERIAL

b) substance belongs to relevant inventory directly involved: Yes

actual quantity: 0,027 **potential quantity:** 0,027

c) substance belongs to relevant inventory indirectly involved: No

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

a) total establishment inventory

CAS number: 67-63-0 **identity:** Isopropyl Alcohol

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): 0,055

use of substance as: STARTING MATERIAL

b) substance belongs to relevant inventory directly involved: Yes

actual quantity: 0,055 **potential quantity:** 0,055

c) substance belongs to relevant inventory indirectly involved: No

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

a) total establishment inventory

CAS number: 7782-84-1 **identity:** Hydrogen Peroxide (35%)

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): 0,1

use of substance as: STARTING MATERIAL

b) substance belongs to relevant inventory directly involved: Yes

actual quantity: 0,1 **potential quantity:** 0,1

c) substance belongs to relevant inventory indirectly involved: No

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

a) total establishment inventory

CAS number: identity: Acidic Smoke

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: No

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

c) substance belongs to relevant inventory indirectly involved: Yes

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

Source of Accident - Situation country: FA ident key: 1986_011_01

situation

industry

initiating event - not applicable -

associated event - not applicable -

activity/unit

major occurrence - not applicable -

initiating event - not applicable -

associated event - not applicable -

component

major occurrence 4003 container; non-pressurised (hopper, tank, drum, bag, etc.)

initiating event 4003 container; non-pressurised (hopper, tank, drum, bag, etc.)

associated event 4003 container; non-pressurised (hopper, tank, drum, bag, etc.)

situation

industry

initiating event 2004 pesticides, pharmaceuticals, other fine chemicals

associated event 2004 pesticides, pharmaceuticals, other fine chemicals

activity/unit

major occurrence 3104 process: physical operations (mixing, melting crystallizing, etc.)

initiating event 3104 process: physical operations (mixing, melting crystallizing, etc.)

associated event 3104 process: physical operations (mixing, melting crystallizing, etc.)

component

major occurrence 4001 reaction vessel; non-pressurised

initiating event 4001 reaction vessel; non-pressurised

associated event 4001 reaction vessel; non-pressurised

B Consequences Full Report

country: FA **ident key:** 1986_011_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 The explosion effects were contained within the building. Though local residents... see Appendix

Full Report B / area concerned - remarks

2 People

establishment popul. emergency personnel off-site population

total at risk

immediate fatalities 1

subsequent fatalities

hospitalizing injuries

other serious injuries

health monitoring

remarks A process operator nearby the deodorization unit when the explosion occurred was... 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 building, containing multi-purpose plant (with reactors, receivers, filters,... 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** No Yes No

- **media interest** No No No

- **political interest** No No No

remarks A nearby main road to the industry was closed. Local residents were warned to cl... see Appendix

7 Discussion of Consequences

C Response Full Report

country: FA **ident key:** 1986_011_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 follow... 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 / 1986_011_01 report

Appendix Short Report / description of accident types:

Hydrogen peroxide was used in a pharmaceutical industry to deodorize an aqueous chemical effluent containing various strong smelling sulphur compounds. The stainless steel treatment vessel was connected to a cast iron holding receiver by both top and bottom connections. The liquid was transferred by the bottom connection and any foam generated during the treatment vented back to the receiver using the top connection. When the treatment method was first adopted, foam had escaped out of the open man lid in the treatment vessel. The man lid was therefore sealed. The foam then passed up the vent system and contaminated the scrubber system. Hence the modification to vent the foam into the receiver. The treatment method for the effluent was provided by the firm's parent company which was specialized in hydrogen peroxide chemistry. The method used was first to add hydrogen peroxide (35%) and then caustic soda solution (25%) to bring the pH up to approximately 9. On some occasions foaming occurred. Management did not fully investigate these incidents; some of the operators were aware of a pressure rise in the treatment vessel if the caustic solution was added too quickly. On a cold Saturday morning in March an explosion occurred within the plant. The lid of the stainless steel vessel was blown off whilst the cast iron receiver was blown to pieces. A process operator nearby at the time was killed. A fire, producing an acidic smoke, then very rapidly spread through the entire building.

Appendix Short Report / description of substances involved:

- Isopropyl Alcohol (C.A.S. CODE: 67-63-0, E.E.C. CODE: 603-003-00-0): amount involved = 55 kg.
- Methyl Alcohol (C.A.S. CODE: 67-56-1, E.E.C. CODE: 603-001-00-X): amount involved = 27 kg.
- Hydrogen Peroxide (C.A.S. CODE: 7722-84-1): amount involved = 100 kg.
- Acidic smoke: composition and amount developed during the fire = not known

Appendix Short Report / description of immediate sources:

The accident occurred in the deodorization unit of a pharmaceutical industry manufacturing intermediates for pharmaceutical and agricultural chemicals based on sulphur industry. This unit was used to deodorize an aqueous chemical effluent containing various strong-smelling sulphur compounds. The unit was in a single building (58x24 metres and 4.2 metres to the eaves, steel framed construction, block/brick walls, steel sheeting roof) containing a multi-purpose plant with reactors, receivers, filters, tanks and assorted services. The components involved were a stainless steel treatment vessel and the connected cast iron receiver.

Appendix Short Report / description of suspected causes:

INITIATING EVENTS AND CONSEQUENCES:

An ignition in vessel caused an explosion followed by a serious fire. Ignition was caused by either (a) static discharge in relief vent line or (b) auto ignition of alcohols vapours-hydrogen peroxide in vessel-receiver.

CAUSES:

The management did not fully investigate the formation of foaming. Researches following the accident showed that the foaming was caused by the decomposition of hydrogen peroxide. This decomposition was catalysed by sulphur compounds in the effluent and was also pH dependant. At about 7.5 pH a rapid exothermic decomposition takes place. The heat produced is capable of vaporizing the various aliphatic alcohols also present in the effluent. This produced a potentially explosive mixture. This mixture would have filled the head space in the treatment vessel and then spilled into the empty receiver. When the Original Report was prepared, the ignition source was not fully identified though static or spontaneous ignition could be involved. The bursting discs failed in relief the vent lines.

Appendix Short Report / description of immediate effects:

EFFECTS ON PEOPLE:

1 person within the establishment was killed by the explosion.

MATERIAL LOSS:

The effects of the explosion were contained within the building. The building, containing a multipurpose plant (with reactors, receivers, filters, tanks and assorted services)

was engulfed by the fire following the explosion. No data are available about the cost of the damages.

COMMUNITY DISRUPTION:

Local residents were warned to close the doors and the windows because of the acidic smoke produced by the fire. The explosion effects were contained within the building. Though local residents were warned to close doors and windows because of acidic smoke produced by the fire, in the Original Report there is no evidence of significant effects outside the establishment.

Appendix Short Report / description of emergency measures taken:

INTERNAL TO THE ESTABLISHMENT:

Evacuation of site personnel. Fire fighting operations were carried out and cooling water was sprayed onto nearby storage tanks.

EXTERNAL TO THE ESTABLISHMENT:

Closure of nearby main road. Local residents were warned to close doors and windows because of acidic smoke produced by the fire.

Appendix Short Report / description of immediate lessons learned:

MEASURES TO PREVENT ANY RECURRENCE OF SIMILAR ACCIDENTS:

After the accident, the following measures were established:

- 1- the unit to be demolished;
- 2- process producing the chemical effluent containing strong-smelling sulphur compounds transferred to another factory;
- 3- a new process for effluent treatment not using hydrogen peroxide to be introduced.

Appendix Full Report A / type of accident:

The decomposition of hydrogen peroxide, catalyzed by sulphur compounds in the effluent, caused the vapourization of the aliphatic alcohols producing a foam potentially explosive. This mixture filled the head space in the treatment vessel and then spilled into the empty receiver. The presence of an ignition source led to the confined explosion of this mixture (code 1307). A fire, then, very rapidly spread through the entire building (code 1202) producing an acidic smoke (code 1401).

Appendix Full Report A / dangerous substances:

The total establishment and the potential directly involved inventories of the substances involved in the accident (hydrogen peroxide [35%], methyl alcohol and isopropyl alcohol) refer to the amounts involved in the accident. The acidic smoke was produced by the fire that followed the explosion. No data are available about the composition and the amount of acidic smoke released during the fire.

Appendix Full Report A / source of accident - remarks:

The accident occurred in the aqueous effluent treatment (deodorizing) facility (code 3104) of a pharmaceutical industry (code 2004) manufacturing intermediates for pharmaceutical and agricultural chemicals mainly based on sulphur chemistry. The components involved were a stainless steel treatment vessel and the connected cast iron holding receiver (codes 4001 and 4003). The deodorization unit was in a building containing a multi-purpose plant (with reactors, filters, receivers, tanks, etc.).

Appendix Full Report A / causes of major occurrence:

The foaming was caused by the decomposition of hydrogen peroxide catalyzed by the sulphur compounds. This reaction was not identified during the process analysis of the deodorization of aqueous organic chemical effluent (code 5307). The source ignition was not fully identified though static (code 5109) or spontaneous ignition could be involved (code 5107). The management did not fully investigate the formation of foaming (code 5302). The bursting discs failed in relief vent lines (code 5102).

Appendix Full Report B / area concerned - remarks:

The explosion effects were contained within the building. Though local residents were warned to close doors and windows because of acidic smoke produced by the fire, in the Original Report there is no evidence of significant effects outside the establishment.

Appendix Full Report B / people:

A process operator nearby the deodorization unit when the explosion occurred was killed.

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 building, containing multi-purpose plant (with reactors, receivers, filters, tanks and assorted services), was engulfed by the fire that followed the explosion. No data are available about the cost of the material losses caused by the accident.

Appendix Full Report B / disruption of community life:

A nearby main road to the industry was closed. Local residents were warned to close doors and windows because of the acidic smoke produced by the fire that followed the explosion.

Appendix Full Report C / lesson learned - prevent:

After the accident, the following measures were established:

- 1- the unit to be demolished;
- 2- process producing the chemical effluent containing strong-smelling sulphur compounds transferred to another factory;

3- a new process for effluent treatment not using hydrogen peroxide to be introduced.