# Utsläpp av reaktionsblandning på en fabrik för produktion av cellulosa nitrat.

#### 920221 MARS 1992 01

Olyckan inträffade på en fabrik för produktion av cellulosanitrat. En operatör öppnade av misstag en kulventil och släppte ut den oreagerade reaktionsblandningen i avloppet, istället för att leda reaktionsblandningen till en omrörare. Avloppstanken var förbunden med en kokare, och reaktionsblandningen fortsatte från den ut i miljön. Larmet gick då reaktionsblandningen gick ut i avloppet och anläggningen stängdes ned och utrymdes.

#### Inblandade ämnen och mängder

	CAS Nr.	Mängd
cellulosa nitrat	9004-70-0	1200 kg
kväveoxider		21 kg
dikvävedioxid (N2O)	10024-97-2	
kväveoxid (NO)	10102-43-9	
kvävedioxid (NO2)	10102-44-0	
salpetersyra	7697-37-2	okänt
svavelsyra	7664-93-0	okänt

#### Skador:

Människor: Inga. Materiella: Inga

Miljö/ekologi: Kortvarigt utsläpp av kväveoxider i luften. Avloppsvattnet fick höga

halter av salpetersyra och svavelsyra, men inga effekter på miljön är

rapporterade.

Infrastruktur: Inga

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

Kortfattat anges förebyggande åtgärder.

# **Report Profile**

#### **Identification of Report:**

**country:** FA **ident key:** 1992\_001\_01

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

Date of Major Occurrence: Time of Major Occurrence

start: 1992-02-21 start: 10:00:00

finish: finish:

#### **Establishment:**

name:

address:

industry: 2001 general chemicals manufacture

General Chemical (Cellulose Nitrate Production)

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 -
e) - not applicable -
d) - not applicable -
e) - not applicable -
Short Report
<b>country:</b> FA <b>ident key:</b> 1992_001_01
Accident Types:
release: Yes explosion: No
water contamination: Yes other: No
fire: No
description:
SAFETY SYSTEMS OR OPERATORS INTERVENTION: see Appendix Short Report / description of accident types
Substance(s) Directly Involved:
toxic: Yes explosive: No
ecotoxic: No other: No
flammable: No
description:
- Cellulose Nitrate (C.A.S. CODE: 9004-70-0): amount involved = 1,200 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 during normal operation in a cellulose nitrate production plant of a general chemical
industry. In the nitration process (esterification) the cellulose reacts with a mixture of nitric acid,
sulphuric acid and water. Th see Appendix Short Report / description of immediate sources

**Suspected Causes:** 

plant or equipment: No environmental: No

human: Yes other: No

description:

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

**Immediate Effects:** 

material loss: Yes

human deaths: No

human injuries: No community disruption: Yes

other: No

ecological harm: Yes

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: 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: Yes

mitigation: Yes

description:

INTERNAL TO THE ESTABLISHMENT:... see Appendix Short Report / description of immediate lessons learned

# **A Occurrence Full Report**

**country:** FA **ident key:** 1992\_001\_01

1 Type of Accident

remarks: During the production of cellulose nitrate, the reaction mixture was fed to

an intermediate stirring apparatus. Due to wrong manipulation of a ball

valve, the unreacted mixture was released to a sewage tank instead to the

centrifuge. As the... see Appendix Full Report A  $\slash\$  type of accident

2 Dangerous Substances

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

cellulose nitrate and nitrogen oxides refer to the amount involved in the

accident. No data are available about the amounts of nitric and sulphuric

acid involved.

3 Source of Accident

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illustration: - not applicable -
remarks: The accident occurred during normal operation in a cellulose nitrate
production plant of a general chemical industry (codes 3101 and 2001). In
the nitration process (esterification) the cellulose reacts with a mixture
of nitric acid, sulphu... 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 (\inftyC):
remarks: - not applicable -
5 Causes of Major Occurrence
main causes
technical / physical - not applicable -
human / organizational 5303 organization: organized procedures (none, inadequate, inappropriate,
5304 organization: training/instruction (none, inadequate, inappropriate)
5401 person: operator error
- not applicable -
- not applicable -
remarks: Despite of operating instructions (codes 5303 and 5304), a worker opened a wrong ball
valve (code 5401) in the intermediate stirring apparatus and the unreacted acid/cellulose
mixture was pumped not in the screening worm centrifuge as plann... see Appendix Full
Report A / causes of major occurrence
6 Discussion about the Occurrence
- not applicable -
Type of Accident country: FA ident key: 1992_001_01
event:
major occurrence 1103 release: fluid release to water
initiating event 1103 release: fluid release to water
associated event - not applicable -
event:
major occurrence 1101 release: gas/vapour/mist/etc release to air
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initiating event 1101 release: gas/vapour/mist/etc release to air
associated event - not applicable -
Dangerous substances
country: FA ident key: 1992_001_01
a) total establishment inventory
CAS number: 7664-93-9 identity: Sulphuric Acid
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: STARTING MATERIAL
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: 10024-97-2 identity: Nitrogen 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): 0,021
use of substance as: ABNORMAL PRODUCT
b) substance belongs to relevant inventory directly involved: Yes
actual quantity: 0,021 potential quantity: 0,021
c) substance belongs to relevant inventory indirectly involved: No
actual quantity: -1 indir_pot_quant: -1
a) total establishment inventory
CAS number: 10102-43-9 identity: Nitrogen Monoxide
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 -
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```
maximum quantity (tonnes): 0,021
use of substance as: ABNORMAL PRODUCT
b) substance belongs to relevant inventory directly involved: Yes
actual quantity: 0,021 potential quantity: 0,021
c) substance belongs to relevant inventory indirectly involved: No
actual quantity: -1 indir pot quant: -1
a) total establishment inventory
CAS number: 10102-44-0 identity: Nitrogen Dioxide
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): 0,021
use of substance as: ABNORMAL PRODUCT
b) substance belongs to relevant inventory directly involved: Yes
actual quantity: 0,021 potential quantity: 0,021
c) substance belongs to relevant inventory indirectly involved: No
actual quantity: -1 indir_pot_quant: -1
a) total establishment inventory
CAS number: 7697-37-2 identity: Nitric Acid
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: STARTING MATERIAL
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: 9004-70-0 identity: Cellulose Nitrate
name from Seveso I Directive: - not applicable -
name from Seveso II Directive: - not applicable -
category from Seveso II: - not applicable -
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other hazards (1): - not applicable -
other hazards (2): - not applicable -
maximum quantity (tonnes): 1,2
use of substance as: NORMAL FINISHED PRODUCT
b) substance belongs to relevant inventory directly involved: Yes
actual quantity: 1,2 potential quantity: 1,2
c) substance belongs to relevant inventory indirectly involved: No
actual quantity: -1 indir_pot_quant: -1
Source of Accident - Situation country: FA ident key: 1992 001 01
situation
industry
inititating event 2001 general chemicals manufacture
associated event - not applicable -
activity/unit
major occurrence 3106 process: power generation (burning fuel, etc.)
inititating event 3104 process: physical operations (mixing, melting crystallizing, etc.)
associated event - not applicable -
component
major occurrence 4009 heat exchanger (boiler, refrigerator, heating coils, etc.)
inititating event - not applicable -
associated event - not applicable -
B Consequences Full Report
country: FA ident key: 1992_001_01
1 Area concerned
affected
extent of effects installation: Yes
establishment: Yes
off-site: local: Yes
off-site; regional: No
off-site; transboundary: No
illustration of effects - not applicable -
remarks Short-term high nitrogen oxides concentration in air. Waste water polluted with ... see Appendix
Full Report B / area concerned - remarks
2 People
establishment popul. emergency personnel off-site population
total at risk
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immediate fatalities

subsequent fatalities
hospitalizing injuries
other serious injuries
health monitoring
remarks No people were injured during the accident.
3 Ecological Harm
pollution/contamination/damage of:
- residential area (covered by toxic cloud) not applicable
- 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 Short-term high nitrogen oxides concentration in air. Waste water polluted with 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 DM ECU DM
material losses 7500
response, clean up, restoration
remarks The accident caused the total loss of production. The cost of the production los 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

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- water No
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- 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 Warning of the neighbourhood in eastern direction by the municipality.... see Appendix Full Repor

### 7 Discussion of Consequences

## **Ecological Components involved**

country: FA ident key: 1992\_001\_01

type: 6102 inland: urban development

threatened: not applicable affected: not applicable

# **C Response Full Report**

country: FA ident key: 1992\_001\_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  $\ensuremath{\text{No}}$ assessment/auditing of management system - specified procedures for No review and update of management policy - specified general training No

- specified emergency No

procedures

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, training f... see Appendix Full Report C / lesson learned - prevent measures to mitigate consequences: After the accident it was deci... see Appendix Full Report C / lesson learned - mitigate

useful references:

- not applicable -

### 5 Discussion about Response

- not applicable -

# Appendices for the FA / 1992 001 01 report

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

SAFETY SYSTEMS OR OPERATORS INTERVENTION:

Alarm system was activated and the boilers feeding pumps were shut-off. The boiler steam supply was interrupted.

ACCIDENT CASE HISTORY DESCRIPTION:

During the production of cellulose nitrate, the reaction mixture (cellulose, nitric acid, sulphuric acid and water) was fed to an intermediate stirring apparatus. This apparatus has two outputs: one for the following screening worm centrifuge and one to the sewage vessel. Due to wrong manipulation of a ball valve, the unreacted acid/cellulose mixture was released to a sewage tank instead to the centrifuge. As the sewage tank was connected with the boiler unit, the unreacted mixture was pumped to 4 boilers whereby the nitrate phase was released into the environment. Waste water was polluted by the acid mixture.

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

- Cellulose Nitrate (C.A.S. CODE: 9004-70-0): amount involved = 1,200 kg.
- Nitrogen Oxides (C.A.S. CODE: 10024-97-2 [N2O], C.A.S. CODE: 10102-43-9 [NO], C.A.S. CODE: 10102-44-0 [NO2]): amount involved = 21 kg (about 17 m3).
- Nitric Acid (C.A.S. CODE: 7697-37-2): amount involved = not known.
- Sulphuric Acid (C.A.S. CODE: 7664-93-9): amount involved = not known.

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

The accident occurred during normal operation in a cellulose nitrate production plant of a general chemical industry. In the nitration process (esterification) the cellulose reacts with a mixture of nitric acid, sulphuric acid and water. The reaction mixture is then fed to an intermediate stirring apparatus and, afterthat, it is transferred to a screening worm machine where separation between acid and treated cellulose takes place. The intermediate stirring apparatus has two outputs: one for the following screening worm centrifuge and one to the sewage vessel.

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

INITIATING EVENT AND CONSEQUENCES:

Each intermediate stirring apparatus had 2 outputs: one for the following screening worm centrifuge and one to the sewage vessel. Due to wrong manipulation of a ball valve, the unreacted acid/cellulose mixture was released to a sewage tank and then it was pumped to 4 boilers whereby the nitrate phase was released into the environment.

CAUSES:

Despite of operating instructions, a worker opened a wrong ball valve in the intermediate stirring apparatus and the unreacted acid/cellulose mixture was pumped not in the screening worm centrifuge as planned but flowed in a sewage tank, which usually transfer the centrifugated mixture in the boiler unit.

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

MATERIAL LOSS:

The accident caused the total loss of production. The cost of the production loss has been estimated in about 7,500 Deutch Marcs.

ECOLOGICAL HARM:

Short-term high nitrogen oxides concentration in air. Waste water polluted with acid mixture but, from the Original Report, there is no evidence of significant ecological harm.

COMMUNITY DISRUPTION:

Warning of the neighbourhood in eastern direction by the municipality.

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

INTERNAL TO THE ESTABLISHMENT:

Alarm system was activated and the boilers feeding pumps were shut-off. The boiler steam supply was interrupted. Evacuation of personnel and plant shut-down.

EXTERNAL TO THE ESTABLISHMENT:

Warning of the neighbourhood in eastern direction by the municipality.

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

INTERNAL TO THE ESTABLISHMENT:

Initiation of disciplinary measures against the guilty worker.

MEASURES TO PREVENT ANY RECURRENCE OF SIMILAR ACCIDENTS:

After the accident, training for all employees was established.

MEASURES TO MITIGATE THE EFFECTS OF THE ACCIDENT:

After the accident it was decided a revision of warning plan and emergency plans, concerning internal use in service and territorial "warning".

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

During the production of cellulose nitrate, the reaction mixture was fed to an intermediate stirring apparatus. Due to wrong manipulation of a ball valve, the unreacted mixture was released to a sewage tank instead to the centrifuge. As the sewage tank was connected with the boiler unit, the unreacted mixture was pumped to 4 boilers whereby the nitrate phase was released into the environment and waste water was polluted by acid mixture (codes 1101 and 1103).

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

The accident occurred during normal operation in a cellulose nitrate production plant of a general chemical industry (codes 3101 and 2001). In the nitration process (esterification) the cellulose reacts with a mixture of nitric acid, sulphuric acid and water. The reaction mixture is then fed to an intermediate stirring apparatus (codes 3104 and 4007)that has two outputs: one for the following worm machine and one to the sewage vessel (code 4003) connected with the boiler unit (codes 3106, 4009).

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

Despite of operating instructions (codes 5303 and 5304), a worker opened a wrong ball valve (code 5401) in the intermediate stirring apparatus and the unreacted acid/cellulose mixture was pumped not in the screening worm centrifuge as planned but flowed in a sewage tank, which usually transfer its contents to the boiler unit.

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

Short-term high nitrogen oxides concentration in air. Waste water polluted with acid mixture.

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

Short-term high nitrogen oxides concentration in air. Waste water polluted with acid mixture but, from the Original Report, there is no evidence of significant ecological harm.

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

The accident caused the total loss of production. The cost of the production loss has been estimated in about 7,500 Deutch Marcs.

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

Warning of the neighbourhood in eastern direction by the municipality.

# Appendix Full Report C / lesson learned - prevent:

After the accident, training for all employees was established.

# Appendix Full Report ${\bf C}$ / lesson learned - mitigate:

After the accident it was decided a revision of warning plan and emergency plans, concerning internal use in service and territorial "warning".