

## Utsläpp till följd av ett operatörsmisslag på en kemikaliefabrik.

910221 MARS 1991\_23

Olyckan inträffade i en av två glasfodrade tankar som innehöll en syralösning (ungefär 29% svavelsyra) för absorption av överskottsammoniak från processen. Denna lösning hölls ständigt vid ett pH på 5-6 genom manuella tillsatser av ammoniumkarbonat. Då olyckan inträffade hade en operatör senfälligt noterat att pH hade stigit och lösningen blivit basiskt. Han tillsatte därför 60% svavelsyra vilket resulterade i en abnorm produktion av koldioxid som sprängde tanken. Innehållet, totalt ca 20 m<sup>3</sup>, rann ut och samlades delvis upp i en bassäng. Resten rann ut i avloppet. Produktionen på alla andra avdelningar stoppades för att under omhändertagandet av avloppet. Därigenom begränsades utsläppet i floden. De lokala miljömyndigheterna underrättades.

### Inblandade ämnen och mängder

	CAS Nr.	Mängd
en flytande lösning med:		totalt 20 kg
ammoniak	7664-41-7	
svavelsyra	7664-93-9	
ammoniumsulfat	7783-20-2	
ammoniumkarbonat	506-87-6	
naftalen	91-20-3	
triklorbensen	120-82-1	spårmängder

### Skador:

Människor:	Inga.
Materiella:	Skador på installationen.
Miljö/ekologi:	Efter att begränsade mängder runnit ut i Bornidafloden togs prover men inga effekter kunde konstateras.
Infrastruktur:	Inga.

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

Mycket kortfattat anges förebyggande åtgärder.

## Report Profile

### Identification of Report:

country: FA ident key: 1991\_023\_01

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

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

start: 1991-02-21 start: 18:00:00

finish: finish:

### Establishment:

name:

address:

industry: 2001 general chemicals manufacture

Organic Chemical (Chemical Intermediates and Dyes 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 -

c) - not applicable -

d) - not applicable -

e) - not applicable -

## Short Report

country: FA ident key: 1991\_023\_01

**Accident Types:**

release: Yes explosion: Yes

water contamination: No other: No

fire: No

**description:**

The accident occurred in one of the two glass lined storage tanks, 35 m3 capacity each, holding the recirculated acid solution (about 29% of sulphuric acid) used to absorb the residual ammonia from the gaseous effluents of the phthalocyanine... see Appendix Short Report / description of accident types

**Substance(s) Directly Involved:**

toxic: Yes explosive: Yes

ecotoxic: No other: No

flammable: Yes

**description:**

The amount of solution released during the accident has been estimated in about 20 m3. No data are available about the single amounts of the substances contained in the solution. These substances were:... see Appendix Short Report / description of substances involved

**Immediate Sources of Accident:**

storage: Yes transfer: No

process: Yes other: No

**description:**

The accident occurred in one of the two glass lined storage tanks containing the recirculated acid solution

used to absorb ammonia from the gaseous effluents of the phthalocyanines process unit. Each 35 m<sup>3</sup> glass lined storage tank was contain... see Appendix Short Report / description of immediate sources

### **Suspected Causes:**

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

**other:** No

**ecological harm:** No

**national heritage loss:** No

**description:**

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

### **Emergency Measures taken:**

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

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

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

**evacuation:** No

**description:**

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

### **Immediate Lessons Learned:**

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

**mitigation:** Yes

**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:** 1991\_023\_01

### **1 Type of Accident**

**remarks:** An operator, by error, suddenly added a 60% sulphuric acid solution to an ammonia solution contained in a glass lined storage tank. This resulted in an abnormal production of carbon dioxide that overpressurized the tank which exploded (code... see Appendix Full Report A / type of accident)

### **2 Dangerous Substances**

**remarks:** The amount of solution released during the accident has been estimated in

about 20 m3. No data are available about the single amounts of the substances contained in the solution. These substances were: ammonia, sulphuric acid, ammonium sulph... see Appendix Full Report A / dangerous substances

### 3 Source of Accident

**illustration:** - not applicable -

**remarks:** The accident occurred in one of the two glass lined storage tanks (codes 4003 and 3201) containing the recirculated acid solution used to absorb ammonia from the gaseous effluents of the phthalocyanines process unit in an organic chemical in... 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** 5107 operation: unexpected reaction/phase-transition

- 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)

5307 organization: process analysis (inadequate, incorrect)

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

5401 person: operator error

**remarks:** The accident was caused by an operator error (code 5401) that realized too late that the solution was became basic (the continuous pH monitoring was not foreseen [code 5307 and 5308]) and added, by error again (codes 5303 and 5304), a 60% s... see Appendix Full Report A / causes of major occurrence

### 6 Discussion about the Occurrence

- not applicable -

**Type of Accident** country: FA ident key: 1991\_023\_01

**event:**

**major occurrence** 1102 release: fluid release to ground

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

**associated event** - not applicable -

## **Dangerous substances**

**country:** FA **ident key:** 1991\_023\_01

### **a) total establishment inventory**

**CAS number:** 120-82-1 **identity:** Trichlorobenzene

**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:** 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:** 91-20-3 **identity:** Naphtalene

**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: identity: Carbon 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): -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: 7783-20-2 identity: Ammonium Sulphate

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: 506-87-6 identity: Ammonium Carbonate

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:** 7664-41-7 **identity:** Ammonia

**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

**Source of Accident - Situation** country: FA **ident key:** 1991\_023\_01

**situation**

**industry**

**initiating event** 2001 general chemicals manufacture

**associated event** - not applicable -

**activity/unit**

**major occurrence** 3201 storage: process-associated (stockholding, etc. on-site of manufacture)

**initiating event** 3201 storage: process-associated (stockholding, etc. on-site of manufacture)

**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** - not applicable -

## **B Consequences Full Report**

country: FA ident key: 1991\_023\_01

## 1 Area concerned

**affected**

**extent of effects installation:** Yes

**establishment:** Yes

**off-site; local:** No

**off-site; regional:** No

**off-site; transboundary:** No

**illustration of effects** - not applicable -

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

Full Report B / area concerned - remarks

## 2 People

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

**total at risk**

**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) 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** The collapse of the tank caused the release of the solution (about 20 m3) but sa... 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 No data are available about the cost of the material losses that occurred (colla... see Appendix

Full Report B / material loss

## 6 Disruption of Community Life

establishment/plant evacuated disabled/unoccupiable destroyed

- nearby residences/hotels No No No

- nearby factories/offices/small shops No No No

- schools, hospitals, institutions No No No

- other places of public assembly No No No

interruption of utilities etc. no / yes duration

- gas No

- electricity No

- water No

- sewage treatment works No

- telecommunications No

- main roads No

- railways No

- waterways No

- air transport No

significant public concern none local level national level

- off site populations Yes No No

- media interest No No No

- political interest No No No

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

## 7 Discussion of Consequences

# C Response Full Report

country: FA ident key: 1991\_023\_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

assessment/auditing of

management system

- specified procedures for

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, provisions... see Appendix Full Report C / lesson learned - prevent

measures to mitigate consequences:

After the accident, improvemen... see Appendix Full Report C / lesson learned - mitigate

useful references:

- not applicable -

### **5 Discussion about Response**

- not applicable -

# Appendices for the FA / 1991\_023\_01 report

## Appendix Short Report / description of accident types:

The accident occurred in one of the two glass lined storage tanks, 35 m<sup>3</sup> capacity each, holding the recirculated acid solution (about 29% of sulphuric acid) used to absorb the residual ammonia from the gaseous effluents of the phthalocyanines process unit. This solution was enriched with ammonium carbonate coming from the ammonia treatment unit. The pH of the solution was manually controlled once per shift and adjusted if necessary by adding sulphuric acid solution so that the pH was maintained within the slightly acidic range (5'6). The solution's pH was periodically checked (every 8 hours) by an operator. When the accident occurred, the operator realized too late that the ammonium sulphate and ammonium carbonate solution was became basic and suddenly added a 60% sulphuric acid solution to it. This resulted in an abnormal production of carbon dioxide that overpressurized the tank which exploded because of inadequate pressure relieving capacity (the hydraulic trap with which the tank was equipped was not sufficient to withstand the peak pressure generated). The collapse of the tank caused the release of the solution (about 20 m<sup>3</sup>), which was partially recovered in the containment basin of the 2 glass lined tanks and partially in the yard. The rest of the solution was collected, through the sewer network, in the emergency basin of ACNA. All plants (except power plant and the oleum production plant) were shut-down in order to reduce the amount of effluents to the sewer network. This allowed the deuration of the ammonia solution released from the exploded tank and accumulated in the emergency basin avoiding, therefore, the pollution of the Bormida river. Samples taken from the river and analyzed by the local environmental authority laboratory (PMP of the U.S.L. N° 7 of City of Savona) confirmed that the amount of solution spilled caused no environmental damage. Nobody was injured.

## Appendix Short Report / description of substances involved:

The amount of solution released during the accident has been estimated in about 20 m<sup>3</sup>. No data are available about the single amounts of the substances contained in the solution. These substances were:

- Ammonia (C.A.S. CODE: 7664-41-7, E.E.C. CODE: 007-001-00-5).
- Sulphuric Acid (C.A.S. CODE: 7664-93-9).
- Ammonium Sulphate (C.A.S. CODE: 7783-20-2).
- Ammonium Carbonate (C.A.S. CODE: 506-87-6).
- Naphthalene (C.A.S. CODE: 91-20-3).
- Trichlorobenzene (C.A.S. CODE: 120-82-1): amount involved = traces.

Also, no data are available about the amount of carbon dioxide generated by the reaction of sulphuric acid with the ammonia solution contained in the glass lined storage tank.

## Appendix Short Report / description of immediate sources:

The accident occurred in one of the two glass lined storage tanks containing the recirculated acid solution used to absorb ammonia from the gaseous effluents of the phthalocyanines process unit. Each 35 m<sup>3</sup> glass lined storage tank was containing a 29% solution of sulphuric acid.

## Appendix Short Report / description of suspected causes:

INITIATING EVENT AND CONSEQUENCES:

The operator realized too late that the ammonium sulphate and ammonium carbonate solution was became basic and suddenly added a 60% sulphuric acid solution to it. This resulted in an abnormal production of carbon dioxide that overpressurized the tank which exploded because of inadequate pressure relieving capacity (the hydraulic trap with which the tank was equipped was not sufficient to withstand the peak pressure generated). The collapse of the tank caused the release of the solution (about 20 m<sup>3</sup>).

CAUSES:

The accident was caused by an operator error that realized too late that the solution was became basic (the continuous pH monitoring was not foreseen) and added, by error again, a 60% sulphuric acid solution, resulting in an internal overpressurization of the tank due to the formation of carbon dioxide. Besides, the tank exploded because the pressure relieving capacity of the provided hydraulic trap was inadequate due to a wrong plant design.

## Appendix Short Report / description of immediate effects:

MATERIAL LOSS:

No data are available about the cost of the material losses that occurred (collapse of the glass lined storage tank and release of about 20 m<sup>3</sup> of solution).

ECOLOGIC HARM:

Samples taken from the nearby Bormida river and analyzed by the local environmental authority laboratory (PMP of the U.S.L. N° 7 of City of Savona) confirmed that the amount of solution spilled caused no environmental damage.

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

INTERNAL TO THE ESTABLISHMENT:

The Internal Emergency Plan was activated. All plants (except power plant and the oleum production plant) were shut-down in order to reduce the amount of effluents to the sewer network. This allowed the deuration of the ammonia solution released from the exploded tank and accumulated in the emergency basin avoiding, therefore, the pollution of the Bormida river.

EXTERNAL TO THE ESTABLISHMENT:

The activation of the Internal Emergency Plan prevented the pollution of the Bormida river. Samples taken from the river and analyzed by the local environmental authority laboratory (PMP of the U.S.L. N° 7 of City of Savona) confirmed that the amount of solution spilled caused no environmental damage.

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

MEASURES TO PREVENT ANY RECURRENCE OF SIMILAR ACCIDENTS:

After the accident, provisions for continuous pH monitoring in the recirculating solution to avoid development in unwanted reactions was established.

#### MEASURES TO MITIGATE THE EFFECTS OF THE ACCIDENT:

After the accident, improvement of mechanical design paying particular attention to pressure relief devices was established.

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

An operator, by error, suddenly added a 60% sulphuric acid solution to an ammonia solution contained in a glass lined storage tank. This resulted in an abnormal production of carbon dioxide that overpressurized the tank which exploded (code 1304). The collapse of the tank caused the release (code 1102) of the solution (about 20 m<sup>3</sup>) but no environmental damage occurred.

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

The amount of solution released during the accident has been estimated in about 20 m<sup>3</sup>. No data are available about the single amounts of the substances contained in the solution. These substances were: ammonia, sulphuric acid, ammonium sulphate, ammonium carbonate, naphthalene and trichlorobenzene (traces). Also, no data are available about the amount of carbon dioxide generated by the reaction of sulphuric acid with the ammonia solution contained in the glass lined storage tank.

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

The accident occurred in one of the two glass lined storage tanks (codes 4003 and 3201) containing the recirculated acid solution used to absorb ammonia from the gaseous effluents of the phthalocyanines process unit in an organic chemical industry for the production of chemical intermediates and dyes (code 2001). Each 35 m<sup>3</sup> glass lined storage tank was containing a 29% solution of sulphuric acid.

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

The accident was caused by an operator error (code 5401) that realized too late that the solution was becoming basic (the continuous pH monitoring was not foreseen [code 5307 and 5308]) and added, by error again (codes 5303 and 5304), a 60% sulphuric acid solution, resulting in an internal overpressurization of the tank due to the formation of carbon dioxide (code 5107). Besides, the tank exploded because the pressure relieving capacity of the provided hydraulic trap was inadequate (code 5307).

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

In the Original Report there is no evidence of significant effects outside the establishment because, even if the collapse of the tank caused the release of the solution (about 20 m<sup>3</sup>), samples taken from the nearby Bormida river and analyzed by the local environmental authority laboratory (PMP of the U.S.L. N° 7 of City of Savona) confirmed that the amount of solution spilled caused no environmental damage. No people were injured.

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

The collapse of the tank caused the release of the solution (about 20 m<sup>3</sup>) but samples taken from the nearby Bormida river and analyzed by the local environmental authority laboratory (PMP of the U.S.L. N° 7 of City of Savona) confirmed that the amount of solution spilled caused no environmental damage.

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

No data are available about the cost of the material losses that occurred (collapse of the glass lined storage tank and release of about 20 m<sup>3</sup> of solution).

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

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

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

After the accident, provisions for continuous pH monitoring in the recirculating solution to avoid development in unwanted reactions were established.

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

After the accident, improvement of mechanical design paying particular attention to pressure relief devices was established.