

Utsläpp från en reaktor på en PVC-fabrik.

890109 MARS 1989_14

Olyckan inträffade vid produktion av PVC i en reaktor som värmdes med vattenånga av 165°-175°C. Reaktionen genomfördes med bristfällig tillsats av ammoniak vilket ledde till ett kraftigt överskott av väteklorid (saltsyra). Överskottet saltsyra destabiliserade mängden bildad PVC-latex vilket ledde till koagulering av PVC-latex. Därmed fallerade omröraren. Ingen varningssignal utgick om detta. En lokal överhettning blev följden, vilket orsakade en värmeutvecklande sönderdelning av PVC. Det koagulerade PVC täppte till alla öppningar, inklusive sprängblecket och säkerhetsventilen. Överskottet av saltsyra började reagera med reaktorkärlets vägg vid hög temperatur. Trots att uppvärmningen stoppats och vattenkyllning satts igång brast kärlet då tjockleken reducerats från 9,8 mm till 2 mm. Det automatiska sprinklersystemet kylde ned kärlet ytterligare och spädde ut de utsläppta kemikalierna.

Inblandade ämnen och mängder

	CAS Nr.	Mängd
en suspension av vinylkloridmonomer och PVC		ca 20 m3
vinylklorid (saltsyra)	75-01-4	
polyvinylklorid	9002-86-2	
väteklorid	7647-01-0	okänt

Skador:

Människor:	Inga.
Materiella:	Anläggningen skadades.
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: 1989_014_01

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

Date of Major Occurrence: Time of Major Occurrence

start: 1989-01-09 start:

finish: finish:

Establishment:

name:

address:

industry: 2001 general chemicals manufacture

Organic Chemical (Synthetic Polymer and Latex 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: 1989_014_01

Accident Types:

release: Yes 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: Yes explosive: Yes

ecotoxic: No other: No

flammable: Yes

description:

- Suspension of Vinylchloride Monomer (C.A.S. CODE: 75-01-4) and Polyvinylchloride [PVC] (C.A.S. CODE: 9002-86-2); amount involved = approximately 20 m3.... 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 the polymerization of vinylchloride in an organic chemical industry for the synthetic polymer and latex production based on ethenylbenzene, butadiene, acrylonitril, acrylates and vinylchloride. The plant was at ... 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: Yes

human deaths: No

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

other: No

ecological harm: No

national heritage loss: No

description:

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

Emergency Measures taken:

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

external services: No **restoration:** No

sheltering: No **other:** No

evacuation: No

description:

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

Immediate Lessons Learned:

prevention: Yes **other:** No

mitigation: No

description:

MEASURES TO PREVENT ANY RECURRENCE OF SIMILAR ACCIDENTS:... see Appendix Short Report / description of immediate lessons learned

A Occurrence Full Report

country: FA **ident key:** 1989_014_01

1 Type of Accident

remarks: Due to an insufficient addition of ammonia to a polymerization reactor for the latex production, a runaway reaction occurred. The uncompensated hydrogen chloride started to react with the material of the reactor and, though the steam supply... see Appendix Full Report A / type of accident

2 Dangerous Substances

remarks: No data are available about the single amounts of vinylchloride and PVC in the suspension. Approximately, about 20 m³ of vinylchloride and PVC were contained in the reactor when the accident occurred. No data are available about the amount ... see Appendix Full Report A / dangerous substances

3 Source of Accident

illustration: - not applicable -

remarks: The accident occurred during the polymerization on vinylchloride (code 3101) in an organic chemical industry (code 2001) for the synthetic polymer and latex production based on ethenylbenzene, butadiene, acrylonitril, acrylates and vinylchl... see Appendix Full Report A / source of accident - remarks

4 Meteorological Conditions

precipitation none: fog: rain: hail: snow:

No No No No No

wind speed (m/s):

direction (from):

stability (Pasquill):

ambient temperature (°C):

remarks: - not applicable -

5 Causes of Major Occurrence

main causes

technical / physical 5105 operation: instrument/control/monitoring-device failure

5106 operation: runaway reaction

- not applicable -

- not applicable -

- not applicable -

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

5307 organization: process analysis (inadequate, incorrect)

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

5401 person: operator error

- not applicable -

remarks: Due to a human error (codes 5303 and 5401), PVC-latex with insufficient ammonia was used, resulting in the coagulation of the suspension. It caused the agitator failure (there were no indication of its failure) and therefore a not detected... see Appendix Full Report A / causes of major occurrence

6 Discussion about the Occurrence

- not applicable -

Type of Accident country: FA ident key: 1989_014_01

event:

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

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

associated event 1101 release: gas/vapour/mist/etc release to air

Dangerous substances

country: FA ident key: 1989_014_01

a) total establishment inventory

CAS number: 75-01-4 identity: Vinylchloride Monomer

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: 9002-86-2 identity: Polyvinylchloride

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: 7646-01-0 identity: Hydrogen Chloride

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

e) substance belongs to relevant inventory indirectly involved: No

actual quantity: -1 indir_pot_quant: -1

Source of Accident - Situation country: FA ident key: 1989_014_01

situation

industry

initiating event 2001 general chemicals manufacture

associated event 2001 general chemicals manufacture

activity/unit

major occurrence 3101 process: chemical batch reaction

initiating event 3101 process: chemical batch reaction

associated event 3101 process: chemical batch reaction

component

major occurrence 4002 reaction vessel; pressurised

initiating event 4002 reaction vessel; pressurised

associated event 4002 reaction vessel; pressurised

B Consequences Full Report

country: FA ident key: 1989_014_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 effects outside the establishment... 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 data are available about the number of people involved in the accident.... 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

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. The... 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 HFL ECU HFL

material losses 1000000

response, clean up, restoration

remarks The cost of the material damages to the reactor and to the plant caused by the e... 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 effects outside the establishment... see Appendix

7 Discussion of Consequences

C Response Full Report

country: FA ident key: 1989_014_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 / 1989_014_01 report

Appendix Short Report / description of accident types:

ACCIDENT CASE HISTORY DESCRIPTION:

The accident occurred during the production of polyvinylchloride (PVC) in a reactor heated with steam at a temperature of 165°175°C. The reaction was carried out without an adequate addition of ammonia and therefore the normal small hydrogen chloride production could not be compensated. Hence, the excess of hydrogen chloride destabilized the suspension of PVC-latex which coagulated. The coagulation of the latex caused the mixer failure but there was no indication of it. Consequently, a local overheating resulted and a decomposition of PVC occurred because the steam temperature (165°175°C) was higher than the PVC decomposition temperature (144°C). Being the PVC decomposition exothermic, the heat caused an expansion of coagulated latex clogged all the pipings including the inlet to the bursting disc and to the safety valve. The uncompensated hydrogen chloride started to react with the material of the reactor (the Duplex stainless steel was not resistant against hydrogen chloride at high temperatures). Though the steam supply had been stopped and the external cooling started (activated by the release of hot gases from the reactor), the vessel burst because the wall thickness was reduced from 9.8 mm to 2 mm. Activation of the sprinkler system enhanced reactor cooling and diluted the hydrogen chloride vapours.

Appendix Short Report / description of substances involved:

- Suspension of Vinylchloride Monomer (C.A.S. CODE: 75-01-4) and Polyvinylchloride [PVC] (C.A.S. CODE: 9002-86-2): amount involved = approximately 20 m3.
- Hydrogen chloride (C.A.S. CODE: 7647-01-0, E.E.C. CODE:017-002-00-2): amount involved = not known (the amount of hydrogen chloride which was dispersed in the atmosphere in any case was estimated to be very low).

Appendix Short Report / description of immediate sources:

The accident occurred during the polymerization of vinylchloride in an organic chemical industry for the synthetic polymer and latex production based on ethenylbenzene, butadiene, acrylonitril, acrylates and vinylchloride. The plant was at a distance of approximately 1,200 metres from the first dwelling houses. The component involved was a polymerization reactor heated with steam at a temperature of 165°175°C.

Appendix Short Report / description of suspected causes:

CAUSES:

Due to a human error, PVC-latex with insufficient ammonia was used, resulting in the coagulation of the suspension. It caused the agitator failure (there were no indication of its failure) and therefore a not detected local overheating occurred. Overheating resulted in a runaway reaction because the steam temperature (about 165°175°C) was higher than the latex decomposition temperature (about 140°C).

Appendix Short Report / description of immediate effects:

MATERIAL LOSS:

The cost of the material damages to the reactor and to the plant caused by the explosion has been estimated in about 1,000,000 Guilders (about 0.43 MECU).

Appendix Short Report / description of emergency measures taken:

INTERNAL TO THE ESTABLISHMENT:

Though the steam supply was stopped and the external cooling of the reactor was applied (the hot gases released from the vessel activated the sprinkler system), the local weakening of the vessel wall around the steam inlet (thickness was reduced from 9.8 mm to 2 mm due to the hydrogen chloride attack) was too fast to prevent the physical explosion of the reactor.

EXTERNAL TO THE ESTABLISHMENT:

The concentration of hydrogen chloride in air was measured outside the establishment but no gas was detected at a distance of approximately 1,000 metres from the plant because the release of gases from the reactor activated the sprinkler system, resulting in cooling of the vessel and delution of the hot mixture that reduced the emission rate of hydrogen chloride into the environment.

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- substitution of the plasticizing agent and use of steam with a maximum temperature of 127°C (latex starts decomposing at 140°C);
- 2- installation of a double signalling device on the mixer for the detection of malfunctions;
- 3- interlock of the steam supply to the mixer so that the steam supply will be automatically shut off in the case of agitator failure;
- 4- installation of two independent temperature sensors. The steam supply will be automatically shut off if any of the sensors indicates a temperature above 100°C or when there is a substantial difference in indications of the two sensors;
- 5- installation of a level switch which will automatically shut off the steam supply when a high level in the reactor is reached;
- 6- installation of a pressure switch (set at 1 bar overpressure) which will automatically shut off the steam supply when a high pressure is reached;
- 7- all these steam shut off actions to be coupled to an alarm signal in control room;
- 8- batch control on quality, pH and persulphate contents to be introduced;
- 9- during the process the pH to be monitored through regular sampling; the possibility of continuous pH-monitoring to be investigated.

Appendix Full Report A / type of accident:

Due to an insufficient addition of ammonia to a polymerization reactor for the latex production, a runaway reaction occurred. The uncompensated hydrogen chloride started to react with the material of the reactor and, though the steam supply had been stopped and the external cooling activated, the vessel burst (code 1304). The vessel burst resulted in a hydrogen chloride release into the environment (code 1101).

Appendix Full Report A / dangerous substances:

No data are available about the single amounts of vinylchloride and PVC in the suspension. Approximately, about 20 m³ of vinylchloride and PVC were contained in the reactor when the accident occurred. No data are available about the amount of hydrogen chloride released during the accident. It must be underlined that hydrogen chloride is both a normal finished product of the reaction and an abnormal decomposition product of polymer.

Appendix Full Report A / source of accident - remarks:

The accident occurred during the polymerization on vinylchloride (code 3101) in an organic chemical industry (code 2001) for the synthetic polymer and latex production based on ethenylbenzene, butadiene, acrylonitril, acrylates and vinylchloride. The component involved was a polymerization reactor heated with steam at a temperature of 165°-175°C (code 4002). The plant was at a distance of approximately 1,200 metres from the first dwelling houses.

Appendix Full Report A / causes of major occurrence:

Due to a human error (codes 5303 and 5401), PVC-latex with insufficient ammonia was used, resulting in the coagulation of the suspension. It caused the agitator failure (there were no indication of its failure) and therefore a not detected local overheating occurred (codes 5105 and 5307). Overheating resulted in a runaway reaction (code 5106) because the steam temperature (about 165°-175°C) was higher than the latex decomposition temperature (code 5308).

Appendix Full Report B / area concerned - remarks:

In the Original Report there is no evidence of effects outside the establishment. The concentration of hydrogen chloride in air was measured outside the establishment but no gas was detected at a distance of approximately 1,000 metres from the plant because the release of gases from the reactor activated the sprinkler system, resulting in cooling of the vessel and delution of the hot mixture that reduced the emission rate of hydrogen chloride into the environment.

Appendix Full Report B / people:

No data are available about the number of people involved in the accident.

Appendix Full Report B / ecological harm:

In the Original Report there is no evidence of significant ecological harms. The concentration of hydrogen chloride in air was measured outside the establishment but no gas was detected at a distance of approximately 1,000 metres from the plant because the release of the gases from the reactor activated the sprinkler system, resulting in cooling of the vessel and delution of the hot mixture that reduced the emission rate of hydrogen chloride into the environment.

Appendix Full Report B / material loss:

The cost of the material damages to the reactor and to the plant caused by the explosion has been estimated in about 1,000,000 Guilders (about 0.43 MECU).

Appendix Full Report B / disruption of community life:

In the Original Report there is no evidence of effects outside the establishment. The concentration of hydrogen chloride in air was measured outside the establishment but no gas was detected at a distance of approximately 1,000 metres from the plant because the release of gases from the reactor activated the sprinkler system, resulting in cooling of the vessel and delution of the hot mixture that reduced the emission rate of hydrogen chloride into the environment.

Appendix Full Report C / lesson learned - prevent:

After the accident, the following measures were established:

- 1- substitution of the plasticizing agent and use of steam with a maximum temperature of 127°C (latex starts decomposing at 140°C);
- 2- installation of a double signalling device on the mixer for the detection of malfunctions;
- 3- interlock of the steam supply to the mixer so that the steam supply will be automatically shut off in the case of agitator failure;
- 4- installation of two independent temperature sensors. The steam supply will be automatically shut off if any of the sensors indicates a temperature above 100°C or when there is a substantial difference in indications of the two sensors;
- 5- installation of a level switch which will automatically shut off the steam supply when a high level in the reactor is reached;
- 6- installation of a pressure switch (set at 1 bar overpressure) which will automatically shut off the steam supply when a high pressure is reached;
- 7- all these steam shut off actions to be coupled to an alarm signal in control room;
- 8- batch control on quality, pH and persulphate contents to be introduced;
- 9- during the process the pH to be monitored through regular sampling; the possibility of continuous pH-monitoring to be investigated.