# Gasutsläpp på en alkyleringsanläggning på ett oljeraffinaderi.

### 901211 MARS 1990\_19

Strax efter 12 uppstod en läcka av isobutan med spårmängder av vätefluorid. Läckan uppstod efter vibrationer orsakat en spricka i den ena av två avtappningskranar. Sprickan uppstod till följd av materialtrötthet . Det inledande utsläppsflödet var ca 12 ton per timme. Efter en stund brast även den andra kranen och flödet fördubblades. Gasen antändes inte omedelbart och läckan identifierades snabbt. Med fjärrstyrda vetiler kunde tillflödet strypas och en gasen ledas till en fackla inom 2 minuter. Det utsläppta gasmolnet antändes av en dieselmotor i närheten och orsakade en mindre brand. Brandlarmet gick och vattengardiner användes för att kyla närliggande utrustning och begränsa gasens spridning. Olyckan var över och branden släckt efter 25 minuter. Räddningstjänsten anlände efter detta.

# Inblandade ämnen och mängder

isobutan CAS Nr. Mängd
isobutan 106-97-8 mindre än 2500 kg
vätefluorid 7664-39-3 spårmängder

Skador:

Människor: Tre personer skadades: en chockades, en förgiftades av isobutan, och

en fick brännskador.

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: 1990\_019\_01

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

Date of Major Occurrence: Time of Major Occurrence

start: 1990-12-11 start: 12:00:00

finish: finish:

### **Establishment:**

name:

address:

industry: 2002 petrochemical, refining, processing

Petroleum Refinery

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 -
e) - not applicable -
Short Report
<b>country:</b> FA <b>ident key:</b> 1990_019_01
Accident Types:
release: Yes explosion: No
water contamination: No other: No
fire: Yes
description:
ENVIRONMENT AND ATMOSPHERICAL CONDITIONS: see Appendix Short Report / description of accident types
Substance(s) Directly Involved:
toxic: No explosive: Yes
ecotoxic: No other: No
flammable: Yes
description:
- Isobutane (C.A.S. CODE: 106-97-8): amount involved = < 2,500 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 Hydrogen Fluoride Alkylation Unit of a petroleum refinery. In the process plant,
isobutane was mixed with olefins (such as propylene and butylene) to produce a polymeric substance called
alkylate which is a mixt see Appendix Short Report / description of immediate sources
Suspected Causes:
plant or equipment: Yes environmental: No
human: No 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: Yes community disruption: No

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: 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: 1990\_019\_01

### 1 Type of Accident

remarks: Owing to vibrations, a newly replaced small bore screwed tapping for an

orifice flowmeter in a hydrogen fluoride alkylation unit underwent fatigue

fracture causing a leak of isobutane with traces of hydrogen fluoride (codes

1101 and 1102). ... see Appendix Full Report A / type of accident

### 2 Dangerous Substances

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

isobutane refer to the amount released during the accident (less than 2.5

tonnes). Hydrogen fluoride was used as a catalyst to combine olefins

(alkenes) such as prop... see Appendix Full Report A / dangerous substances

### 3 Source of Accident

illustration: - not applicable -

remarks: The accident occurred in a HF alkylation unit (code 3102) of a petroleum

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refinery (code 2002). The process plant involved was the alkylation unit
where isobutane was mixed with olefins (such as propylene and butylene) to
produce a polymeric... 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): 2
direction (from): SE
stability (Pasquill): F
ambient temperature (\inftyC):
remarks: Gentle wind (2 metres/sec) from South East under "F" stability class.
5 Causes of Major Occurrence
main causes
technical / physical 5104 operation: corrosion/fatigue
- not applicable -
- not applicable -
- not applicable -
- not applicable -
human / organizational 5308 organization: design of plant/equipment/system (inadequate,
inappropriate)
- not applicable -
- not applicable -
- not applicable -
- not applicable -
remarks: The accident was caused by the fatigue fracture (due to vibrations) of a newly replaced
(about 11 hours in service) 1/2" schedule 160 nipple in flange orifice screwed tapping
(code 5104). Also, the design of this component was probably not ... see Appendix Full
Report A / causes of major occurrence
6 Discussion about the Occurrence
- not applicable -
Type of Accident country: FA ident key: 1990_019_01
event:
major occurrence 1204 fire: flash fire (burning vapour cloud, subsonic flame front)
initiating event - not applicable -
associated event - not applicable -
Dangerous substances
country: FA ident key: 1990_019_01
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a) total establishment inventory

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CAS number: 106-97-8 identity: Isobutane
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): 2,5
use of substance as: STARTING MATERIAL
b) substance belongs to relevant inventory directly involved: Yes
actual quantity: 2,5 potential quantity: 2,5
c) substance belongs to relevant inventory indirectly involved: No
actual quantity: -1 indir_pot_quant: -1
a) total establishment inventory
CAS number: 7664-39-3 identity: Hydrogen Fluoride
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: 1990_019_01
situation
industry
inititating event 2002 petrochemical, refining, processing
associated event - not applicable -
activity/unit
major occurrence 3102 process: chemical continuous reaction
inititating event 3102 process: chemical continuous reaction
associated event - not applicable -
component
major occurrence 4011 general pipework/flanges
inititating event 4011 general pipework/flanges
associated event - not applicable -
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# **B** Consequences Full Report

country: FA ident key: 1990\_019\_01 1 Area concerned affected extent of effects installation: Yes establishment: No off-site; local: No off-site; regional: No off-site; transboundary: No illustration of effects - not applicable remarks In the Original Report there is no evidence of significant effects outside the i... see Appendix Full Report B / area concerned - remarks 2 People establishment popul. emergency personnel off-site population total at risk 3 immediate fatalities subsequent fatalities hospitalizing injuries 1 other serious injuries 2 health monitoring remarks Three people were affected by the accident: one from shock, one from inhalation ... 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:

-  $\mbox{\bf historical sites}$  not applicable -  $\mbox{\bf historic monuments}$  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 minor damages to materials (pipework... 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  $\,\mathrm{No}\,\,\mathrm{No}\,\,\mathrm{No}$ interruption of utilities etc. no / yes duration - gas No - electricity No - water No - sewage treatment works No - telecommunications No - main roads No - railways No - waterways No - air transport No significant public concern none local level national level - off site populations Yes No No - media interest No No No - political interest No No No remarks In the Original Report there is no evidence of significant effects outside the i... see Appendix 7 Discussion of Consequences C Response Full Report

country: FA ident key: 1990\_019\_01

### 1 Emergency Measures

taken - on site - not applicable - - not applicable -

- not applicable - - not applicable -

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- 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 / 1990\_019\_01 report

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

ENVIRONMENT AND ATMOSPHERICAL CONDITIONS:

Gentle wind (2 metres/sec) from South East under "F" stability class.

At 12:18 hr an isobutane leak with hydrogen fluoride traces occurred in the HF alkylation unit. It occurred when one of the two small bore pipe tappings into a large 10" (250mm) pipeline underwent fatigue fracture owing to vibrations. This tapping was used to allow process stream into a flow transmitter. The initial leak rate (at the operating pressure of about 16 barg) was about 11.8 tonnes/h. Shortly after the first failure, the second tapping nipple fractured and the total release rate became 23.6 tonnes/h. The gas did not immediately ignite and the leak was quickly identified both by plant instrumentation and visually. The activation of remotely operated valves allowed the isolation of the process piping and the diversion of the contents of the isolated section to a flare within 2 minutes. The escaped gas cloud ignited probably on a diesel engined painters mobile hoist after a few minutes, resulting in a small flash fire. The isolation and venting was so successful that the accident was over in 25 minutes with the fire extinguished.

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

- Isobutane (C.A.S. CODE: 106-97-8): amount involved = < 2,500 kg.
- Hydrogen Fluoride (C.A.S. CODE: 7664-39-3, E.E.C. CODE: 009-002-00-6): amount involved = traces.

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

The accident occurred in the Hydrogen Fluoride Alkylation Unit of a petroleum refinery. In the process plant, isobutane was mixed with olefins (such as propylene and butylene) to produce a polymeric substance called alkylate which is a mixture of C7 and C8 branched hydrocarbons. The component involved was a small bore pipe tapping for a process flowmeter installed on a process line. The accident occurred during normal operation. The operating pressure in the process line was about 16 barg.

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

INITIATING EVENT AND CONSEQUENCES:

Owing to vibrations, a 1/2" (12mm) scheduled 160 nipple in flange orifice screwed tapping fatigue fractured. The fitting was new (only 11 hours in service). The isobutane leak occurred at approximately 16 barg. The escaped gas cloud, probably ignited on a diesel engined painters mobile hoist that was operating nearby, resulted in a small flash fire.

CAUSES:

The accident was caused by the fatigue fracture (due to vibrations and, probably, to an inadequate component design) of a 1/2" scheduled 160 nipple in flange orifice screwed tapping.

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

EFFECTS ON PEOPLE:

3 people were injured by the accident: one from the shock, one from inhalation of isobutane and the third with burns caused by the flash fire. All were taken to hospital in a precautionary way but only the operator with burns was detained overnight.

MATERIAL LOSS:

Pipework lagging, electric cables scaffold boards were damaged during the accident but no data are available about the cost of the material losses.

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

INTERNAL TO THE ESTABLISHMENT:

Full site emergency alert. The internal emergency teams put into operation the water monitor sprays during vapour dispersion and after the ignition. Cooling was applied to the nearby plant vessels in order to prevent B.L.E.V.E. The activation of remotely operated valves allowed the isolation of the process piping and the diversion of the contents of the isolated section to a flare.

EXTERNAL SERVICES

The external county emergency services were called but the accident was over and fire extinguished before they could deploy their equipment.

### 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- replacement of the flow metering device with a non-intrusive one;
- 2- review of the use of mobile diesel-powered plants in the area of the process units with the purpose of reducing its use;
- 3- extensive vibration monitoring to identify any equipment causing excessive

vibrations

4- fully survey of pipework supports on plant.

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

Owing to vibrations, a newly replaced small bore screwed tapping for an orifice flowmeter in a hydrogen fluoride alkylation unit underwent fatigue fracture causing a leak of isobutane with traces of hydrogen fluoride (codes 1101 and 1102). The escaping gas cloud probably ignited on a diesel engined painters mobile hoist after a few minutes, resulting in a small flash fire (code 1204).

### Appendix Full Report A / dangerous substances:

The total establishment and the potential directly involved inventories of isobutane refer to the amount released during the accident (less than 2.5 tonnes). Hydrogen fluoride was used as a catalyst to combine olefins (alkenes) such as propylene and butylene with isobutane to produce a polymeric substance called alkylate which is a mixture of C7 and C8 branched hydrocarbons. No data are available about the amount of hydrogen fluoride released (only traces, however).

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

The accident occurred in a HF alkylation unit (code 3102) of a petroleum refinery (code 2002). The process plant involved was the alkylation unit where isobutane was mixed with olefins (such as propylene and butylene) to produce a polymeric substance called alkylate (a mixture of C7^C8 branched hydrocarbons). The component involved was a small bore pipe tapping for a process flowmeter (code 4011). The accident occurred during normal operation. The operating pressure was 16 barg.

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

The accident was caused by the fatigue fracture (due to vibrations) of a newly replaced (about 11 hours in service) 1/2" schedule 160 nipple in flange orifice screwed tapping (code 5104). Also, the design of this component was probably not adequate (code 5308).

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

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

#### **Appendix Full Report B / people:**

Three people were affected by the accident: one from shock, one from inhalation of isobutane and the third with burns caused by the flash fire. All were taken to hospital in a precautionary way but only the operator with burns was detained overnight.

### Appendix Full Report B / ecological harm:

In the Original Report there is no evidence of significant ecological harms.

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

No data are available about the cost of the minor damages to materials (pipework lagging, electric cables, scaffold boards damaged) caused by the flash fire.

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

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

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

After the accident, the following measures were established:

- 1- replacement of the flow metering device with a non-intrusive one;
- $\hbox{2-review of the use of mobile diesel-powdered plants in the area of process units with the purpose of reducing its use;}$
- 3- extensive vibrations monitoring to identify any equipment causing excessive vibrations;
- 4- full survey of pipework supports on plant.

F