

Explosion och brand på en kemikaliefabrik för produktion av fluorföreningar.

900320 MARS 1990_18

Olyckan inträffade på en anläggning för produktion av difluoranilin, en mellanprodukt som används i farmaceutisk industri. Till följd av en oförutsedd reaktion skenade reaktionen och reaktionsblandningen självantändes. Reaktionskärlet exploderade och en brand spred sig till en förrådstank med xylen som fattade eld. Anläggningen utrymdes och företagets interna brandkår fick snart hjälp av räddningstjänsten att bekämpa branden.

Den aktuella processen inbegriper en reaktion där diklornitrobensen (DCNB) reagerar med kaliumfluorid och bildar difluornitrobensen (DFNB). Reaktionen sker i närvaro av katalysator i lösningsmedlet dimetylacetamid (DMAC). Den genomförs vid 165°C och atmosfärstryck. Det är väl känt att nitroföreningarna DCNB och DFNB sönderfaller under våldsamma betingelser vid temperaturer över 220°C. Man förutsåg inte några sådana omständigheter. Ett par veckor före olyckan hade lösningsmedlet DMAC kontaminerats med vatten. Man antog att vattnet hade avlägsnats, men tillräckligt med vatten fanns kvar i lösningsmedlet för att en del DMAC skulle hydrolyseras till ättiksyra. Det är under normala betingelser svårt att hydrolysera DMAC till ättiksyra. Vad man inte kände till var att fluoraromatiska föreningar katalyserar denna hydrolys. Olyckan inträffade då man för första gången använde denna kontaminerade mängd DMAC. Laboratorieförsök har visat att halter på 2-10% ättiksyra i DMAC leder till en reproducerbar värmeutvecklande reaktion vid 140-160°C, dvs vid driftsbetingelserna ifråga. Denna reaktion drev upp temperaturen från 160°C till 220°C och satte i sin tur igång den betydligt våldsammare nedbrytningen av nitroföreningarna. Metallurgiska undersökningar av resterna av reaktionskärlet gav vid handen att kärlet sprack vid 20-25 bar och 500°C.

Inblandade ämnen och mängder

	CAS Nr.	Mängd
2,4-difluoronitrobensen		15000 kg
2,4-dikloronitrobensen	89-61-2	15000 kg
kaliumfluorid	7789-23-3	15000 kg
dimetylacetamid (lösningsmedel)	127-19-5	mer än 15000 kg
tetrametylammoniumklorid (katalysator)	75-57-0	15000 kg
xylen	1330-20-7	225 000 kg
vätefluorid	7664-39-3	okänt
andra förbränningsprodukter		okänt

Skador:

Människor: En illa utsatt arbetare som dränktes in med reaktionslösningen och föll 6 meter kom undan med brutet ben, men avled av post-operativt trauma 20 dagar senare. Ytterligare 5 personer blev lindrigt skadade.

Materiella: Stora delar av anläggningen förstördes, medan närliggande anläggningar fick påtagliga skador. Anläggningen byggdes inte upp igen. Utanför anläggningen krossades fönster upp till 1,2 km bort. Den omedelbara omgivningen blev svårt kontaminerad. Bilar i närheten fick vindrutor och lack skadade av vätefluorid.

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_018_01

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

Date of Major Occurrence: Time of Major Occurrence

start: 1990-03-20 start: 03:20:00

finish: finish:

Establishment:

name:

address:

industry: 2002 petrochemical, refining, processing

Petrochemical (800 hectare site comprising Petroleum Refinery and various Chemical Plants)

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: 1990_018_01

Accident Types:

release: Yes explosion: Yes

water contamination: No other: No

fire: Yes

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:

Inside the reactor there were about 15,000 Kg of dichloronitrobenzene (DCNB), difluoronitrobenzene (DFNB), dimethylacetamide (DMAC) and tetramethylammoniumchloride (TMCA) but no data are available about the single amounts of each substance.... 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 an establishment (located on an area of 800 hectare) including an integrated oil refinery and a number of independent chemical plants. The process plant involved in the accident produced fluoroaniline by means of tw... see Appendix Short Report / description of immediate sources

Suspected Causes:

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

human: No **other:** No

description:

CAUSES:... see Appendix Short Report / description of suspected causes

Immediate Effects:

material loss: Yes

human deaths: Yes

human injuries: Yes **community disruption:** Yes

other: No

ecological harm: No

national heritage loss: No

description:

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

Emergency Measures taken:

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

external services: Yes **restoration:** No

sheltering: No **other:** No

evacuation: Yes

description:

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

Immediate Lessons Learned:

prevention: Yes **other:** No

mitigation: No

description:

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

immediate lessons learned

A Occurrence Full Report

country: FA ident key: 1990_018_01

1 Type of Accident

remarks: During the production of difluoronitrobenzene (DFNB) in a reactor, a runaway reaction occurred (code 1304) due to the decomposition of DFNB and dichloronitrobenzene (DCNB). The reactor vented, flames were seen to ignite at the top of the ve... see Appendix Full Report A / type of accident

2 Dangerous Substances

remarks: Inside the reactor there were about 15,000 Kg of dichloronitrobenzene (DCNB), difluoronitrobenzene (DFNB), dimethylacetamide (DMAC) and tetramethylammoniumchloride (TMCA) but no data are available about the single amounts of each substance.... see Appendix Full Report A / dangerous substances

3 Source of Accident

illustration: - not applicable -

remarks: The accident occurred in an establishment (located on an area of 800 hectare) including an integrated oil refinery and a number of independent chemical plants (code 2002). The process plant involved in the accident produced fluoroaniline by... 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): 9

direction (from): SSW-WSW

stability (Pasquill):

ambient temperature (°C):

remarks: During the explosion, wind direction ranged between South-South-West and West-South-West and the average wind speed between 4.5 m/sec and 9 m/sec. No rain during or after the accident for several days.

5 Causes of Major Occurrence

main causes

technical / physical 5102 operation: component/machinery failure/malfunction

5107 operation: unexpected reaction/phase-transition

- not applicable -

- not applicable -

- not applicable -

human / organizational 5307 organization: process analysis (inadequate, incorrect)

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

- not applicable -

- not applicable -

- not applicable -

remarks: The accident occurred as the result of a chain of events. The failure of two valves separating the distillation section from the rest of the plant and the subsequent gross water contamination were the first initiating events (code 5102). Th... see Appendix Full Report A / causes of major occurrence

6 Discussion about the Occurrence

- not applicable -

Type of Accident country: FA **ident key:** 1990_018_01

event:

major occurrence 1307 explosion: VCE (vapour cloud explosion; supersonic wave front)

initiating event - not applicable -

associated event - not applicable -

event:

major occurrence 1202 fire: pool fire (burning pool of liquid, contained or uncontained)

initiating event - not applicable -

associated event 1402 other: combustion products into ground

event:

major occurrence 1201 fire: conflagration (a general engulfment fire)

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

associated event 1401 other: combustion products into air

Dangerous substances

country: FA **ident key:** 1990_018_01

a) total establishment inventory

CAS number: 1330-20-7 **identity:** Xylene

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): 225

use of substance as: NORMAL FINISHED PRODUCT

b) substance belongs to relevant inventory directly involved: Yes

actual quantity: 225 **potential quantity:** 225

c) substance belongs to relevant inventory indirectly involved: No

actual quantity: -1 indir_pot_quant: -1

a) total establishment inventory

CAS number: 75-57-0 identity: Tetramethylammonium 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): 15

use of substance as: STARTING MATERIAL

b) substance belongs to relevant inventory directly involved: Yes

actual quantity: 15 potential quantity: 15

c) substance belongs to relevant inventory indirectly involved: No

actual quantity: -1 indir_pot_quant: -1

a) total establishment inventory

CAS number: 7789-23-3 identity: Potassium 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): 15

use of substance as: STARTING MATERIAL

b) substance belongs to relevant inventory directly involved: Yes

actual quantity: 15 potential quantity: 15

c) substance belongs to relevant inventory indirectly involved: No

actual quantity: -1 indir_pot_quant: -1

a) total establishment inventory

CAS number: identity: Other Combustion Products

name from Seveso I Directive: - not applicable -

name from Seveso II Directive: - not applicable -

category from Seveso II: - not applicable -

other hazards (1): - not applicable -

other hazards (2): - not applicable -

maximum quantity (tonnes): -1

use of substance as: ABNORMAL PRODUCT

b) substance belongs to relevant inventory directly involved: No

actual quantity: -1 potential quantity: -1

c) substance belongs to relevant inventory indirectly involved: Yes

actual quantity: -1 indir_pot_quant: -1

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: ABNORMAL PRODUCT

b) substance belongs to relevant inventory directly involved: No

actual quantity: -1 potential quantity: -1

c) substance belongs to relevant inventory indirectly involved: Yes

actual quantity: -1 indir_pot_quant: -1

a) total establishment inventory

CAS number: 127-19-5 identity: Dimethylacetamide

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): 15

use of substance as: STARTING MATERIAL

b) substance belongs to relevant inventory directly involved: Yes

actual quantity: 15 potential quantity: 15

c) substance belongs to relevant inventory indirectly involved: No

actual quantity: -1 indir_pot_quant: -1

a) total establishment inventory

CAS number: identity: 2,4-difluoronitrobenzene

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): 15

use of substance as: ON-SITE INTERMEDIATE

b) substance belongs to relevant inventory directly involved: Yes

actual quantity: 15 potential quantity: 15

c) substance belongs to relevant inventory indirectly involved: No

actual quantity: -1 indir_pot_quant: -1

a) total establishment inventory

CAS number: 89-61-2 identity: 2,4-dichloronitrobenzene

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): 15

use of substance as: STARTING MATERIAL

b) substance belongs to relevant inventory directly involved: Yes

actual quantity: 15 potential quantity: 15

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_018_01

situation

industry

initiating event - not applicable -

associated event - not applicable -

activity/unit

major occurrence - not applicable -

initiating event - not applicable -

associated event - not applicable -

component

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

initiating event - not applicable -

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

situation

industry

initiating event 2002 petrochemical, refining, processing

associated event 2002 petrochemical, refining, processing

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 4001 reaction vessel; non-pressurised

initiating event 4001 reaction vessel; non-pressurised

associated event 4001 reaction vessel; non-pressurised

B Consequences Full Report

country: FA **ident key:** 1990_018_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 A large part of the plant was destroyed while nearby plants suffered serious str... see Appendix

Full Report B / area concerned - remarks

2 People

establishment popul. emergency personnel off-site population

total at risk 6

immediate fatalities

subsequent fatalities 1

hospitalizing injuries

other serious injuries 5

health monitoring

remarks One operator was on the plant at the time of the explosion. Although he was cove... 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 Though during the fire combustion products were released inair and deposited ont... see Appendix

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 A large part of the CFA plant was destroyed while nearby plants suffered serious... see Appendix

6 Disruption of Community Life

establishment/plant evacuated disabled/unoccupiable destroyed

- **nearby residences/hotels** No No No
- **nearby factories/offices/small shops** No No No
- **schools, hospitals, institutions** No No No
- **other places of public assembly** No No No

interruption of utilities etc. no / yes duration

- **gas** No
- **electricity** No
- **water** No
- **sewage treatment works** No
- **telecommunications** No
- **main roads** No
- **railways** No
- **waterways** No
- **air transport** No

significant public concern none local level national level

- **off site populations** No Yes No
- **media interest** No No No
- **political interest** No No No

remarks The accident broke windows and caused minor roof damages up to 1.2 km away from ... see Appendix

7 Discussion of Consequences

C Response Full Report

country: FA ident key: 1990_018_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:

The area of the installation w... see Appendix Full Report C / lesson learned - mitigate

useful references:

The estimated overpressures fr... see Appendix Full Report C / lesson learned - references

5 Discussion about Response

- not applicable -

Appendices for the FA / 1990_018_01 report

Appendix Short Report / description of accident types:

ACCIDENT CASE HISTORY DESCRIPTION:

The plant was initially commissioned in 1975 for the manufacture of chlorofluoaniline (CFA) but was also used for manufacturing fluoroaromatic compounds. The whole site contained plants covered by the requirements of Article 5; this specific plant did not however fall under the requirements of Article 5. The manufacturer had nevertheless prepared a safety report, which was submitted to the competent Authority at the correct time. This report categorized the process as relatively low risk (the reaction was only mildly exothermic and not very sensitive to small operational variations). The process included the production of difluoronitrobenzene (DFNB) by reacting dichloronitrobenzene (DCNB) with potassium fluoride at a temperature of 165 °C and atmospheric pressure. DFNB was purified by centrifuge and distillation and was subsequently hydrogenated to difluoroaniline (DFA), an intermediate for the pharmaceutical industry. DCNB and DFNB were identified as substances which could decompose violently at temperatures above 220 °C but no circumstances were foreseen which could result in the temperature of the mixture being raised by such a large amount above the normal operating temperature. A few weeks before the accident, the distillation mixture had been contaminated with water through two leaking valves. It was believed that the water had been removed by distillation. During the heating phase the operators realized that the temperature was rising fast, but could do little to control it. The reactor vented, flames were seen to ignite at the top of the reactor and then an explosion occurred, followed by a serious fire. Tank storage of xylene was ignited at an early stage and prolonged the fire.

Appendix Short Report / description of substances involved:

Inside the reactor there were about 15,000 Kg of dichloronitrobenzene (DCNB), difluoronitrobenzene (DFNB), dimethylacetamide (DMAC) and tetramethylammoniumchloride (TMCA) but no data are available about the single amounts of each substance. The amount and type of combustion products released into air (such as particle soots) are not known. Also, no data are available about the amount of hydrogen fluoride produced by the combustion of fluoroaromatics.

- 2,4-Difluoronitrobenzene [DFNB]: amount involved = 15,000 Kg.
- 2,4-Dichloronitrobenzene [DCNB] (C.A.S. CODE: 89-61-2): amount involved = 15,000 Kg.
- Potassium Fluoride (C.A.S. CODE: 7789-23-3): amount involved = 15,000 Kg.
- Dimethylacetamide (DMAC) used as solvent (C.A.S. CODE: 127-19-5): amount involved = over 15,000 Kg.
- Tetramethylammoniumchloride (TMAC) used as catalyst (C.A.S. CODE: 75-57-0): amount involved = 15,000 Kg.
- Xylene (C.A.S. CODE: 1330-20-7): amount involved = 225,000 Kg.
- Hydrogen Fluoride (C.A.S. CODE: 7664-39-3, E.E.C. CODE: 009-002-00-6): amount involved = not known.
- Other Combustion Products: type and amount involved = not known.

Appendix Short Report / description of immediate sources:

The accident occurred in an establishment (located on an area of 800 hectare) including an integrated oil refinery and a number of independent chemical plants. The process plant involved in the accident produced fluoroaniline by means of two reaction stages. The second reaction was made in a 15 tonnes batch reactor (R7601) normally operating at 165 °C and atmospheric pressure. The overall height of vessel 4.195 and its outside diameter was 2.5 m. It had a design pressure of 5 barg and a test pressure of 18.93 barg. Following the reactor explosion, a fire occurred that involved a xylene storage tank.

Appendix Short Report / description of suspected causes:

CAUSES:

The accident occurred as the result of a chain of events. The failure of the two valves and the subsequent gross water contamination were the first critical initiating events. There was an attempt to remove the water using a second distillation on the water/toluene intercut. Failure to remove water may have been due to phase separation of water in the base of the main distillation column. The dimethylacetamide (DMAC) solvent was hydrolyzed to acetic acid. It was known that DMAC does not easily hydrolyse to acetic acid, but fluoroaromatic compounds acted as catalysts (this catalytic property was not previously known) causing an increased acetic acid production. Acetic acid was accumulate in the DMAC because of the similar boiling points. It is worth noting that the accident occurred when the batch loaded into the reactor was the first one to completely use recycled DMAC following its contamination with water. Laboratory investigations have shown that 2-10% w/w acetic acid in DMAC gives a reproducible rapid exothermic reaction at 140-160 °C, producing a high yield of higher weight molecular substances with evolution of gas (CO₂). This lower temperature exothermic reaction drove the temperature up to that which initiated the violent decomposition of the nitrobenzene compounds. Metallurgical examinations indicated that the vessel failed at about 20-25 bar and 500 °C, conditions far above its design pressure and substantially higher than its test pressure. Cooling through both the external jacket and the open vent to a knock-out pot could not cope with the violent decomposition and prevent the pressure build-up in the reactor.

Appendix Short Report / description of immediate effects:

EFFECTS ON PEOPLE:

One operator was on the plant at the time of the explosion. Although he was covered by reactants/products and fell a distance of 6 metres, he suffered nothing worse than a broken leg and was recovered strongly. Unexpectedly, he died 20 days later from post-operative complications. The other 2 plant operators and 3 operators in a nearby

control room from an adjacent plant received relatively minor injuries. During the plant demolition, strict controls were used to monitor the workers.

MATERIAL LOSS:

A large part of the CFA plant was destroyed while nearby plants suffered serious structural damage (missile were thrown up to 500 metres away). There was little material damage outside the plant complex (broken windows and minor roof damages up to 1.2 km away). The immediate area of the installation was heavily contaminated and slight etching of windscreens and paintwork of a couple of car was caused by hydrogen fluoride precipitation. The plant was subsequently demolished.

COMMUNITY DISRUPTION:

The accident broke windows and caused minor roof damages up to 1.2 km away.

MAP OF THE ACCIDENT AREA AND MAX. DENSITY OF POPULATION:

The extent of the effects is shown on a map attached to the Original Report.

Appendix Short Report / description of emergency measures taken:

INTERNAL TO THE ESTABLISHMENT:

The plant was evacuated. Fire was initially fought by company fire brigade and then by local authority fire brigade (27 pumps and 128 firefighters were activated).

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- Procedures for assessing the potential for runaway reaction should include guidance on: (a) emphasizing the need for control of the composition of batch process recycles and development of suitable analytical methods; (b) the importance of recognizing potential deviations from standard reaction conditions which might invalidate any presumption that known dangerous conditions could not be achieved;
- 2- the company design parameters for batch reactors should be re-examined to minimize possible pressure build up;
- 3- there should be approved auditing of examination and inspection procedures and the methods of assessment for: (a) mechanical integrity of vessels; (b) control systems;
- 4- future plans for rebuilding this plant are unknown. The future use of DMAC as a Halex solvent is being considered by the company.

Appendix Full Report A / type of accident:

During the production of difluoronitrobenzene (DFNB) in a reactor, a runaway reaction occurred (code 1304) due to the decomposition of DFNB and dichloronitrobenzene (DCNB). The reactor vented, flames were seen to ignite at the top of the vessel and then an explosion occurred (code 1307), followed by a fire (code 1201). A xylene storage tank in an adjacent plant was ignited (code 1202). During the fire, combustion products were released into air (code 1401) and deposited onto ground (code 1402).

Appendix Full Report A / dangerous substances:

Inside the reactor there were about 15,000 Kg of dichloronitrobenzene (DCNB), difluoronitrobenzene (DFNB), dimethylacetamide (DMAC) and tetramethylammoniumchloride (TMCA) but no data are available about the single amounts of each substance. The quantity and type of combustion products released into air (such as particle soots) are not known. Also, no data are available about the quantity of hydrogen fluoride produced by the combustion of fluoroaromatics.

Appendix Full Report A / source of accident - remarks:

The accident occurred in an establishment (located on an area of 800 hectare) including an integrated oil refinery and a number of independent chemical plants (code 2002). The process plant involved in the accident produced fluoroaniline by means of two reaction stages. The second reaction was made in a 15 tonnes batch reactor (codes 3101 and 4001). Following the reactor explosion, a fire occurred that involved a xylene storage tank (code 4003).

Appendix Full Report A / causes of major occurrence:

The accident occurred as the result of a chain of events. The failure of two valves separating the distillation section from the rest of the plant and the subsequent gross water contamination were the first initiating events (code 5102). The DMAC contamination led to its decomposition and the reaction heated the mixture to the decomposition temperatures for DCNB and DFNB, a strong exothermic reaction (code 5107). Process analysis and design plant were not adequate (code 5307 and 5308).

Appendix Full Report B / area concerned - remarks:

A large part of the plant was destroyed while nearby plants suffered serious structural damages (missiles were thrown up to 500 metres away but were confined within the refinery site). There were blast effects on-site and to the company's adjacent Research Centre up to 500 metres away. There was little material damages outside the plant complex (broken windows and minor roof damages up to 1.2 km away). The area of the installation was heavily contaminated.

Appendix Full Report B / people:

One operator was on the plant at the time of the explosion. Although he was covered by reactants/products and fell a distance of 6 metres, he suffered nothing worse than a broken leg and was recovered strongly. Unexpectedly, he died 20 days later from post-operative complications. The other 2 plant operators and 3 operators in a nearby control room from an adjacent plant received relatively minor injuries. During the plant demolition, strict controls were used to monitor the workers.

Appendix Full Report B / ecological harm:

Though during the fire combustion products were released in air and deposited onto ground, in the Original Report there is no evidence of significant ecological harms.

Appendix Full Report B / material loss:

A large part of the CFA plant was destroyed while nearby plants suffered serious structural damage (missile were thrown up to 500 metres away). There was little material damage outside the plant complex (broken windows and minor roof damages up to 1.2 km away). The immediate area of the installation was heavily contaminated and slight etching of windscreens and paintwork of a couple of car was caused by hydrogen fluoride precipitation. The plant was subsequently demolished.

Appendix Full Report B / disruption of community life:

The accident broke windows and caused minor roof damages up to 1.2 km away from the installation.

Appendix Full Report C / lesson learned - prevent:

After the accident, the following measures were established:

- 1- Procedures for assessing the potential for runaway reaction should include guidance on: (a) emphasizing the need for control of the composition of batch process recycles and development of suitable analytical methods; (b) the importance of recognizing potential deviations from standard reaction conditions which might invalidate any presumption that known dangerous conditions could not be achieved;
- 2- the company design parameters for batch reactors should be re-examined to minimize possible pressure build up;
- 3- there should be approved auditing of examination and inspection procedures and the methods of assessment for: (a) mechanical integrity of vessels; (b) control systems;
- 4- future plans for rebuilding this plant are unknown. The future use of DMAC as a Halex solvent is being considered by the company.

Appendix Full Report C / lesson learned - mitigate:

The area of the installation was heavily contaminated by fluoroaromatic compounds and the plant was demolished. During the plant demolition, strict controls (including atmospheric sampling and medical supervision [blood and urine tests]) were used to monitor the demolition workers.

Appendix Full Report C / lesson learned - references:

The estimated overpressures from the blast damages and their comparison with TNT charges are shown on two tables attached to the Original Report.