Explosion of a tank in TDI production unit

November, 28th, 2002

Mestre – Italy

toluene diisocyanate

TDI

stirrer

cooling

domino effect

THE INSTALLATIONS IN QUESTION

Generality

The company was found on 01/05/2001 after the acquisition of the polyurethane division from an other major Italian company. The installation is located inside a chemical pole in an industrial area, which is about 2,5 km far away from a residential area, 1 km from a village and 4 km from a city. Besides the plant there are other plants/ storage facilities, inside or adjoining the ancient installation, owned by almost 11 important Seveso companies. The plant has a production capacity of 118,000 tons/year. A total of 248 persons are employed, in particular the TDI plant is operated by 102 persons. The plant is under Seveso II Directive (upper tier plant).

The process cycle foresees:

- Production of Dinitrotoluene (DNT)/ sulphuric acid recycling: Dep. TD1/TD7

  DNT is obtained through the reaction between toluene and nitric acid in presence of sulphuric acid, which acts as promoter of the reaction and as dehydrating agent for the water formed as a by-product during the reaction.

  The department TD7 was set up in 1996 to substitute the department for the purification of sulphuric acid by means of toluene and urea, which was closed down and partially dismantled.

- Production of 2,4-toluendiamine (TDA): Dep. TD3

  TDA is obtained through the reaction between dinitrotoluene (DNT) and hydrogen in presence of palladium as a catalyst, water is formed as by-product of the reaction.

- Production of Phosgene: Dep. TD4

  Phosgene (COCl2) is obtained through the reaction between carbon monoxide (CO) and Chlorine (Cl2) in gas phase over a catalyst made of active coal.

  CO and Cl2 are transferred by pipeline respectively from Dep. 12 and CS23.

- **Production of Toluene di-isocyanate (TDI): Dep. TD 5**

  Toluene diisocyanate is obtained through the reaction between 2,4 toluenediamine (TDA) and Phosgene in presence of dichlorobenzene (DCB) as solvent, by-products of the reaction are hydrochloric acid and high-boiling compounds (tars).

- Storage and shipment of TDI: Dep. TD6

  Storage and shipping area in barrels or road tankers. The purified TDI is first transferred to a tank in which ionol (colour stabiliser) is added, then stored in tanks where, if necessary, the pH value is corrected by adding benzoil chloride. The TDI is then transferred from these tanks either to the barrel filling plant or the loading ramp for road-tankers and rail-tankers or for on-site storage near the South tank park

- Production of carbon monoxide and hydrogen: Dep. TD12

Description of the process unit involved

The accident occurred in a section of high-boiling tars of the TDI department TD5. In the department TD5 toluene di-isocyanate (TDI) is produced through the reaction of 2,4-toluendiamine (TDA) and phosgene.

The reaction is performed in 3 successive steps with increasing temperature from approximately 80°C to 170°C, with decreasing pressure and with production of hydrogen chloride acid as a by-product. TDA is fed to the reaction in DCB solution at 12%, while phosgene is fed in stechiometric excess (5:1 in moles) in relation with TDA. Chloride acid and phosgene not reacted are taken away from the reaction in gas phase to be separated: phosgene is remitted in cycle, while chloride acid in transferred to other departments.

TDI reaction product remains in DCB solution with high-boiling tars. This solution is sent successively to the distillation, after which a TDI - high-boiling tars mixture is obtained. This mixture is then evaporated in D521, to produce TDI with low high-boiling tars contents (1%) from the top, and a TDI /high-boiling tars mixture in report 1:1 from the bottom. The evaporator D521 is forced circulation cooled by a vapour boiler at 18 bar. Its operation parameters are: 180°C and 850 mm w.c. absolute.

The TDI /high-boiling tars mixture in report 1:1 from the bottom of the evaporator is sent to tank D522 to cool it to 90°C, which is equipped with a stirrer and water refrigerated coils manually regulated. The mixture is then sent to the tanks D 528/1-2-3 for storage, which feed the section of high-boiling tars treatment, where in a vacuum batch process is carried out a discontinuous recovery of a part of TDI from the same mixture (a simplified scheme of TDI section is shown in fig. 1).

The TDI is recovered by evaporation in the concentrator D 525/1, equipped with a stirrer, steam heated coils and maintained at vacuum pressure. It works at 10 mm Hg of residue P, and 130-150°C of T. Concentrator D 525/1 is fed by the tanks D 528/1-2-3 working also as compensation tanks. The TDI vapours are then condensed and then the liquid is transferred for storage, the residual gas is sent through a separator and then suctioned by the 3stage vacuum units P 509/1-3.

The concentrate present in D 525/1 is composed of 18-20% TDI and for the remaining part of high-boiling tars is diluted with toluene, mixed and transferred over a pump in tank D 541, where it is continuously stirred at a temperature of 115 - 120°C to get a sufficiently fluid and stable mass to be sent into the incinerator B 502/2 for combustion.

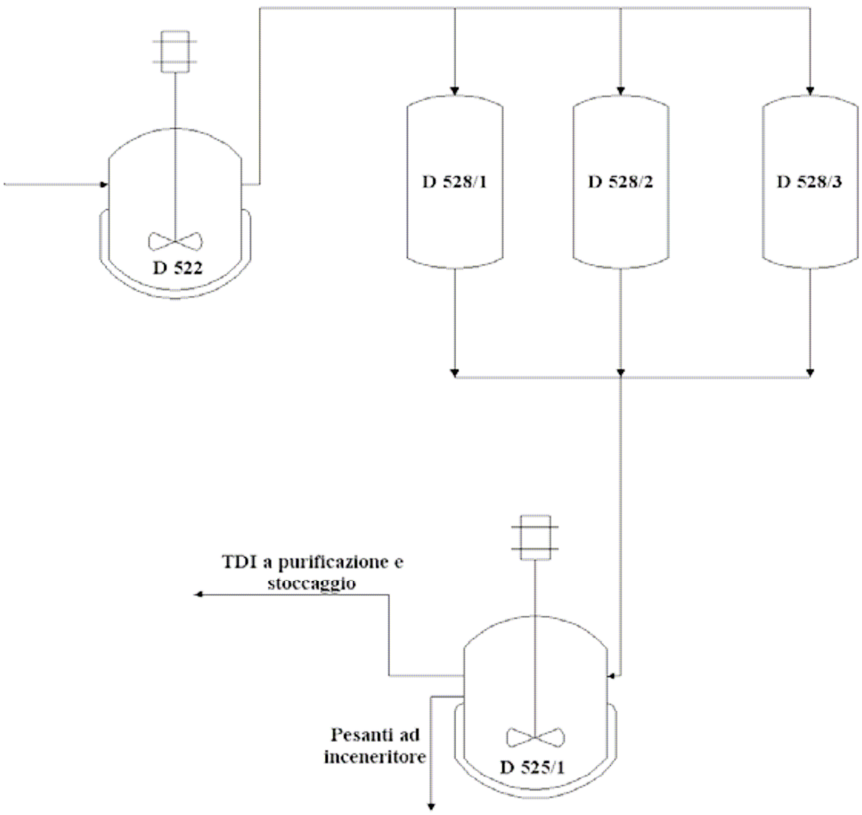

Fig. 1 - Simplified scheme of TDI section

THE ACCIDENT, ITS BEHAVIOUR, ITS EFFECTS AND CONSEQUENCES

The accident :

The event occurred inside the Department TD5 for the processing of high boiling tars of the TDI plant, and in particular in the tank D 528 1-2 for the temporary storage of bottoms of D 521 expecting to be distilled in D525/1.

Two days before the accident, at about 17:40, the shift assistant of department TD 4-5 shut down the stirrer P 507 of tank D 522 due to the excessive noise of the reduction gear of the motor, caused by an insufficient lubrication (registered in the logbook). Following the shutting down of the stirrer P 507, the temperature in tank D 522 started to rise gradually and stabilised at 125°C according to the value recorded by the DCS (Distributed Control System) switchboard assistant. These values cannot be considered reliable due to the fact that the instrument TI was calibrated to measure temperatures up to 120°C. Tank D 522, which receives the high-boiling tars and the TDI from the evaporator D 521, operates at a maximum temperature of approximately 95°C in normal operating conditions.

In the day before the accident, at 7:30 hrs, the feed to tank D 522 is reduced from 4000 kg/h to 1900 kg/h, maintaining the water circulation in the cooling coils of tank D 522 constant. The reduction of the feed charge reduced the temperature in tank D 522 to 65°C.

At approximately 12:00 hrs the temperature of tank D 522 rose again in connection with the increased load of the evaporator D 521, which went up from the previous 1900 kg/h to 7000 kg/h. For the remaining part of the day and until approximately 17:30 hrs on the day after, when the stirrer was started again, the DCS registered a temperature beyond the top of the measurement scale (above 120°C).

At 4:00 hrs in the day of the occurrence, the shift personnel registered a temperature rise in tanks D528/1-2-3, and in the work-sheet the temperature registered for tanks D 528/1-2-3 were respectively 136-142 and 131°C. The operating temperature normally foreseen for the tanks is 105°C.

The switchboard operator reported to the shift assistant an abnormal batch distillation, characterised by the fastness and a low amount of distilled product; the shift assistant explained that the T increase already persisted by some time. The temperature of concentrator D 525/1 was 139°C instead of 105-110° expected at the beginning of the distillation. The operation procedure did not indicate the measures to be adopted in case of high temperatures in D 522 and D 528/1-2-3.

In the meantime, at 16:30 in the same day, the tank 528/2 filled to 60% reached the temperature of 170°C. The design temperature of the equipment D528/1-2-3 is 150°C.

When the stirrer was started again, at about 17:30, the homogenisation of the mixture in D522 led to a T decrease also in D 528/1, that was the only one under loading. But, at 18:00 hrs the temperature in tank D 528/2 reached once more to 181°C and it was not possible to discharge tank D 528/2 because distillation was in progress in D525/1, and tank D541 feeding the incinerator B 502/2 was full and could not receive the high-boiling tars from D 525/1.

Only at 18:35, when the distillation process in D 525/1 finished, it was possible the discharge into D 541, which has the capacity to receive the content of D 525/1.

At 18:50 valve XV 5316 was opened to start the discharge operation of tank 528/2 into tank D 525/1; in that point tank D 528/2, with a nominal capacity of 10m3, was 59.5% full and the temperature was 220.7°C. The attempt to discharge tank D 528/2 did not succeed, due to the fact that the inhomogeneous product inside the tank contained solid matter which blocked the discharge of the tank. Inside the tank unwanted chemical reactions had been going on for hours with development of gas and increase of the temperature and viscosity of the reaction mass. Moreover, discharge procedure of D528/2, considering the opening-closing valves logic, did not permit its loading with product at lower temperature.

Four external contractors went to the distillation unit D 525/1 to verify the conditions inside through a visual inspection window installed on the dome cap. A dense white smoke inside the distillation unit did not allow the workers to look inside the equipment, and the pipe connecting tank D 528/2 to the rupture disk was particularly hot.

At 19:25 a second attempt to discharge the tank was made, but failed. The temperature on the control panel indicated 220°C, while there was no system to measure the pressure inside the vessel.

At 19:30 the four external contractors were still verifying the hydraulic guard in the plant when a strong whistle was heard and white smoke, leaking from the flanged coupling located on the delivery tube of the distillation unit D 525/1, was seen. Instinctively the four external contractors tried to escape but a strong explosion was heard, at 19:42 hrs tank D 528/2 exploded. The tank contained a mixture of TDI and TDI high-boiling tars. Due to the pressure wave of the explosion one of the escaping workers fell, while all the workers were hit and covered by a dense, warm, semi-solid substance with a high viscosity and a granular structure.

After a few (dozen) seconds a fire developed. The explosion ignited a fire involving the terminal part (southern side) of the framework of the "TDI high-boiling tars processing" department. The fire was mainly fed by 20 tons of diathermic oil (Aerthem 320) and one ton of toluene, after the rupture of the corresponding pipes. The fire affected the second of the three TDI - high-boiling tars storage tanks, D 528/1 (85% full when the accident occurred), causing its mechanical failure and a second explosion at approximately 20:25 hrs.

The explosion of tank D 528/1 extinguished the main fire leaving only some residual secondary fires.

According to the estimates made by the operator the quantities of chemical substances involved and released during the accidental event are:

Substance name	Amount	Physical state
TDI and high-boiling tars	15 ton	liquid/solid
Toluene	1 ton	liquid
Diathermic oil	20 ton	liquid

The safety data sheet of the diathermic oil does not classify the oil as an hazardous substance (falling under the scope of the annexes of legislative decree 334/99).Shutting down and restarting the oven is a lengthy process in which the oven has to cool down, before it can be restarted. Restarting has to be done gradually, starting with the pilot burners, after which the main burners can be started.

The consequences :

The consequences of the event were limited, not involving significant off-site consequences, even if the accident generated distress in the population, which was taken into account by the media and the public authorities.

Material effects

The explosion of tank D 528/2 generated a pressure wave with an extremely rapid expansion speed and the release of the hot liquid contained in the tank which solidified at ambient temperature. The pressure wave had a destructive effect on equipments and plant parts in the vicinity of the tank with projection of metal fragments, damage to the support frames of the plant equipment, rupture/damaging of connection pipes and electrical cables and utilities. TD5 department damaged is shown in fig. 2.

The fire was fed by the rupture of the toluene pipe and by the rupture of the diathermic oil (Aertherm) pipe installed at a height of 8 meters, and propagated to tank D 528/1 containing TDI - high-boiling tars which was 85% full when the explosion occurred. It is assumed that the explosion of tank D 528/1 was caused by overpressure generated from the decomposition reactions of TDI, thermally activated by the temperature of the flames and thermal radiation hitting the tank. As for tank 528/2, the high temperature triggered and accelerated the same exothermic decomposition reactions between TDI and high-boiling tars, releasing carbon dioxide.

The associated effect of the pressure wave, generated by the explosion of tank D 528/1 followed by the strong air movement generated by the blast wave, and the effect of the carbon dioxide formed by the chemical reactions described above, caused the displacement of the flame sources, extinguishing most of the fires, avoiding the creation of domino effects to other plants, which could cause major damage to the plant structures. Damages due to 1st and 2nd explosions of tank D 528/2 and tank D 528/1 respectively, are shown in fig. 3 and 4.

Human effects

Personnel present on-site: when the event occurred there were 30 internal employees and 6 external technicians for activities on the TD1-2 plant; of these only 4 external contractors needed medical treatment as specified below :

- Worker 1 : 3 days of incapacity to work due to pharyngeal hyperaemia and facial erythema
- Worker 2 : 31 days of incapacity to work due to I and II degree burns on the scalp
- Worker 3 : 31 days of incapacity to work due to the consequences of exposure to toxic industrial substances.
- Worker 4 : 53 days of incapacity to work due to the after effects of a trauma, caused by a contusion associated with a distortion of the right knee, and state of reactive anxiety

The 4 external workers who were performing controls in proximity of the plant equipment, were involved in the accident but were only partially exposed to the effects of the explosion of tank D 528/2. All received first medical treatment at the infirmary of the petrochemical establishment, and then at the emergency department of the hospital in the nearest city.

The medical reports of the emergency department contain following diagnosis :

- persons involved off-site : the population was not involved in the accidental event
- no fatalities and hospitalised injuries were registered

Environmental effects

Consequent to the accident, the personnel of the Antipollution Department of the Water Authority performed a series of controls on the drains of the site connected to a lagoon. Considering the position in which the accident occurred, it was considered appropriate to concentrate the controls on the community sewage drain SM15 (in particular, on the section drain SM15/3 directly connected to the TDI production department, and on the drain SM15/22 of the central biological sewage treatment plant of the installation, which might have suffered consequences from the event).

The analysis of TDI (toluene di-isocyante) and aromatic amines showed the presence of TDI with concentrations corresponding to 5280 mg/l and traces of aromatic amines. The concentration values of dichlorobenzenes (chlorinated solvents not mentioned elsewhere) and of organic aromatic solvents (toluene)- all compounds used in the production process involved in the accident - were also particularly high.

The accident caused a temporary but consistent pollution of the lagoon water. The polluting substances were channelled into the lagoon via the general drain SM15 of the establishment, spreading in the aquatic environment and modifying the chemical characteristics of the water in the lagoon up to 1 km from the establishment.

The characteristics of the fire and the atmospheric conditions, characterised by very slight wind and stability, probably favoured an umbrella like fallout pattern of the pollutants around the establishment, which resulted quite uniform. The TDI fire and of the other substances present in the installation caused an increase of the substances typical for combustion processes (nitrogen oxides, carbon oxide and hydrocarbons in a minor proportion), even if the absolute values measured are comparable with the values measured during traffic peak hours in stable meteorological conditions.

The increase of toluene is much more significant and to a minor extent the increase of Ethyl-benzene and Xylenes. Moreover the values measured for styrene, methylene chloride, trichloroethylene, perchloroethylene, trimethylbenzene do not differ much from the values indicated in literature for highly urbanised and industrialised areas.

It is important to note the absence of dichlorobenzenes in all air samples of the urban areas, even the ones taken in the most critical fallout phase, whereas dichlorobenzenes were found in significant concentrations in proximity of the accident place even the morning after the fire. The concentrations of dioxins, furans, and PCBs similar to dioxins, measured in the total particulate were undoubtedly low, the total values were comparable with the background concentration levels indicated by literature for urban areas.

Fig. 2 - TD5 department damaged

Fig. 3 – tank D 528/2 : 1st explosion

Fig. 4 – tank D 528/1 : 2nd explosion

European scale of industrial accidents

By applying the rating rules of the 18 parameters of the scale made official in February 1994 by the Committee of Competent Authorities of the Member States which oversees the application of the 'SEVESO' directive, the accident can be characterized by the following 4 indexes, based on the information available.
The parameters which compose these indexes and the corresponding rating method are indicated in the appendix hereto and are available at the following address: http://www.aria.ecologie.gouv.fr/

The level of the hazardous substances index is 3 because 5 tons of TDI were released. The level of the human and social index is 2 because 4 workers were injured.

The accident has been considered a 'major accident' according to the criteria set in Annex VI of the Seveso II Directive:

- Substances involved :
  Any fire or explosion or accidental discharge of a dangerous substance involving, a quantity of at least 5 % of the qualifying quantity laid down in column 3 of Annex I.

- Damage to property :
  damage to property in the establishment at least ECU 2 million,
  damage to property outside the establishment; at least ECU O,5 million.

About 15 tons of TDI have been involved, so exceeding the limit indicated in Annex VI: 5 tons (5% of 100 tons). Damage to property was estimated almost 2,8 millions Euros, exceeding the 2 millions Euros that represents the limit in Annex VI.

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

The principal causes assumed are the following:
- interruption of the stirring movement in tank D 522
- missing operative instructions concerning the management of abnormal conditions caused by high temperature in tanks D 522 and D 528 1/2/3
- missing information on the hazards involved in managing the abnormal process conditions relating to the specific case
- missing pressure measurement instruments in tanks D 528 1/2/3

According to the information given by the operators and from the analysis of the plant data on the section involved in the accident, it is assumed that the accident was caused by an unwanted condensation reaction between the high-boiling tars and TDI, thermally activated first in tank D522 and then developed in tank D 528/2, with the release of heat and carbon dioxide causing the mechanical explosion of tank D 528/2 due to overpressure.
The high temperatures and the prolonged residence time of the mass in D 528/2 (approximately 13 hours), supported the development of exothermic condensation reactions associated with the formation of carbon dioxide and a significant pressure increase.

When the explosion occurred the internal temperature of tank D 528/2 was above 220°C and clearly the tank was in extreme overpressure conditions. When the event occurred the tank was filled to 60% of its design capacity of 10 m^3.
A study has been performed by the Company on the thermal stability of the substances involved in the accident, and in particular on the results of the adiabatic calorimetric tests (ARC) performed on a tar sample collected immediately after the accident from tank D 522, with the goal of understanding the behaviour of the substances involved in the accident.
The tests were made by heating a known quantity of material, composed by high-boiling tars and TDI, in an adiabatic thermal system, and registering the temperature and pressure evolution over time. This test simulated the heating process of the product in D 528/2 involved by the explosion.

The test results agree basically with the values registered by the DCS during the accident, and demonstrated the development of two distinct reactions, one exothermic reaction (fig. 6 and 7) and another one developing carbon dioxide (fig. 5).
The rupture disk failed due to a plug produced by the solidification of foams of the "boiling" mass inside the pipe connecting the tank with the rupture disk, and with the venting manifold.

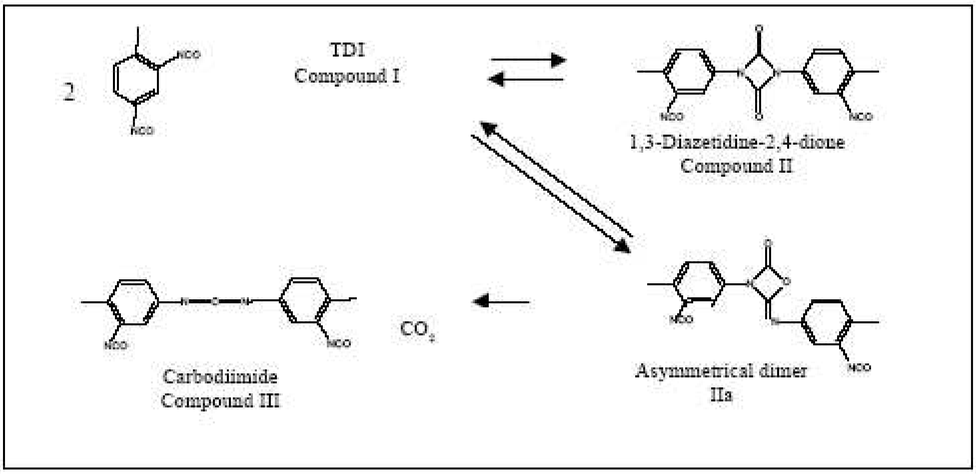

Fig. 5 - TDI dimerization with developing of carbon dioxide

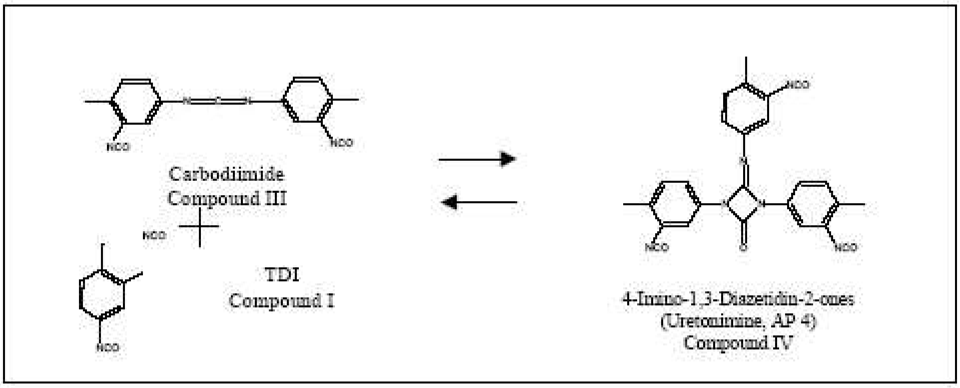

Fig. 6 - TDI exothermic reaction with dimer

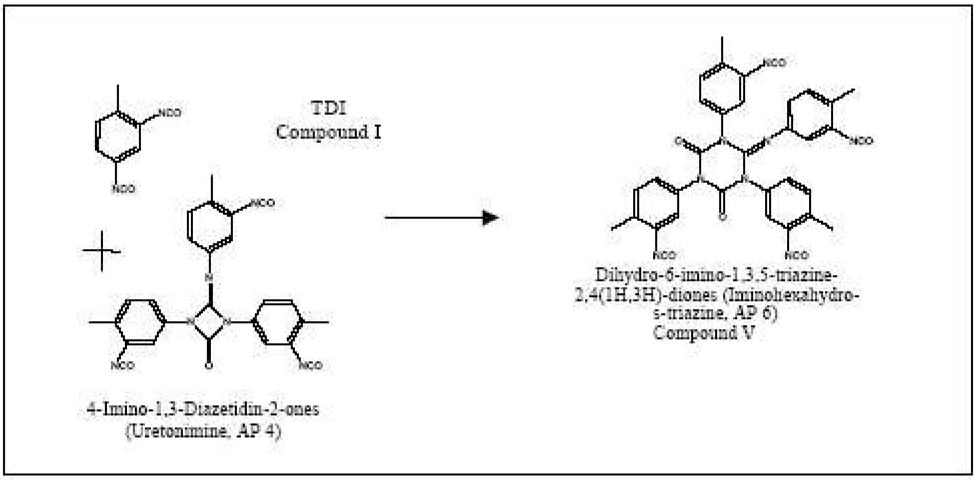

Fig. 7 - TDI exothermic reaction with trimer

ACTION TAKEN

Emergency measures

At 19:47, following the signalling of the emergency by the workers of the plant, the shift technician of near establishment in charge of emergency signalling, alerted the works fire brigade and then the national fire brigade. All equipment was

secured and the fire put under control by approximately 20:30 hrs, thanks to the rapid response of the works fire brigade located inside the chemical pole at a distance of 700-800 meters from the accident place, associated with the intervention of the national fire brigade of the near city, and the rapid response of the plant personnel who activated the emergency shut down of the plant over the automatic shut down systems.
Internal emergency plan

Consequent to the explosion and the subsequent fire, in the control room the assistant on duty in department TD1-3 activated the general alarm and the emergency shut down procedure for securing the plant, while the assistant on duty in plant TD 4-5 put on the self-contained breathing apparatus and performed a series of operations for securing the plant.

At 19:47 hrs the national fire brigade was alerted over the telephone; at 19:49 hrs the preliminary alarm was activated in the department; at 19:52 the general alarm was activated in the whole installation. From 19:59 hrs to 20:06 hrs the procedure of communicating the event via fax to the public authorities was activated.

The extinguishing operations were performed by the fire brigade of near establishment employing extinguishing foam, while the fire brigade of near city carried out the cooling of the adjoining plants and equipment with water hydrants, the containment of the gas emissions with water curtains and the monitoring of temperatures with infrared-cameras. At 20:45 the fire could be considered as extinguished. At 22:45 the on-site emergency was called off.

External emergency plan

At 20:30 hrs the acoustic alarm for the population was activated. At 21:30 the off-site emergency was called off. The members of the fire brigade, equipped with an infrared-camera, monitored the temperature of the structures and of the equipment during the fire and at the same time provided the cooling of the structures and equipment affected by the fire. Composition of the emergency response teams: near company fire brigade intervened with a team of 12 persons; the national fire brigade intervened with a team of 52 persons.

Official action taken

A penal action was started against some mangers of the TDI plant. Some minor civil actions for biological damage were also started. Authority charged with Safety at Work laws enforcement applied sanctions against three managers. The Ministry for the Environment requested the conclusion of the assessment of the SMS foreseen by Seveso implementation (D. Lgs. 334/99).

Corrective actions taken by the Company

Following the accidental event of November 2002, a thorough safety assessment of the plant, starting from the cause analysis, has been further developed by the Company, using different up to date methodologies. The studies and analysis listed below, applied to the high-boiling tars section and to the entire TDI production process, followed by the implementation of technical and procedural changes, should lead to an high safety standard reached and maintained, in particular with regards to process control, management of failures and accident prevention.
The characteristics of the high-boiling tars processing section of department TD5, and particularly concerning the chemical behaviour of the products processed, correlated with the parameter of residence time, temperature and composition, lead to consider the accident dynamics anomalous, due to the fact that it could not have happened in any other section of the department or in any other phase of the processing cycle.

LPP (Loss Prevention Programme) Guidelines for the analysis of the compliance of the process with the accident prevention principles.
This methodology was developed by the technological centre of the company, based on the experience gained in the establishments of the company groups, and other major companies operating worldwide.
The compliance with these guidelines allows the performance in terms of safety and operating reliability in general to be improved.
These guidelines often reflect the entire experience and knowledge gained on the management of process plants and the process anomalies that may occur in any of the activities involved in the management of a chemical plant (design, process control, operation, safety procedures, equipment).

Analysis of the management systems of the combustion plants.
As for the foregoing guidelines this tool is used inside the company to compare the combustion systems (heating furnaces, steam generators) with the most advanced technologies in the field of safety and reliability.
During the audit the problems concerning the management of the furnaces, the safety systems (alarms, shut-down systems), the control systems and the process parameters were analysed, using the most advanced international standards as reference and complying with Italian and European norms.

Layer of Protection Analysis (LOPA)
The LOPA analysis is a simplified form of risk analysis that analyses the risk of an undesired event over the magnitude of the event frequencies, effect gravity and event probability.
The LOPA process builds a risk analysis process using all data available from the company technological centre, from the databases of the company, from the plant histories and using the specific knowledge of the process engineers of the plants (from the same or other companies).

The analysis demonstrates that the implemented safety systems are adequate to obtain acceptable risk levels.

Investigation into the problems concerning chemical reactivity
All aspects concerning chemical reactivity of the substances present in the TDI production cycle were examined very closely; product incompatibilities and eventual instabilities were analysed.
Chemical reactivity matrixes and reference guidelines, based on company's experience, have been issued for the personnel of all company installations and in particular for those producing isocyanates.
A detailed analysis was performed on the reactivity of TDI and high-boiling tar mixtures with respect to different parameters, such as temperature, residence time and composition, referring also to the accident occurred.

Definition of Process Safety Cardinal Rules
Development and implementation of the cardinal rules concerning the process safety during production of dinitrotoluene, toluene di-amine, toluene di-isocyanate and phosgene.
These rules have been developed based on the experience of the Company and other leading companies gained in plant management; the rules indicate in a clear and concise way the criticality of different process phases, pointing out the operations to be avoided, with the goal of operating at the highest safety levels.

Pre start-up Audit
As foreseen by the procedures of the company, an audit was performed on the plant to check if there were the necessary safety conditions to restart the plant following the recent shut-down for maintenance.
The audit was carried out on the entire plant, with particular attention on the high-boiling tars processing section upstream the introduction of chemical reagents in the process; the performance of all foreseen test procedures on equipment and piping subject to maintenance was audited, and adequate training of the operative plant personnel was verified with specific checklists.
The implementation of the procedures contained in the operative manual was verified with a particular focus on the safety standards.

Updating of the operative manual
The entire operative manual of the department was revised, not only with regards to the high-boiling tars treatment section, which was the main reason of the revision, but also for all departments of the plant.

Management of change (MoC)
All technical or procedural changes have to be assessed through a MoC procedure analysing the consequences of the change with specific checklists with the participation of all roles involved.

LESSONS LEARNED

The accident put in evidence some SMS issues that, even if general and already identified in other cases, still had an important role in the event occurred.
They are showed on a specific format (table 2) used in the Italian approach, which makes reference to a check list of SMS elements (see Annex 1), consistent with the main articulation given for the SMS by the Annex III of "Seveso II" Directive.
An analysis of the actual accident pointed out the faults in SMS, as illustrated in Table 2.

Table 2 - Accidental Causes: analysis of plant and management factors

		Title: Explosion of a tank in a TDI production unit of a chemical plant

Accident occurred in section TD5 of the plant, aimed to high-boiling TDI compounds treatment. At 7.40 p.m. an internal overheating (T up to 230℃) of one storage tank of the compounds – D528/2 – caused by a runaway reaction between chlorinated tars and TDI, led to tank explosion, after the operators have tried to unload the same tank, without success. Vapour cloud released ignited after 5 minutes causing a fire, which burned almost 10-20 tons of toluene and high-boiling tars. Fire involved equipments in sight, with domino effect on a 2nd tank – D528/1 – which exploded after 1 hour, due to external radiation and internal overpressure. Overpressure wave from the 2nd explosion switched off the fire in course. A toxic cloud was formed, and four operator, injured for inhalation, were recovered. The explosions damaged different equipments and structure inside the unit. Internal and external emergency plans were immediately activated. Fire plumes caused suspected impact to the atmosphere and to the groundwater, monitored continuously by the regional agency for the protection of the environment.

3.i **3.iii**	Identification of substances and processes hazards; definition of safety requirements and criteria. Planning and updating of technical and/or managerial solutions for the reduction of risks	Inadequate re-examination of safety criteria and requirements for critical equipments. Tank D522 (for cooling impure TDI mixing) could be subject to inadequate thermal regulation, because of the presence of cooling-coils inside manually regulated, and due to the delicacy of the necessary controls. In the same way, tars storage tanks D528 could be subject to inadequate unloading, because of the peculiarity of the mixture treated (viscosity) and of the discontinuous process for transferring the product to the concentrator.	
3.ii	Identification of possible accidental events, safety analysis and residual risk	An adequate risk assessment could put in evidence the possibility of abnormal temperature increase inside the tars storage tanks D528, and the consequent exothermic reaction between TDI and tars	
4.i	Identification of plants and equipment to be subject to inspection plans	Inadequate identification of all equipments and elements subject to verify planning. Control instrumentation, safety systems (rupture disc) and mixer had to be submit to maintenance and periodic control, furthermore they had to be available during normal plant process. Instead: the mixer of D522 was under maintenance, the TI of D522 was broken (it always set bottom scale value) so it was no possible to determine the temperature value; the LI of D528/2 was out of use, the rupture disc of D525 was broken by time	

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3.iii	Planning and updating of technical and/or managerial solutions for the reduction of risks		Considering the possibility of T increase inside the tanks, and the hazardous mixture treated, it was needful to provide for an automatic alarm/lock-out
4.iii	Operating procedures and instructions in normal, abnormal and emergency conditions		Operating procedures in abnormal conditions had to include the necessary operations in the case of high-temperature (instead the operators appeared inactive during failure of mixer and instrumentation).
6.iv	Alarm and communication systems and support to the external intervention		Alarm systems not adequate. Delay in the communication of the event to the external authorities (from the first failure detection, at 2.00 p.m., to the last explosion, at 9.00 p.m., 7 hours passed).

Annex 1: Elements of SMS check-list

1. The document on prevention policy

1.i Definition of prevention policy
1.ii Verification of the SMS structure and its integration with the establishment organization
1.iii Policy Document Contents

2. Organisation and personnel

2.i Definition of responsibilities, resources and planning of activities
2.ii Information activity
2.iii Training and formation activities
2.iv Human factors, operator/plant interfaces

3. Evaluation and identification of major hazards

3.i Identification of substances and processes hazards; definition of safety requirements and criteria.
3.ii Identification of possible accidental events, safety analysis and residual risk
3.iii Planning and updating of technical and/or managerial solutions for the reduction of risks

4. Operational control

4.i Identification of plants and equipment to be subject to inspection plans
4.ii Process documentation
4.iii Operating procedures and instructions in normal, abnormal and emergency conditions
4.iv Maintenance procedures
4.vi Materials and services procurement

5. Management of change

5.i Technical and organizational plant modifications
5.ii Documentation updating

6. Emergency planning

6.i Accident analysis, planning and documentation
6.ii Roles and responsibilities
6.iii Controls and verifications of the management of emergency situations
6.iv Alarm and communication systems and support to the external intervention

7. Monitoring performance

7.ii Performance evaluation
7.ii Accident and near-accident analysis

8. Audit and review

8.i Safety audits
8.ii Review of safety policy and of Safety Management System.