Outbreak of fire in the supply duct of a chemical reactor

May, the 20th, 2000

Issoire – [Puy-de-Dôme] France

- Fire
- Glycols
- Static electricity
- Dimensioning
- Start-up
- Property damage
- Electrical continuity
- Inerting

THE INSTALLATIONS IN QUESTION

The site :

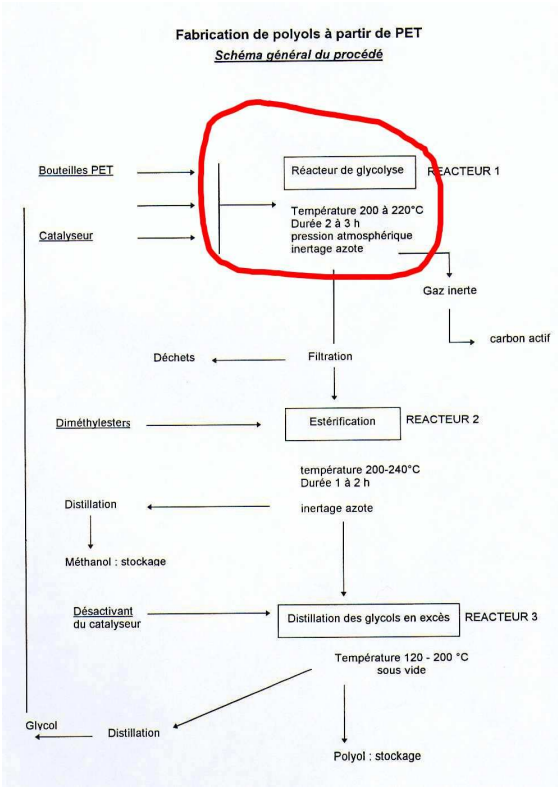
The company, located in a recently created industrial zone in Issoire, France, specialises in the manufacture of polyurethane foam derived from recycled food-grade bottles made of polyethylene terephthalate (PET), for use in building construction applications. The PET is reclaimed by chemical transformation in order to produce polyols/polyester.

The manufacture of polyesterol comprises three main stages:

× Glycolysis reaction of the PET: The PET bottles, which have been pre-ground, and the catalyst are introduced into a reactor containing the mix of glycols. Glycolysis takes place at 210℃-225℃ for approximately 3 hours in an inert atmosph ere.

× Interesterification reaction: the glycolysat is filtered and then transferred to a second reactor, where interesterification takes place by a mixing of diesters at a temperature of 205℃. Methanol forms during this reaction. It is distilled, separated and stocked for use as a fuel in the boiler that provides heat energy for the operation of the installation.

× Distillation of free glycols: the excess glycol is eliminated by vacuum distillation at a temperature gradient between 130℃ and 175℃.



The company operates using a patented process. Start-up of the unit firstly involved lengthy laboratory studies, followed by the construction of a micro-pilot (150 kg capacity). This first pilot facility allowed the laboratory tests to be reproduced with no apparent deviation. A half-scale industrial pilot facility (1,000 kg capacity) was then constructed and operated for 2 years without incident. The large amount of data collected was used in the dimensioning of the industrial unit.

The establishment received authorisation by prefectorial order dated July 7th, 1998, in particular for the storage of diphenylmethane diisocyanate, plastic materials (PET bottles, polyols and raw materials in tanks) and the manufacture or regeneration of plastic materials.

THE ACCIDENT, ITS BEHAVIOUR, EFFECTS AND CONSEQUENCES

The accident

The accident occurred on Saturday, May 20th, during the first tests of reactor R1. The company's technical manager and chemical engineer were present, as well as representatives of the Contracting Authority and the Main Contractor. A Saturday had been chosen to allow the tests to be carried out without any environmental or safety constraints (work sites in progress, etc.).

When the accident occurred, only the principal reactor (R1), which is used for glycolysis, was operating. The steam plant and the cold water production station were operating normally. Reactor R1 had been loaded normally, with 12 t of a precise mixture of 3 glycols and its temperature was 223℃, for a temperature control programmed at 21 5 ℃. The reactor was under an inert atmosphere and under constant N-flux, the vent on the condenser outlet was open. In normal operation, monitoring and control appeared correct and no operating anomaly was indicated.

The protocol of the test procedure called for repeated manipulations, in order to check the functioning of the commands in manual and automatic mode, particularly the PET supply.

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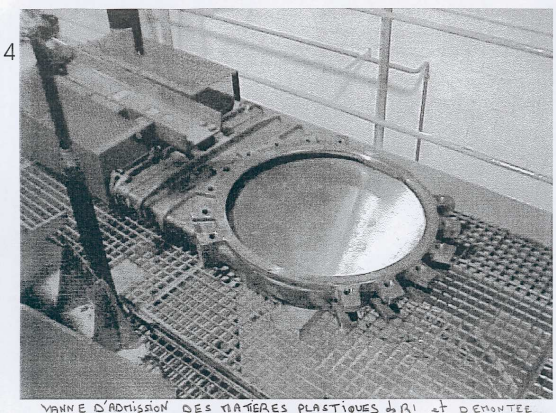

The inlet valve being open, the catalyst was inserted through the branch connection installed on the reactor. Following insertion of the catalyst and before initialisation of the insertion of the bottles, a fire started in the inlet duct. It immediately spread to the duct's acoustic liner. The liner, which was combustible, spread the fire, and "deflagrated", producing blazing droplets. Two dry chemical extinguishers were immediately used to put out the fire, which proved difficult to reach. The guillotine valve was locked and the N-flux in the reactor was sharply increased.

Over and above these measures, and faced with increasing flames on the duct liner, the operator decided to call the fire brigade and emergency services. When they arrived, however, they could see only persistent smoke. In order to make the site safe, they "flooded" the reactor in a multipurpose dry chemical, using a high-power nozzle. A water curtain was set up between the outer facade of the building and the methanol storage tanks, in order to protect the tanks from the consequences of any subsequent re-ignition of the fire.

The consequences :

The damages caused by the fire itself are as follows:

- ✓ Destruction of the supply duct,
- ✓ Destruction of the separator and damage to all sensors and electrovalves,
- ✓ Partial destruction of the guillotine valve,
- ✓ Destruction of the thermal insulation and all electrical, computer and pneumatic cabling on the upper zone of reactor R1,
- ✓ Structural damage to the building, mainly to the roofing and the structure situated near the fire.

The damage caused by the fire required extensive cleaning, repair of the electrical cabinets and circuits, the replacement of robots and electronic equipment (such as pressure and temperature sensors), as well as the replacement of all the unprotected thermal insulation in place. As the water used on the outside had damaged a series of sensors and electrovalves on the methanol tanks, the safety devices were replaced. A methanol pump was also destroyed by the water. The materials contained in the reactor were subject to stresses rendering them unusable and will be removed by a specialist company.

The cost of the damage, which was mainly caused by the extinction methods used, is estimated to be 3 million French francs, 2 million francs of which will result from operating losses. The cost of strengthening the safety systems amounts to approximately 400,000 French francs.

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 characterised by the following 4 indices, based on the information available.

The parameters that comprise these indices and the corresponding rating method are indicated in the appendix hereto and are available at the following address: http://www.aria.ecologie.gouv.fr

Property damage in the establishment (parameter €15), evaluated at 3 MF and production losses (parameter €16) estimated at 2 MF, explain the 'economic consequences' index rating of 1.

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

A fire broke out in the supply duct, which immediately heated up. The outer acoustic liner deteriorated, caught fire, spread the fire, melted and formed "droplets". Two types of fire occurred:

- The initial fire, which was caused by spontaneous ignition and the combustion of glycol vapours and condensed glycol,
- An induced fire that spread, due to combustion of the acoustic liner.

The fire broke out for the following reasons:

- The presence of condensed glycols and glycol vapour in the PET supply duct and the presence of oxygen in the supply duct,
- The temperature of the mix of glycols in the reactor, which was too close to the temperature of spontaneous combustion of diethylene glycol. The temperature in the reactor was 223°C and the temperature of the v apours was 220°C (the point of spontaneous combustion of DEG b eing 232°C),
- Aggravating factors such as:
  - The possible presence of traces of catalyst in the supply duct, which would favour combustion,
  - The absence of ground straps linking the different metal parts of the supply duct, even though the connections were made without splices and the supply duct was earthed (the absence of ground straps could explain a spark of static electricity),
  - A discharge flow that may have been be too weak, thus favouring the return of glycol vapours back into the supply duct,
  - The ease with which the protective liner caught fire (possible hypothesis of combustible gas forming in the supply duct, being gas resulting from the decomposition of the liner or its mounting adhesive).

ACTION TAKEN

Considering certain non-modifiable parameters, particularly the nature of the products and the temperature of the reactions, the operator has decided to:

- Eliminate the oxidant by high-pressure injection of nitrogen in the PET supply duct, to prevent combustion from occurring,

- Eliminate the presence of glycol vapours in the supply duct by strengthening the extraction at the condenser outlet, in order to prevent combustion,

- Stay as far below the temperature of spontaneous combustion of diethylenene glycol as possible, by maintaining the temperature of the mix at 205°C during the entire duration of the insertion of the PET, by controlling the thermal inertia coupled with the weight of the equipment, products and the influence of the thermal insulation,

- Prevent the presence of catalyst in the supply duct: the catalyst, which is extremely soluble in cold glycol, will now be introduced in the form of a solution, by a dosage pump, via an unused tap of the reactor in a completely closed cycle,

- Prevent any sparks caused by static electricity by connecting the components of the supply duct using a bonding jumper and earthing,

- Prevent the spread of fire caused by combustion of the liner, by removing the liner,

- Install a powerful exhaust fan above reactor R1 and at the level of the separator, in addition to the natural ventilation already existing on the upper part of the roofing,

- Install the control room high in an elevated position, and in the immediate vicinity of the emergency exits, in order to ensure the safety of personnel located too close to the zones in which the reactions take place,

- Replace the current system for inserting the bottles by a continuous and hermetic procedure, in order to prevent oxygen from accumulating in the PET supply duct, with installation of a dry chemical extinguisher system inside the supply duct itself.

LESSONS LEARNED

The fire occurred during the systems testing and validation phase, and the operator cannot be blamed in this respect, as that is the reason for carrying out these tests. It does demonstrate, however, the difficulties of transposing a correctly functioning pilot unit to the industrial phase. The sole reproach that can be made to the operator was his failure to immediately contact the inspectorate of classified installations.

A synthesis report concerning this accident was sent to the inspectorate of classified installations by representatives of the company on June 5, 2000, in accordance with article 38 of decree No. 77-1133 of September 21st, 1977. The causes and consequences of the fire, in addition to the measures foreseen or already in place to prevent any further incident, have been analysed.