

## Thermal runaway in a copolymerisation reactor

July 22<sup>nd</sup> 2000

## Leak in a polymerisation reactor

May 15<sup>th</sup> 2000

**Villers St Sépulcre (60) – France**

Chemistry  
Polymerisation  
Butadiene / Styrene  
Acrylonitril  
Leak  
Thermal runaway  
Material failure  
Human failure  
Organisation / Lack of  
maintenance  
Automation / Level probe

### THE INSTALLATIONS CONCERNED

#### The site :

The site of Villers St Sépulcre which employed 270 people, was specialised in the production of plastic materials:

- ✓ The S.A.N (Styrene Acrylonitril) were obtained by polymerisation of styrene and acrylonitril. These are the intermediary products for the production of A.B.S (Acrylonitrile Butadiene Styrene) and other plastic materials.
- ✓ The A.B.S are obtained by polymerisation of Acrylonitril, Butadiene and Styrene.

Three types of operations were conducted on the site: polymerisation, finishing and composition. The polymerisation took place in agitating reactors, of various sizes, the length of the process varying from 1 to 15 hours. Following polymerisation, the latex and aqueous residues were transferred to storage tanks while awaiting further treatment. The finishing operations consisted of separating the polymer from its liquid medium by flocculation, to obtain a dry powder. The composition operations involve the addition of pigments and various additives to the powder resulting from finishing to give the properties and characteristics required.

Annual production capacities were as follows:

- ✓ S.A.N resins: 33 000 t
- ✓ A.B.S resins: 15 000 t
- ✓ Granular A.B.S: 45 000 t

A.B.S have two essential properties: good shock resistance and good mechanical resistance. They are used in numerous applications: automobile manufacturing, household products, the leisure industry...

Activities were regulated by authorisation from the Prefect dated February 26<sup>th</sup> 1993 for an annual production capacity of 109 000 t. The site is covered by the European SEVESO II for the storage of acrylonitril (250 t) and butadiene (340 t).

## THE ACCIDENTS, THE SEQUENCE OF EVENTS AND THE CONSEQUENCES

The accidents of May 15<sup>th</sup> and July 22<sup>nd</sup> 2000 both took place in the polymerisation sector.

### The accident of May 15<sup>th</sup> 2000:

The reactor concerned (R 13) was a reactor of 55 m<sup>3</sup>, equipped with an agitator with paddles and counter-paddles as well as a heating and cooling system by a "jacket" circuit. This latter was connected to heat exchangers supplied with cold water, by cooling towers, or by steam from the plant circuit (maximum temperature of the reactor: 80 °C). It was equipped with valves and with bursting dishes specified at 15 bars as well as with a de-gassing system connected to the flare-stack network of the plant. It also had, at the base, a pneumatically controlled drainage valve, used to evacuate the washing water. This valve was extended by a watertight sleeve fitted with a solid plug with a watertight gasket.

Prior to any polymerisation, a series of tests were conducted to ensure that all the safety systems were operational. When the reactor had been opened, it was subjected to pressure tests.

The reactor was then loaded: for the production of polybutadiene, 25 tonnes of water were introduced, plus 15 tonnes of butadiene, an emulsifier and an initiator. The water was brought to 80 °C. The butadiene was introduced in liquid phase under a pressure from 8 to 10 bars. The progress of the reaction, which can last up to 15 hours, was linked to a reduction of pressure in the reactor from more than 10 bars to roughly 3 bars. The exothermal effect was at its maximum between 4 and 10 hours of polymerisation.

In the case of these highly exothermal reactions, agitation and temperature are essential parameters. The latter is precisely adjusted by setting the parameters for flow and temperature of the cooling water. At the end of the reaction, the butadiene which has not reacted is recovered by stripping.

On May 15<sup>th</sup>, around 3h45, during a butadiene polymerisation reaction conducted in the reactor R 13, a leak of butadiene occurred at the base of the reactor at the level of the solid plug located below the drainage valve. The operators in the control room detected the sudden opening of the drainage valve from a blinking alarm. For the management it did not seem a major problem, the circuit being closed by a sleeve and a solid plug.

The operators tried several times to close the valve, without succeeding. One of them went to the reactor to check the position of the valve and close it. The operator, who could not reach the valve on account of the fog of foam emitted from the lower part of the reactor, smelled the odour characteristic of butadiene. At that moment, the leak set off the alarm from the network of gas detectors, one of which being located just beside the reactor. Some of these alarms were set at a level above the upper threshold for the alarm (40 % of the lower explosion limit).

The POI (Internal emergency plan) was initiated and the management took the decision to open the de-pressurisation valve towards the flare-stack circuit located on the dome of the reactor. The pressure in this dropped, reducing the leak to zero in less than 30 minutes. The flare-off lasted for 1 hour and 15 minutes. Detectors returned to a zero detection position one hour after the onset of the incident.



Source : Drire Picardie























### The consequences :

Atmospheric checks conducted by the fire brigade in a radius of 5 km around the site, did not reveal any significant traces of butadiene. The management estimated that around 340 kg of this product had been released to the open air. This incident caused no material damage or bodily harm.

### EUROPEAN SCALE OF INDUSTRIAL ACCIDENTS

Using the scoring rules of the 18 parameters on the scale approved in February 1994 by the Committee of Competent Authorities of the Member States in application of the 'SEVESO' directive, the accident can be characterised by the four following indices, taking into account the available information.

The accident of May 15<sup>th</sup> is characterised by the following indices:

Dangerous materials released							
Human and social consequences							
Environmental consequences							
Economic consequences							

The parameters comprising these indices are available at the following address.: <http://www.aria.ecologie.gouv.fr>

The leak of butadiene was estimated at 340 kg or 0,7% of the Seveso threshold for this substance (50 t). The index relating to dangerous materials released for this percentage is equal to 2 (see. parameter Q1).

### [The accident of July 22<sup>nd</sup> 2000:](#)

The reactor concerned (R 23) had a capacity of 75 m<sup>3</sup> and comprised essentially the same equipment as reactor R 13. Its maximum temperature was 150 °C, its maximum pressure was 7 bars. In addition it had a capability referred to as "fast empty" of 195 m<sup>3</sup> allowing, in case of emergency, to rapidly evacuate the contents of the reactor and to drown it.

Around 22h40, during a S.A N. copolymerisation reaction, the operator in the control room detected an abnormal temperature rise in reactor R 23 (125 °C). The display screen in the control room confirmed the need for cooling.

An operator therefore went to the cooling tower to see the water level in the basin and observed that the low point had been reached. The supply of industrial water was not taking place. His attempts to provide an additional water supply did not allow him to re-start the cooling pumps.

The operator in the control room initiated the emergency procedure prescribed in the case of a runaway of the reactor: three loads of cold water with a unit volume of 2 m<sup>3</sup> were introduced to the reactor to bring the temperature down to 121 °C maximum. As the temperature was above 125 °C and each load of cold water only reduced the temperature by 0.7 °C, this procedure proved ineffective. Furthermore, the volume of the reactor did not allow for further additions of water.

It was therefore decided, as the emergency procedure prescribed, to introduce a reaction inhibitor to avoid the solidification of the product before voiding the reactor into the "fast empty" receptacle placed below the reactor, this involving 65 t styrene-acrylonitril mixture. At the moment of the emptying, the limits of this procedure had been reached. (temperature of 140 °C, pressure of 5.2 bars).




### [The consequences :](#)

This second accident did not result in any material damage, bodily harm or consequences to the environment.

### EUROPEAN SCALE OF INDUSTRIAL ACCIDENTS

Using the scoring rules of the 18 parameters on the scale approved in February 1994 by the Committee of Competent Authorities of the Member States in application of the 'SEVESO' directive, the accident can be characterised by the four following indices, taking into account the available information.

The accident of July 22<sup>nd</sup> is characterised by the following indices:

Dangerous materials released		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Human and social consequences		<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Environmental consequences		<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Economic consequences		<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

The parameters comprising these indices can be found at the following address: <http://www.aria.ecologie.gouv.fr>

S.A.N are copolymers of styrene-acrylonitril of which the acrylonitril content varies from 10 to 28%. Styrene is a Seveso substance for which the threshold is 50 000 t (inflammable substance: R10). The threshold for acrylonitril is 200 t (easily inflammable: R11 and toxic substance: R23/24/25). In accepting the least penalising hypothesis, or 10% of acrylonitril, the quantity of styrene released was 58.5 t et and that of acrylonitril was 6.5 t forming a mixture of 65 t. The quantity of styrene released corresponds to 0.12% of the threshold and that of the acrylonitril to 3.25% of the threshold. The index relating to this percentage is equal to 3 (see parameter Q1).

## THE ORIGIN, THE CAUSES AND THE CIRCUMSTANCES OF THE ACCIDENTS

### The accident of May 15<sup>th</sup> 2000:





The analysis of the accident highlights three contributing factors:

- ✗ The failure of the control of the pneumatic drainage valve with, in particular, a leak of the retaining ring of the push button which commanded it. The pressure then became sufficient to force the opening of the valve,
- ✗ Defect in the gasket of the solid plug below the valve,
- ✗ Faulty placing of the solid plug with a number of incorrect bolts and inadequate tightening. Furthermore, the solid plug had not been subjected to prior pressure tests.

#### The accident of July 22<sup>nd</sup> 2000:

The runaway of the reactor was due to a lack of water in the jacket circuit of the reactor, leading to an insufficient heat exchange. This lack of water was itself due to a lack of water in the cooling tower basin leading to a drop in the flow towards the heat exchanger of the reactor. The temperature of the badly regulated reactor rose, causing a runaway of the copolymerisation reaction.

A closer inspection of the basin of the cooling tower revealed a failure of the level probes for “low” and “very low” levels placed in the basin which allowed for the detection of any abnormal drop in the water level. Disassembly of the probes with vibrating blades showed that they were clogged up. The failure of the “low” level probe therefore prevented the automatic opening of the water supply valve to the basin. As regards the “very low” level probe, it was so clogged up that the alarm was not set off in the control room. The authorisation to initiate the production cycle was not therefore blocked during the prior tests on the reactor.

## THE MEASURES TAKEN

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Source : Drire Picardie

### The accident of May 15<sup>th</sup> 2000:

Since this accident, the installation concerned has not been returned to service. <thought has been given to the question of maintaining production of polybutadiene on the site. This production is henceforth handled on another production site belonging to the same group in Holland. The supply of polybutadiene to the site is provided by road tankers from the Dutch site. The company therefore no longer stores butadiene on the site.

However, a decree from the Prefect dated 14<sup>th</sup> November 2000 subordinates the possible return to service of the butadiene production unit to the respect of certain dispositions, relating in particular to:

- × Organisation of risk prevention,
- × Preparation of clear operational standing orders,
- × Preventative maintenance of the installations,
- × Periodic verification of safety measures concerning the correct operation of the installations,
- × Operating measures for the installations,
- × Equipment and set operating parameters which are important for safety (IPS)

### The accident of July 22<sup>nd</sup> 2000:

Immediately following the accident, reactor R 23 was closed off. Later, the operator cleaned the level probes.

Furthermore, a programme for checking the state of the probes was instituted during each cleaning operation for the reactors, or every 15 days. A testing programme for the alarms and for the "low" and "very low" probes, which were also to be tested before commencing every production cycle. The management of the plant also intended to install level probes using different technologies.

The installation concerned was returned to service on July 26<sup>th</sup> late in the evening after having been subjected to the checks and tests described above.

## **THE LESSONS LEARNED**

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These two accidents were characterised by faulty organisation of maintenance of the installations on the part of the management. Above and beyond these shortcomings, the initiation of a real safety management system as provided for by ministerial order dated May 10<sup>th</sup> 2000 appears to be the best way to prevent further accidents of this kind.