

## HOW THE STUDY OF ACCIDENT CASE HISTORIES CAN PREVENT RUNAWAY REACTION ACCIDENTS TO OCCUR AGAIN

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The study of accident case histories is of utmost importance to prevent the repetition of the same accidents or of accidents with the same causes. This is especially true in the field of runaway reaction accidents.

In the study of accident case histories, the following considerations should be addressed:

- Description of the process and of the chemistry involved.
- Description of the accident circumstances and consequences.
- Identification of the accident causes with special attention to the chemistry.
- Review of the relevant literature to determine if the same accident has occurred earlier.
- Comparison of the accident circumstances with other accidents/incidents where the same cause/chemistry was involved.
- Lessons learned: considerations and factors, which would provide a warning to prevent the same type of accident to occur again.

In this paper, the above approach will be applied to the following accidents:

- the Seveso accident (1976)
- the Bhopal accident (1984)
- the Griesheim accident (1993)
- the frequent Phenol + Formaldehyde runaway reaction
- the accidental bulk polymerisation of reactive monomers with consideration of vinyl acetate and acrylic acid.

It will be shown that the study of accident case histories could greatly reduce the rate of occurrence of runaway reaction accidents.

Keywords: Runaway Reactions, case histories.

### INTRODUCTION

The Seveso II regulation requires that for any chemical process concerned by the regulation, a hazard study be completed where the accident case histories known in the same process elsewhere or in related processes should be collected and analysed. This new requirement will ensure that the lessons learned from accidents occurred in the chemical industry as a whole, will help to improve process safety at least in the European Community.

The study of accident case histories will develop. Some processes with bad safety records will be identified and labelled as unsafe. Ignoring this information or neglecting to collect it and to analyse it, will increase liability in case of occurrence of a well known accident scenario.

The study of accident case histories is of great interest in the field of runaway reaction accidents. It helps to identify the contributing factors and scenarios of the accidents, allowing reaching general conclusions, which may apply to related processes or chemistry.

In the manufacture of fine chemicals or pharmaceuticals, some frequent reactions or the use of particular reactants, may present a hazard. It is therefore useful to record incidents and accidents to learn the lessons from it, to prevent these problems to occur again.

A simple method to collect the information on accidents and incidents would be the following:

- Provide a description of the process and of the chemistry involved.
- Describe the accident circumstances and consequences.
- Identify the accident causes with special attention to the chemistry.

- Review the relevant literature to determine if the same accident has occurred earlier.
- Compare the accident circumstances with other accidents or incidents where the same cause/chemistry was involved.
- Identify the considerations and factors, which would provide a warning to prevent the same accident to occur again.

This method of analysis will be exemplified considering well known accidents thoroughly described in the literature or frequent accidents occurring always the same, thus proving the interest of this exercise to prevent accidents from occurring again.

### THE SEVESO ACCIDENT ON 10 JULY 1976

This accident had a very important influence on the regulation applied to the chemical industry in the European Community.

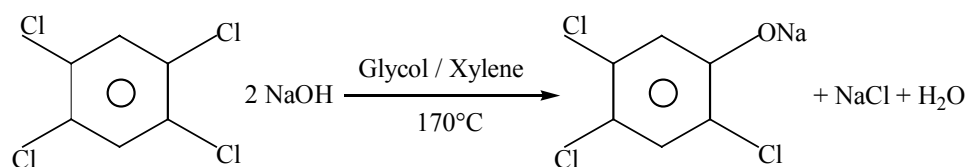
The Seveso accident occurred in a process to produce 2,4,5 trichlorophenol by alkaline hydrolysis of 1,2,4,5 tetrachlorobenzene.

As pointed out by Grewer<sup>1</sup> there are two different processes to carry out this reaction. The "old" process is the so-called "Methanol process", a German process where methanolic caustic soda is used for the hydrolysis reaction. This process, very similar to the process involved in the Griesheim accident, is a pressure process operating under the solvent autogeneous pressure i.e. 20 barG in a temperature range of 165°C-180°C<sup>1</sup>.

A slightly different process, the Boehringer process<sup>2</sup> operates at a temperature of 140°C thus with a lower pressure but with longer cycle time.

According to Grewer<sup>1</sup> the drawbacks of this process are that no reflux cooling is possible under the process pressure and that caustic soda is not completely soluble in methanol at the process temperature, causing the caustic soda heat of dissolution to add to the heat of reaction of the hydrolysis reaction of  $\Delta H = -180$  kJ/mole. This process had four known incidents before the Seveso accident.

The Seveso process is the "Glycol – Xylene" process carried out under ambient pressure. The synthesis reaction is:



This process is a total batch process. At the beginning of the operation, 3235 kg of Ethylene Glycol, 603 kg of Xylene, 2000 kg of solid 1,2,4,5 tetrachlorobenzene and 1000 kg of solid sodium hydroxide, were charged into a 10 m<sup>3</sup> stirred reactor equipped with a condenser and a water separator to remove water from the condensate and return xylene into the reactor. The equivalent ratio NaOH / 1,2,4,5 TCB is 2,7. There is an excess of 0.7 equivalent caustic soda with respect to 1,2,4,5 TCB.

The choice of solvents appears to be correct. Caustic soda is soluble in glycol and the organic reactant and product are soluble in xylene. Xylene allows the removal of water by azeotropic distillation. This helps the hydrolysis reaction to go to completion. The reaction mixture should be homogeneous, except for the sodium chloride by product, which should be solid after water removal.

The reaction mixture was heated to 170°C using 12 barG steam with a saturation temperature of 190°C. The reaction mixture was kept at 170°C for four hours and the water – xylene azeotrope was distilled. Then all the xylene and 500 kg of glycol were distilled off by vacuum distillation. Then, on the Saturday of the accident, as the hydrolysis of the phenate

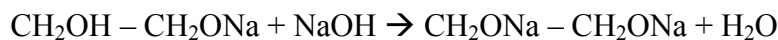
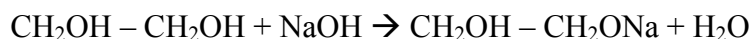
with aqueous HCl could not be carried out immediately, and had to be delayed until the following Monday, the steam valve to the heating coil was closed and stirring was stopped 15 minute later at 05:00. This was done to keep the reactor warm over the week-end to prevent the phenate crystallisation. A runaway reaction caused the bursting disc to open at 12:37 i.e. 7.5 hours later, while the reactor was unattended. The whole reactor inventory was released and sprayed over the neighbourhood with a tetrachlorodibenzodioxin content of 3500 ppm. Approximately 2 kg TCDD were released during the reaction vessel blow-down.

There are many variations in the process description published by various authors and details are missing like the reactor volume and material of construction, the reaction temperature, the temperature at which the reactor was left on Saturday morning, whether the steam valve was leaking or not, whether the atmospheric pressure had been re-established with nitrogen or the reactor connected to the atmosphere through some vent line or the reactor completely isolated<sup>1, 3, 4, 5</sup>.

A precise drawing of the process is not even available, nor the size of the famous bursting disc. Considering the cost of this accident for the chemical industry as a whole, these details should be made available.

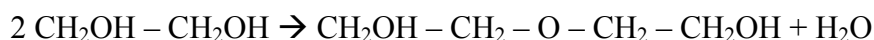
#### WHAT ARE THE CAUSES OF THE SEVESO ACCIDENT ?

The Seveso accident was caused by the thermal instability of the final reaction mixture after distillation of the xylene and a part of the glycol charge, under vacuum. Most probably the cause of the instability is the presence of anhydrous caustic soda in excess and glycol in the final reaction mixture. In such conditions glycol is not only a solvent but reacts with caustic soda to produce sodium glycoxide and water<sup>5</sup>.



Dehydration of the reaction mixture by vacuum distillation of the xylene/water azeotrope helps this reaction to proceed.

Diethylene glycol is also formed under alkaline conditions.

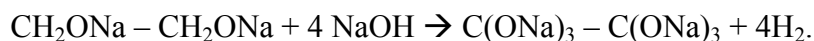
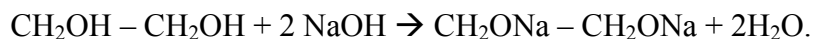


Other reactions are known at higher temperature:

In 1859, by heating a mixture of KOH and glycol at 250°C, Wurtz<sup>6</sup> obtained potassium oxalate and hydrogen.



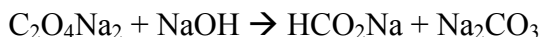
In 1904, by heating an equimolar mixture of ethylene glycol and caustic soda at 230°C-284°C, Nef<sup>7</sup> obtained hydrogen, di and tri ethylene glycol, methanol, ethanol, sodium formate, sodium acetate, sodium oxalate and sodium carbonate. The following reaction mechanism was proved by new experiments carried out at 250°C-350°C by Fry and Schulze<sup>8</sup>:



Then, the sum of the above reactions is as follows:



Then:



Thus one can write the following reaction:



The gas produced by these reactions is mainly hydrogen. The gas production onset temperature is about 150°C. Gas production increases with temperature and some other gases are obtained in smaller quantity: ethylene, ethane, CO, CH<sub>4</sub>, at higher temperature. The decomposition exotherm onset temperature under temperature scan conditions in open and closed test cell is about 230°C-250°C. However the exothermic decomposition of sodium glycoxide and polyglycoxide in glycol and polyglycol solutions is autocatalytic. In isothermal exposures in open VSP test cell, the exotherm initiation may be obtained at 190°C after a long induction period. The autocatalytic nature of sodium glycoxide decomposition may also be deduced from the reaction mechanism as written above.

Cardillo and Girelli<sup>9</sup> studied the reaction of glycol and diethylene glycol with different proportions of caustic soda. Mixtures with 10 % to 30 % caustic soda exhibited exotherms onset temperature of 225°C-230°C. The sample heat of decomposition was 90 to 160 J/g for glycol and 150 to 200 J/g for diethylene glycol.

In the production of polyglycols, accidents occurred during the vacuum distillation of polyglycols over their sodium glycoxides. The sodium polyglycoxide happened to decompose in the column bottom. In the USA, the DIERS in a round robin exercise, studied the decomposition of tetraethylene glycol sodium salt in a tetraethylene glycol solution. The decomposition was best obtained in open cell tests as recommended by the DIERS.

In the Seveso accident, depending on the sodium glycoxide concentration in the reaction mixture, the glycoxide decomposition may have been active at temperatures as low as 160°C or 170°C and may have accelerated later after an induction period. There is no need to assume overheating of the reaction mass or a leak of steam in the limpet coil.

## LESSONS LEARNED

In this accident, the cause of the runaway reaction is to have allowed the final reaction mixture after dehydration and evaporation of the solvents, to stay in the reactor at the process temperature for a long period of time, without checking the reaction mixture thermal stability over this period of time.

The rupture disc was not sized on a runaway reaction scenario. Therefore there was no release containment system. The R.D. design basis was to protect the reactor from overpressure during nitrogen push transfer of the reaction mass. It is frequent in multipurpose plants that the emergency relief vents are designed on scenarios independent of the chemistry being made. i.e. the fire case, full heating etc., not necessitating a release containment system. Should a runaway reaction occur, a two-phase flow of the reaction mixture could be sprayed over the neighbourhood. Therefore it would be necessary to review any emergency relief vent to check if a release containment system is necessary in case of runaway reaction. This is a very demanding program.

## THE BHOPAL ACCIDENT IN THE NIGHT OF SUNDAY 2 DECEMBER 1984

The facility of Union Carbide India Ltd (UCIL) in Bhopal was built to manufacture Carbaryl by reaction of methyl isocyanate on alpha naphthol.

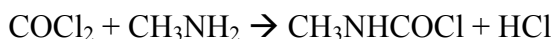
There were five main plants on the site:

- a carbon monoxide plant
- a phosgene plant where phosgene was produced by reaction of CO with chlorine
- the MIC plant where phosgene was reacted with monomethylamine (MMA) to produce methyl isocyanate
- the Sevin plant where alpha naphthol was produced and reacted with MIC to produce carbaryl
- a pesticide formulation plant.

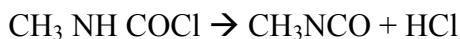
This facility was situated in a town of 800.000 inhabitants.

Only the MIC plant was involved in the disaster. This plant was described in various papers and books concerning this accident and in ref. <sup>4</sup> and <sup>5</sup>.

In the MIC plant, phosgene and MMA are reacted in a gas phase reactor at high temperature to produce methyl carbamoyl chloride (MCC):



The outflow of the reactor is quenched with chloroform, the process solvent. After separation of unreacted phosgene, MCC is thermally decomposed into MIC and HCl in a pyrolyzer:

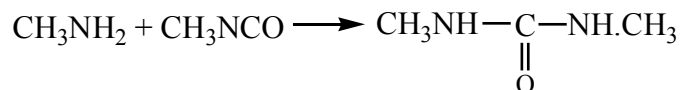
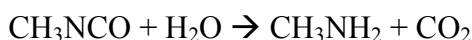


Finally MIC is separated from chloroform by distillation in the MIC refining still. Only high purity MIC is sent to the MIC storage vessels.

There were three MIC underground storage tanks. One, n° 619 was empty, the two other tanks were in use. The MIC storage vessels are horizontal cylinders of 57 m<sup>3</sup> nominal capacity each, designed for vacuum and 2.8 barG at 121°C. The storage vessels are pressure vessels allowing a nitrogen pressure of 0.7 to 1,7 barG, to prevent any liquid ingress and help pumping. The MIC was pumped and circulated through a refrigeration unit using chloroform as heat-transfer fluid. The material of construction was 304L stainless steel. The MIC storage vessels were equipped with a combination of a rupture disc and a pressure safety valve in series, with a set pressure of 2,8 barG. The PSV outlet was collected to a vent gas header directed to a scrubber with a circulation of caustic soda solution. The vent gas scrubber capacity was of 4 tonnes of MIC in 30 minutes, then less than 2 tonnes per hour due to the absence of cooling. To obtain this capacity, it was necessary to add 50 % caustic soda to the scrubber when necessary. Both the process vent header and the relief vent header were collected to the scrubber and could also be diverted to the plant flare, as a back-up of the scrubber. The gas scrubber exit was through a 30 m high stack directed to the atmosphere.

The MIC plant was shut-down on 22 October 1984 and was never restarted. The 610 storage tank inventory was 41 tonnes of impure MIC contaminated by 750 kg to 1300 kg chloroform, probably coming from wrong operating conditions in the MIC refining still during plant shut-down. The MIC storage tank cooling system was taken out of service in June 1984. The accident occurred on 2 December 1984 i.e. six weeks after the plant shut-down. Experimental study of the runaway reaction led to the conclusion that 500 kg to 1000 kg water must have entered the tank.

The reaction of MIC with water gives CO<sub>2</sub> and MMA, which further react with MIC to produce DMU:



The heat produced by the above reactions caused MIC polymerisation and the formation of many by-products. The vessel pressure increased due to CO<sub>2</sub> production and MIC vapour pressure. When the PSV discharged, there was probably significant liquid carry over. An estimate of 36 tonnes of material was released, of which 25 tonnes of MIC vapour. The storage vessel did not rupture. The PSV release mass flow-rate was well above the vent gas scrubber capacity. Obviously, the vent gas scrubber design basis was far from taking into account a release mass flow-rate of 10 tonnes/hour of a two-phase flow of the storage vessel inventory. The presence of 7-10 % MMA hydrochloride in the tank residue proved the presence of HCl in the tank, probably coming from upstream in the process.

#### WHEN DID THE WATER ARRIVE IN 610 STORAGE TANK ?

It is obvious that the water came after the plant shutdown. As there was no circulation in the storage tank after the refrigeration unit shut-down, the water could remain separated in a layer and unreacted for a long time at ambient temperature.

#### WHERE DID THE WATER COME FROM ?

Considering accidents with isocyanates in general, they occur during plant shut-down due to the use of washing water for cleaning equipments during shut-down. Examples are valve explosions where water or isocyanates came into contact, explosion in pumps, eruption in containers where water and isocyanates are inadvertently mixed. The water may have been cleaning water or water coming from leaks in the plant on heat exchangers and admitted in the 610 storage tank after plant shut-down.

#### HOW COULD THIS OCCUR ?

This process was a high-tech continuous process with inventories of toxic and flammable products. It was consistent with a large continuous consumption of MIC. If the MIC demand was only occasional, due to problems down-stream, the plant could only start and stop just for the timely MIC consumption, and to fill the underground storage tanks. During the transient shut-down conditions, the MIC purity may have been out of specifications.

This plant design came from the USA in the seventies, from a region where the chemical industry was developed, and large inventories of toxic and flammable materials not considered as a hazard. This type of awareness came later, after the Bhopal accident. Such a disaster had never occurred before.

#### LESSONS LEARNED

The scenario which led to the Bhopal disaster was very simple and common. If the production of large inventories of such reactive and toxic products had been avoided, if such a process had been installed far from populated areas, the consequences would have been minor.

This accident proves that continuous processes are not less dangerous than batch processes and that they don't exclude large inventories of toxic chemicals.

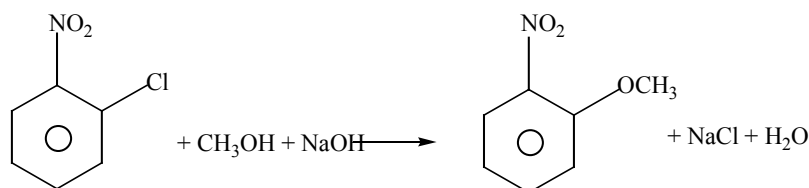
The occurrence of a runaway reaction due to water ingress in the MIC storage vessel was not taken into account in the vent scrubber design, nor was the possibility of liquid carry-over in the relief system vent line. A proper release containment system was not provided.

#### **THE GRIESHEIM ACCIDENT ON FEBRUARY 22, 1993**

On February 22, 1993, a runaway reaction occurred at the Griesheim plant of Hoechst A.G. during which about 10 tons of a reaction mixture were released through a pressure safety valve. The two-phase release was carried over by the north wind and spread over the south part of the factory, the river Main banks and two suburbs of Frankfurt: Schwanheim and

Goldstein. The area concerned by the yellow deposit was of 300.000 m<sup>2</sup>. It was the most serious accident occurred in this company over 130 years<sup>10</sup>.

The process concerned was the reaction of ortho chloro nitrobenzene with methanolic caustic soda to produce ortho nitroanisole.



This reaction was carried out in a 36 m<sup>3</sup> reaction vessel at a reaction temperature of 80°C and an absolute pressure of 10 bar<sup>11, 12</sup>. The process was a semi-batch process in which 2800 litres of methanol and 5800 litres of o-nitrochlorobenzene were charged to the reaction vessel under stirring. The agitator was then turned off and the liquid level in the reaction vessel was checked manually by opening the manhole cover. The agitator was then restarted and the reactor inventory was heated to about 80°C. Then 15800 litres of cold 15 % wt methanolic caustic soda were introduced over five hours while keeping the reaction mixture temperature at 80°C by cooling through a jacket.

Nitrogen blanketing of the reactor gas phase was achieved after the cold initial charge by applying an additional 3 bar nitrogen pressure to the reactor gas phase, to reduce the oxygen concentration to less than 8 % vol. This oxygen partial pressure was allowed to prevent secondary reactions. Thus no solvent reflux was provided and the process was a pressure process.

The accident enquiry proved that on the operation of the night of 21 to 22 February which was the night of "Rosenmontag" the following failures occurred:

- the agitator was not restarted after checking the reactor liquid level.
- During the introduction of the cold methanolic caustic soda, heating was applied to the reactor to obtain the usual temperature of 80°C whereas cooling was normally necessary.
- After sampling of the reaction mixture to check conversion, the agitator was unfortunately restarted. This was done when the conversion ratio of o-nitrochlorobenzene was only 45 % in the reaction mixture. On mixing the reactor inventory a runaway reaction occurred where the temperature could reach at least 160°C and the pressure 16 barG. The reactor was equipped with a pressure safety valve with a set pressure of 16 barG. The PSV was actuated and its size was large enough to allow liquid carry over. The heat of reaction of the desired reaction was of 140 kJ/mole o-nitrochlorobenzene between 80°C and 120°C, corresponding to an adiabatic temperature rise of ca.100°C. However secondary decomposition reactions involving the nitro group were initiated when the agitation was restarted, with a heat of reaction of 390 kJ/mole<sup>13</sup>. This was also proven by the chemical analysis of the yellow deposit showing significant concentration in azo and azoxy derivatives<sup>10</sup>. It was argued that the side reactions were possible due to a lack of oxygen in the reaction mixture because the reactants were in separate layers in the reactor. The other cause is the high temperature obtained during the runaway reaction.

#### WHAT ARE THE GENERIC CAUSES OF THE ACCIDENT ?

The most frequent cause of accident in semi-batch processes is the absence of agitation during introduction of the controlling reactant. This was achieved in the Griesheim accident.

This process could have been identified as safety critical since an aromatic nitrocompound was reacted under strong alkaline conditions. It is known that the thermal stability of organic nitrocompounds is lowered by a large extent under alkaline conditions.

The process was operated manually whereas one would expect a computer control for such a process in a 36 m<sup>3</sup> reactor.

There was an alarm if the agitator failed but probably no alarm if the agitator was not started when necessary. This is a frequent short-coming in semi-batch processes.

There was a pressure safety valve on the reactor for another reason and therefore no release collection system was provided. However, should a runaway reaction occur, a two phase release of the vessel inventory was possible.

#### DID THIS ACCIDENT OCCUR BEFORE ?

The answer is yes. In a document provided by Sumitomo Chemical Ltd<sup>14</sup>, a list of chemical accidents occurred in Japan between 1971 and 1981 is given, among which the following:

In a process to manufacture o-nitroanisole from o-chloronitrobenzene, by adding o-nitrochlorobenzene in caustic methanol solution, abnormal reaction occurred when the stirrer was restarted after the stoppage. Nine were injured.

#### LESSONS LEARNED

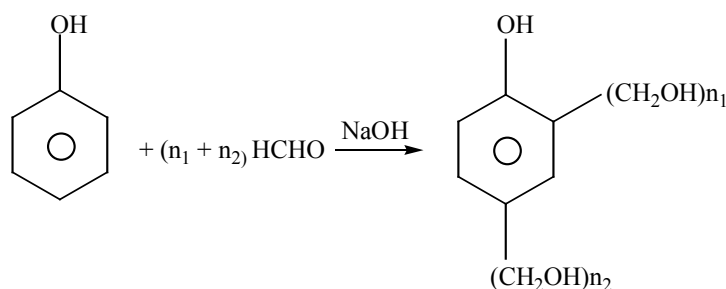
- A process where an organic nitrocompound is reacted under strong alkaline conditions should be considered as safety critical.
- In a semi-batch process with high exotherm potential, agitation should be controlled by a computer and safety interlocks. No action should be undertaken if the agitator is not running.
- Pressure safety valves on reactors with a runaway reaction potential, should be reviewed to check for the necessity of a release containment system.
- The products of the runaway reaction, involving side reactions or subsequent decomposition reactions are very different from the desired reaction products. So are their toxic properties. Therefore, the need for a release containment system should not be discussed on the basis of the normal reaction products but on those of the runaway reaction.
- The accidents occurred on the same process should be known by the plant manager and considered in safety reviews.
- This accident had an unexpected mediatic impact – see ref.<sup>15</sup> – and probably caused the withdrawal of the company from the chemical industry.
- A commission was created by the federal government of the FRG to determine the minimum knowledge required to be allowed to run a process<sup>16</sup>. This was added to the German regulation. This accident had an influence on the regulation applied to the Chemical Industry in Germany.

#### THE PHENOL + FORMALDEHYDE RUNAWAY REACTION

The phenol + formaldehyde reaction is commonly used in the chemical industry to manufacture formo-phenolic resins. This reaction caused many runaway reaction accidents<sup>17</sup>. The hazards of this reaction was exemplified in previous papers<sup>18, 19</sup> by considering a Resole base catalysed reaction where the formaldehyde to phenol molar ratio was  $R = 1,897$ . This process includes two separate reaction steps: the methylation reaction and the salification of the methylolated phenol.

In the methylation step, formaldehyde is reacted with phenol to obtain a methylolated phenol, in the presence of a catalytic quantity of caustic soda.

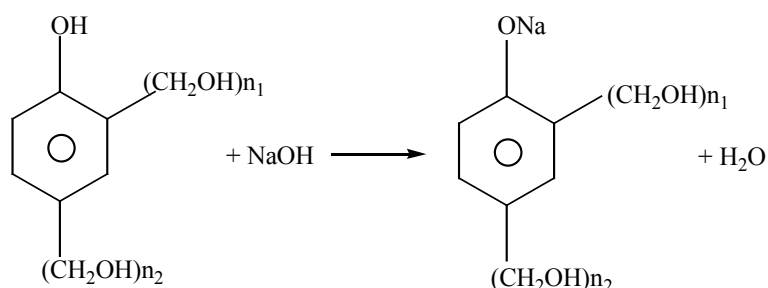




The reaction is carried out in a stirred reactor equipped with a condenser. The reactor can be heated or cooled through a jacket.

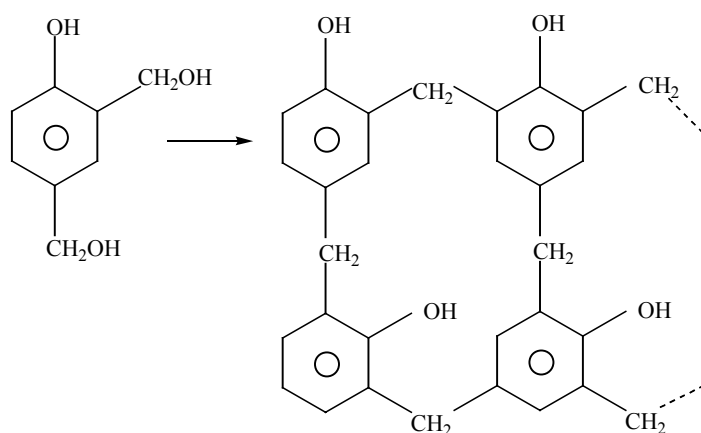
Phenol is charged to the reactor with the catalytic amount of caustic soda. The reaction mixture temperature is set to 60°C and 37 % wt formaldehyde aqueous solution is introduced over two hours under temperature control by cooling. The reaction mixture is then kept at 60°C to allow the reaction to come to completion. Then the reactor is cooled to 50°C.

In the salification step, a stoichiometric amount of 30 % wt caustic soda is introduced over 30 minutes under temperature control at 50°C, to obtain a phenate.



There is a well known dangerous process deviation which consists of forgetting to introduce the catalytic quantity of caustic soda in the methylation step, not detecting the mistake and starting the introduction of the stoichiometric amount of caustic soda in the salification step. Obviously, the reactant of the salification step is the catalyst of the previous methylation step. Should this process deviation occur, the exothermic methylation reaction is initiated when the whole inventory of formaldehyde is present and unreacted. The fast temperature rise will trigger the polymerisation reaction causing the reactor to pressurise and often to explode, together with the gelification of the reactor inventory.

The gelification reaction is:



The absence of catalyst in the methylation step may remain undetected because it has no effect on the reactor temperature which is controlled at 60°C. An experimental study of this worst case scenario based on Vent Sizing Package experiments was carried out, where a

pressure surge to 37 bar abs. and a maximum heat-rate of 680°C/min. were obtained. See figure 1. The reaction mixture is a high vapour system. The venting requirement for the worst case scenario is a rupture disc of 1 metre in diameter for 30 tonne inventory reactors, like those exploding in the recent period. Atmospheric venting is necessary to prevent the vent blockage by the reaction mixture gelification.

Other process deviations may also cause problems in relation to reactant accumulation or reaction mixture instability. The methylation final reaction mixture may polymerise a few degree Celsius above 60°C. The corresponding adiabatic temperature rise is 100°C.

During formaldehyde injection in the methylation step, accumulation of the controlling reactant and its subsequent reaction may initiate the reaction mixture polymerisation above 60°C. The causes of formaldehyde accumulation are: too low a temperature, too high a reactant feed rate, no agitation.

The loss of cooling or a wrong temperature control may also cause the reaction mixture polymerisation. The methylation final reaction mixture is not stable even at ambient temperature and cannot be safely stored or transported. Gelification proceeds slowly at ambient temperature.

The process considered is therefore safety critical and a number of safety interlocks are recommended to prevent runaway reaction accidents:

1. Interlocks to prevent wrong reactant introduction in the methylation step.
  - The formaldehyde introduction must not be allowed if the catalytic quantity of caustic soda has not been previously introduced.
  - The formaldehyde introduction must be interrupted if the cooling demand is not obtained in the reactor jacket cooling loop.
  - The catalyst must not be introduced after the beginning of formaldehyde injection.
  - The introduction of the controlling reactant, formaldehyde, must be prevented or interrupted if there is no agitation.
2. Interlocks to prevent the controlling reactant accumulation:
  - Low temperature interlock interrupting the formaldehyde introduction.
  - Limitation of the formaldehyde feed-rate by a diaphragm.
3. Interlocks to prevent the reaction mixture polymerisation by too high a temperature:
  - High temperature interlock interrupting formaldehyde introduction and providing full cooling capacity on the reactor jacket.

In addition, the methylation final reaction mixture must not be kept for a long period of time without temperature control in a large reactor at the process temperature or under ambient temperature, because the polymerisation proceeds slowly and may speed up.

The merit of high integrity interlocks may be taken into account to reduce runaway reaction accident scenarios, thus reducing the reactor venting requirement.

### **THE ACCIDENTAL BULK POLYMERISATION OF REACTIVE MONOMERS**

The bulk polymerisation of reactive monomers like vinyl acetate, acrylic acid and others, is not currently used in industrial processes, due to the violence of the reaction. However this type of reaction is frequently involved in polymerisation accidents concerning the storage of recycled monomers and premix vessels.

Recycled monomers are obtained in processes where the polymerisation conversion ratio is not 100 %. The unreacted monomers are recovered and stored to be recycled in the polymerisation process. These monomers may contain a very low polymerisation inhibitor concentration and some traces of polymerisation initiator. They are much less stable than commercial inhibited monomers.

The use of premix of polymerisation initiator dissolved in the monomers appears to be frequent in polymerisation processes. This allows the introduction of the polymerisation initiator in the polymerisation process, not necessitating the use of a solvent to dissolve the initiator.

These premix with a high concentration of initiator are very unstable and give very violent polymerisation. The accidents are also frequent. This can be easily understood.

The kinetic behaviour of radical chain polymerisations has been presented by Flory<sup>20</sup>. In this theory, the rate of monomer consumption is referred as the rate of polymerisation.

$$R_p = -\frac{d[M]}{dt} = k_p [M][P]$$

where [M] is the monomer concentration, [P] is the polymer radical concentration and  $k_p$  is the propagation rate constant.

According to the theory of Flory, the rate of polymerisation is controlled by the initiator concentration<sup>20, 21</sup>.

$$R_p = -\frac{d[M]}{dt} = k_p [M] (k_d f [I] / k_t)^{1/2}$$

where  $k_d$  is the initiator decomposition rate constant,  $k_t$  the termination rate constant, [I] the initiator concentration,  $f$  the fraction of initiator radicals successfully reacting with the monomer.

Consequently, the rate of polymerisation is an Arrhenius function with first order with respect to the monomer concentration and half order with respect to the initiator concentration which controls the population of polymer radicals.

Considering the maximum rate of polymerisation, the higher the initiator concentration, the faster the maximum rate of polymerisation. This explains the very violent polymerisation observed in premix vessel polymerisation accidents, where very high initiator concentration is present. See figure 2.

In the case of commercial monomer storage, the induction period is the time necessary for the monomer thermally generated radicals to consume the inhibitor concentration<sup>20</sup>

$$t = \frac{[Z]}{k_o e^{-E/RT} \cdot [M]} \quad t = \frac{m[Z]}{k_o e^{-E/RT} \cdot [M]}$$

depending on whether one or more monomer radicals react with each molecule of inhibitor Z. This way not be the case if a polymerisation catalyst is present and if the inhibitor is eliminated first. Then the isothermal induction period is:

$$t = \frac{m[Z]}{k_o e^{-E/RT} \cdot [M] + k_{do} e^{-E_d/RT} [I]}$$

In this case, the polymerisation inhibitor is consumed by the monomer thermal generation of radicals and by the decomposition of the polymerisation initiator. Under moderate temperature where the polymerisation initiator is active and the thermal generation of monomer radicals negligible compared to that of the initiator, the above equation reduces to:

$$t = \frac{m[Z]}{k_{do} \cdot e^{-E_d/RT} [I]}$$

In this case, the polymerisation isothermal induction period is an Arrhenius function of the inhibitor and polymerisation initiator concentrations with an activation energy  $E_d$  characteristic of the polymerisation initiator.

This allows a much shorter polymerisation isothermal induction period than in commercial monomer storage. Consequently the probability of having a polymerisation incident in premix vessels or in recovered monomer storage vessels is much higher than in commercial monomer storage vessels and the polymerisation is faster or more violent. Therefore these process situations should be excluded where possible or carefully controlled.

## CONCLUSION

The accident case histories discussed in this paper as well as the consideration of two processes where well identified runaway reaction scenarios are known, emphasise the interest of a good understanding of process relevant chemistry.

An effort devoted to the study of the process relevant literature could certainly help to prevent such accidents. A special attention should be paid to possible or frequent process deviations such as the absence of agitation, abnormal residence time, cooling or cleaning fluid ingress to the process side.

The side reactions occurring in case of process deviation should be taken into account. Abnormal toxic products may be obtained together with increased reaction exotherm.

When an emergency relief vent is provided, based on a runaway reaction scenario, the design of a release containment system with sufficient capacity should be included in the project. Also, the revision of existing vents with consideration of possible runaway reaction scenarios should lead to the installation of release containment systems. The assessment of the release toxic properties should take into account possible side reactions and not only the normal synthesis reaction. This could influence the design and size of the release containment system.

The general conclusion that continuous processes are safer than semi-batch processes should be revised taking into account the Bhopal accident circumstances. An oversized continuous process producing toxic products may lead to very unsafe conditions due to the product or intermediate inventories. The reduction or elimination of toxic products inventories should be considered as a priority and should be taken into account in process design.

The care taken to the core process design should also be applied to more neglected operations such as reactant recycling, premix preparation, product storage facilities. Again, a good knowledge of the product properties and of the chemistry involved is necessary.

The use of high integrity safety interlocks should be preferred to manual operation, to prevent simple process deviations such as the absence of agitation, or control catalyst introduction in a reaction mixture.

The above conclusions are only a small part of the lessons learned from the study of these well-known accidents. They emphasise the interest of this activity to complement hazards studies based on risk assessment methods.

## LITERATURE

1. Grever Th., "Thermal Hazards of Chemical Reactions", Industrial Safety Series, vol. 4, 324-328, Elsevier.
2. Braun R., Schönbacher A., "Simulation von Semibatchprozessen am Beispiel einer komplexen chemischen Reaktion", Chemische Reaktionen, Erkennung und Beherrschung sicherheitstechnisch relevanter Zustände und Abläufe. Praxis der Sicherheitstechnik, vol. 4, 35 Tutzing-Symposium (1997), 157-169, Dechema e.V.
3. Bretherick, Handbook of Chemical Reactive Hazards, p. 680.

4. Ralph King, "Safety in the Process Industries", Butterworth Heinemann, 1990, 83-89.
5. V.C. Marshall, "Major Chemical Hazards", John Wiley and Sons, 1987, 356-369.
6. Wurtz A., "Mémoire sur les glycols ou alcools diatoniques". Ann. Chim. Phys., 3, 400 (1859).
7. Nef J. U., "Ueber das Verhalten der Glycole und des Glycerins gegen Aetzalkalien und gegen Oxydationsmittel", Annalen, 335, 310 (1904)
8. Fry H.S., Schulze E.L., "The liberation of hydrogen from carbon compounds. IV The interaction of glycol and glycerol with fused caustic alkalies", J. Am. Chem. Soc., 50, 1131 (1928).
9. P. Cardillo, A. Girelli, "Comportamento termico di miscele NaOH/glicol etilenico e NaOH/glicol dietilenico. La chimica e l'industria, 64, n° 12, 781 (1982).
10. Vennen H., "Störfälle in Serie ?", Hoechst im Dialog, 1993.
11. Klais O., Wörsdörfer U., Westphal F., "Griesheim runaway reaction – Thermochemical investigation" in "Safety and Runaway Reactions, Major accident Hazards Bureau, Joint Research Centre, European Commission, 1997, 23-30.
12. Klais O., Wörsdörfer U., "Ergebnisse der thermochemischen Untersuchungen zum Störfall im Werk Griesheim". Praxis der Sicherheitstechnik vol. 4, Dechema e.V., Frankfurt am Main, 1997, 41-81.
13. Klais O., Wörsdörfer U., Westphal F., "Thermochemische Untersuchung zum Störfall Griesheim", Chem. Ing. Tech. 66 (1994) n° 9, 1169-1170.
14. Sumitomo chemical Ltd, "Accident case histories of reactive materials" – case n° 36, 1973.
15. Kepplinger H.M., Hartung U., "Störfall – Fieber. Wie ein Unfall zum Schlüsselereignis einer Unfallserie wird", Alber-Broschur-Kommunikation. Verlag Karl Alber GmbH, Freiburg/München (1995).
16. TAABMU, "Technischer Ausschuss für Anlagensicherheit" "Leitfaden Erkennen und Beherrschen exothermer chemischer Reaktionen" TAA-GS-05, 12.04.1994.
17. The British Plastic Federation Thermosetting Material Group, "Guidelines for the Safe production of Phenolic Resins". British Plastic Federation, London, 1979.
18. Gustin J.L., Fillion J., Treand G., El Biyaali K., "The phenol + Formaldehyde runaway reaction, vent sizing for reactor protection". J. Loss Prev. Process Ind. 6 (2) 1993, 103-113.
19. Gustin J.L., "Choice of Runaway Reaction Scenarios for vent sizing based on pseudo-adiabatic calorimetric techniques". 1<sup>st</sup> Symposium on Runaway Reactions, Pressure Relief Design and Effluent Handling, March 11-13, 1998, New Orleans, Louisiana. A.I.Ch.E., New York. G.A. Melhem and H.G. Fischer editors.
20. Ham G.E., "Kinetics and Mechanisms of Polymerisations", Marcel Dekker Inc., New York, 1967.
21. Gustin J.L., "Understanding vinyl acetate polymerization accidents", I.Chem.E. Symposium Series n° 144, 387-403.

FIGURE 1

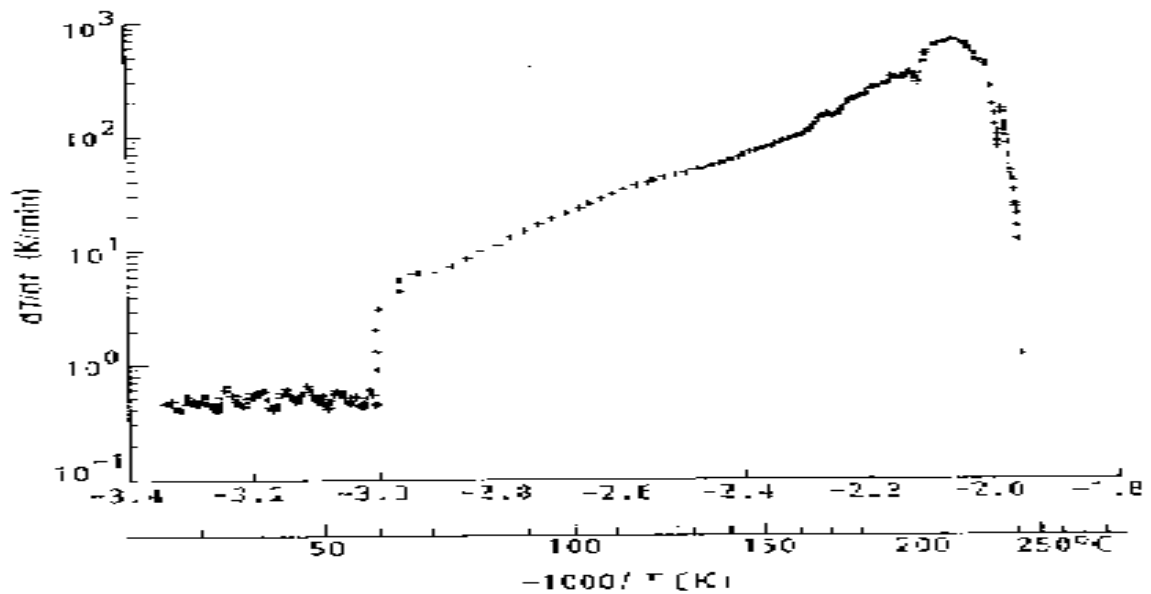


Figure 1: VSP test. Heat rate curve of the worst credible scenario Phenol + Formaldehyde runaway reaction as described.

FIGURE 2

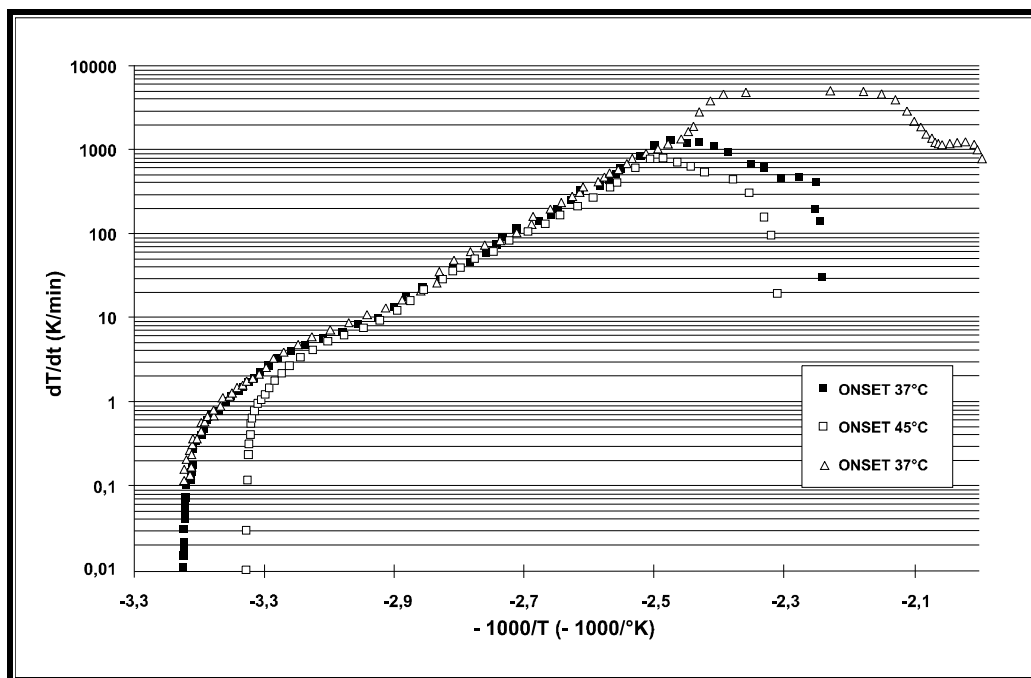


Figure 2: VSP closed cell experiment. Polymerisation of vinyl acetate monomers with 1.8 % w/w dilauroyl peroxide initiated by a constant temperature exposures at 37°C and 45°C. Heat rate curves.