Incident Title	Synthesis Reaction Temperature Runaway (Near Miss)	
Incident Type	Runaway Reaction	
Date	4th January 1992	
Country	UK (England)	
Location	Grimsby (Lincolnshire)	
Fatalities	**Injuries**	**Cost**
0	0	Unknown

Incident Description

Credit: IChemE Loss Prev. Bulletin 273

A plant producing chemical intermediates for manufacture of active drug ingredients experienced a runaway chemical reaction. The process involved synthesis of 2-chloro-6-nitrodiphenylamine by reacting dichloronitrobenzene (DCNB) with aniline ($C_6H_5NH_2$) in the presence of sodium carbonate (Na_2CO_3 or "soda"). This synthesis reaction is mildly exothermic with an adiabatic temperature rise of 25 °C (45 °F). The decomposition reaction has an adiabatic temperature rise of 938 °C (1720 °F). Aniline provides a layer of protection against decomposition as evaporation of the aniline removes the heat of reaction (boiling point of aniline is 184 °C or 363 °F at NTP).

The process is operated batchwise in a jacketed continuously stirred tank reactor (CSTR). The jacket is used for both heating and cooling (pressurised water/steam for heating, water for cooling). The reactor had a vertical glass riser vent pipe with a tee section. The vertical branch of the tee incorporated 2 busting discs (BDs) and a vent pipe discharging to atmosphere. The other branch carried reactor vapour to a condenser and receiver. After charging soda to the reactor from bulk storage, molten DCNB at 70 – 80 °C (158 – 176 °F) is added from bulk storage while stirring. The batch is then heated to ~ 150 °C (302 °F) and a light vacuum is drawn to enable unreacted aniline to distil off. The jacket is then turned off and the heat of reaction increases the temperature to the target 160 °C (320 °F) where it is held until completion.

On the night of the incident, the reactor temperature was climbing slowly and reached the upper limit of the temperature sensor range while the reactor was still at atmospheric pressure. The aniline had started to distil off by itself and quickly began boiling vigorously. The jacket was found to be operating at a higher pressure than normal but an attempt to depressure the jacket by opening the drain valve was aborted due to the deafening noise generated by the venting steam. Soon afterwards, the reaction mix was seen rising up the glass riser and a decision was taken to evacuate the building. Two bursting discs ruptured, releasing fumes and black particulate matter to atmosphere for around 20 minutes. Several joints on the glass riser failed relieving black, tar-like decomposed material to the floor of the reactor hall.

Incident Analysis

Basic cause was abnormally high synthesis reaction end temperature.

Critical factors included: 1) A historical 10% batch size increase resulted in a small rise in synthesis reaction end temperature, 2) Reactor temperature exceeded measurable range (prevented early warning of runaway).

Root causes included: 1) Inadequate process design (inadequate boiling barrier; no distillate reflux or quench system), 2) Inadequate thermometry (insufficient range), 3) Inadequate process control (no auto temperature control), 4) Inadequate management of change (batch size increase).

Lessons Learned

1) A boiling barrier is only sufficient if it can remove all the decomposition reaction energy and if the process can cope with the rate of boiling from the energy released, 2) Decomposition reaction severity can be estimated from energy potential (e.g. adiabatic temperature rise); probability can be estimated from maximum temperature of synthesis reaction (MTSR) and time required to reach maximum rate of decomposition at adiabatic conditions (TMR_{ad}).

More Information

1) "Historical Runaway Reaction Case Study (January 1992)", M. Rantell, IChemE Loss Prevention Bulletin 273 (2020).

Industry Sector	Process Type	Incident Type
Pharmaceutical	Active drug ingredients	Runaway Reaction
Equipment Category	**Equipment Class**	**Equipment Type**
Not equipment related	Not applicable	Not applicable

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