

## Excess Cooling Can Cause a Runaway Reaction

A process at a British dye factory required addition of nitrosyl sulfuric acid (NSA) to a 600-gal (~2.3-m<sup>3</sup>) batch reactor containing an amine and sulfuric acid at 30–40°C. The manual feed to the reactor typically took about five hours to complete, and the resulting reaction was exothermic. This process had been in operation for many years without a problem until, in 1996, the batch reactor exploded.

Initially, the batch was overheated to almost 50°C during NSA addition. The feed was stopped and the batch was cooled to 25°C (below the required temperature range). NSA addition resumed, and when complete, the batch temperature could not be controlled by the available cooling methods, exceeding the maximum temperature reportable by the temperature instrument. The runaway reaction overpressurized the reactor and it exploded. The explosion propelled the lower part of the reactor off its supports and onto the building floor. The reactor agitator landed on the roof, and the top of the reactor was thrown about 500 ft (150 m). Fortunately, no one was injured, but the accident cost the company £2 million.



▲ Runaway reactions at other process facilities in Jacksonville, FL (top), and Morganton, NC (bottom), also caused extensive damage.

### Did You Know?

- The rate of most exothermic reactions increases with temperature. If the reaction temperature is too low, the reaction will slow and unreacted material may accumulate. If the reaction temperature then increases, the unreacted material may react and potentially exceed the reactor cooling capacity.
- At high temperatures, chemical reactions other than those that are intended, including decomposition reactions, may become significant. These reactions may release more energy, and the reaction products may include gases that can increase the pressure inside the reactor.
- It is believed that approximately 30% unreacted NSA accumulated in the reactor during the time that the batch was too cold. Studies and simulations indicate that this accumulation might not have been sufficient to cause the runaway. However, the energy available from the unreacted NSA made the reactor more vulnerable to runaway. Another heat source, such as a steam leak to the reactor jacket, may have been sufficient to trigger the reaction.
- It is important to ensure that reaction systems are in good working order, since equipment leaks and other malfunctions can cause, or contribute to, incidents.

### What Can You Do?

- Know the effect of temperature on the rate of exothermic reactions, such as polymerization, nitration, sulfonation, acid-base, and oxidation reactions, to help prevent reactant accumulation and runaway reactions.
- Be aware that both the upper and lower temperature limits are critical for safety. In addition to reactants accumulating at low temperatures, liquids may freeze or become very thick and solids may precipitate out of solution.
- Understand the consequences of deviating from critical safety parameters, including temperature, pressure, flowrate, and mixing, and know what action to take if a deviation occurs.

Reference: Partington, S., and S. Waldram, "Runaway Reaction During Production of an Azo Dye Intermediate," *ICHEME Symposium Series*, No. 148, pp. 81–93 (2001).

**A process that is too cool may not be safe!**

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