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HOW TO PREVENT RUNAWAY REACTIONS

CASE STUDY: PHENOL-FORMALDEHYDE REACTION HAZARDS

CHEMICAL SAFETY
CASE STUDY

EPA is issuing this *Case Study* as part of its ongoing effort to protect human health and the environment by preventing chemical accidents. Under CERCLA, section 104(e) and the Clean Air Act (CAA), EPA has authority to conduct chemical accident investigations. EPA is striving to learn the causes and contributing factors associated with chemical accidents to prevent their recurrence. Major chemical accidents cannot be prevented solely through command and control regulatory requirements, but by understanding the fundamental root causes, widely disseminating the lessons learned, and integrating them into safe operations. EPA will publish *Case Studies* and *Alerts* to increase awareness of possible hazards. It is important that facilities, State Emergency Response commissions (SERCs), Local Emergency Planning Committees (LEPCs), emergency responders and others review this information and take appropriate steps to minimize risk.

PROBLEM: Many industrial chemical processes involve exothermic (heat generating) reactions. Uncontrolled, or runaway, reactions can occur as a result of various situations, such as mischarged raw materials, failure of a reactor's cooling system or the presence of contaminants. If the heat generation exceeds the reactor's ability to remove it, the reaction can accelerate - or run away - and cause the temperature and pressure to increase. A sudden energy release from such an uncontrolled reaction has the potential to harm workers, the public, and the environment. The following Case Study aims to increase awareness of possible hazards connected with exothermic reactions.

Columbus, Ohio
Sept. 10, 1997

At approximately 10:42 a.m. on Wednesday, Sept. 10, 1997, an explosion occurred in a resins production unit at Georgia-Pacific Resins, Inc. in Columbus, Ohio. The blast was reported to be felt at least 2 miles and possibly as far as 7 miles away according to various news accounts and other reports. As a result of the explosion, one worker was killed and four others injured. The explosion extensively damaged the plant. Local news reported that a vocational school and several homes and businesses within a 3/4-mile radius were evacuated as a precaution by the local fire department for several hours (*Dispatch*, September 11, 1997). The explosion also resulted in the release of a large quantity of liquid resin and smaller quantities of other chemicals within the facility. Three fire fighters were injured during the response, treated for first-degree chemical burns, and released.

Accident Investigation

Under a 1997 Memorandum of Understanding (MOU) to investigate chemical accidents and report on the lessons learned, EPA and the Occupational Safety and Health Administration (OSHA) collaborated to analyze the evidence. The purpose of this effort was to understand the circumstances associated with the accident to prevent a recurrence at this and other facilities.

Phenol-formaldehyde reactions are common industrial processes. The reaction of phenol or substituted phenol with an aldehyde, such as formaldehyde, in the presence of an acidic or basic catalyst is used to prepare phenolic resins. Phenolic resins are used in adhesives, coatings, and molding compounds. The type of catalyst used, the ratio of reactants, and the reaction conditions determine the molecular structure and physical properties of the resin produced. Typically, phenol-formaldehyde reactions are highly exothermic and sensitive to a variety of physical and chemical conditions. Once a reaction is initiated, heat generated by the reaction increases the reaction rate generating more heat. Because the reaction rate is typically an exponential function of temperature, the rate of heat generation will accelerate. Without intervention, a thermal runaway will occur, producing a large amount of heat in a very short time. Once the reaction begins to accelerate, the pressure of the system will typically increase suddenly due to gas production and/or the vigorous evaporation of liquid. If the reaction continues to accelerate, the pressure buildup may reach and exceed the ultimate strength of the reactor and cause it to explode.

Typically, phenolic resin batch processes are equipped with an agitator, heating/cooling jacket, a water-cooled condenser, and a vacuum system (Kirk-Othmer, p.614). The heat of reaction is removed by the evaporation of water or other liquid from the process, condensation of the liquid in the overhead condensation system, and return of the liquid to the reactor vessel. Emergency relief on the reactor is usually provided by rupture disks. In a conventional novalak process, molten phenol is placed into the reactor, followed by a precise amount of acid catalyst. The formaldehyde solution is then added. For safety reasons, slow continuous or stepwise addition of formaldehyde is preferred over adding the entire charge at once (Kirk-Othmer, p. 614).

The manufacture of phenolic resins has resulted in a number of accidents dating back to 1957. A search of accident databases and the literature reveals that numerous incidents have resulted in worker fatalities and injuries and significant property damage. **Table 1** is a summary of the incidents that have occurred during the past 10 years.

Table 1 Phenol-Formaldehyde Reaction Incidents at Various Companies

Date of incident	State	Description	Effects
September 10, 1997	OH	A 8,000 gallon reactor exploded during production of a phenol-formaldehyde resin.	1 worker fatality, 4 employees injured, 3 firefighters treated for chemical burns. Evacuation of residents for several hours.
August 18, 1994	OH	Pressure buildup during manufacture of phenolic resin, pressure increased, rupture disks popped. Product was released through emergency vent. The cause of accident was reported as failure to open condensate return line.	Residents evacuated for 5 hours.
February 29, 1992	GA	A 13,000 gallon reactor exploded during production of a phenol-formaldehyde resin. Explosion occurred during initial stages of catalyst addition.	4 employees injured, 1 seriously. 1 firefighter treated for chemical burns. Evacuation of 200 residents for 3 hours.
November 11, 1991	OH	Temperature increased in chemical reactor, releasing phenol formaldehyde resin.	None reported.
October 16, 1989	WI	Manufacture of phenolic resins and thermoset plastics; release of phenol and formaldehyde from process vessel.	None reported.
August 28, 1989	NY	Manufacture of phenolic resins; release of phenol and phenolic resin from process vessel; “operator error” cited as cause.	1 injured.
July 25, 1989	VA	Specialty paper manufacturing; release of phenolic resin and methanol from process vessel.	None reported.

Georgia-Pacific was manufacturing a phenolic resin in an 8,000-gallon batch reactor when the incident occurred. An operator charged raw materials and catalyst to the reactor and turned on steam to heat the contents. A high temperature alarm sounded and the operator turned off the steam. Shortly after, there was a large, highly energetic explosion that separated the top of the reactor from the shell. The top landed 400 feet away. The shell of the reactor split and unrolled, and impacted against other vessels. A nearby holding tank was destroyed and another reactor was partially damaged. The explosion killed the operator and left four other workers injured.

The investigation revealed that the reactor explosion was caused by excessive pressure generated by a runaway reaction. The runaway was triggered when, contrary to standard operating procedures, all the raw materials and catalyst were charged to the reactor at once followed by the addition of heat. Under the runaway conditions, heat generated exceeded the cooling capacity of the system and the pressure generated could not be vented through the emergency relief system causing the reactor to explode.

Lessons Learned

Controlling an exothermic reaction depends on the interaction among the kinetics and reaction chemistry; the plant equipment design; and the operating environment. Facilities must consider the following factors to better understand and address the potential hazards and consequences of reactive systems:

Thorough hazard assessment - The chemical and process hazards and the consequences of deviations must be thoroughly understood, evaluated, documented, and appropriately addressed through preventive measures. The adequacy of safety systems to prevent deviations must be carefully evaluated, including consideration of worst case situations. Several layers of safety systems, whether complementary or redundant should be considered to enhance reliability. One way that facilities can carry out this evaluation is to use formal process hazard analysis (PHA) techniques, such as what-if or fault tree analysis. The Center for Chemical Process Safety (CCPS) of the American Institute of Chemical Engineers (AIChE) has prepared guidance on PHA methodologies. (See CCPS, 1992)

Complete identification of reaction chemistry and thermochemistry - For some exothermic reactions, the time to runaway is very short. Overpressurization can occur when gas or vapor is produced as a byproduct of the reaction or any decomposition reactions. The kinetics of the runaway reaction will be reaction specific and may differ in various runaway situations. While general studies found in the literature can be useful for screening thermal hazards, the characteristics of the particular reactions must be determined experimentally. Experimental data should be used to define process boundaries in terms of the pressure, temperature, concentration, and other parameters as well as the consequences of operating outside of these boundaries.

Administrative controls- If administrative controls, such as training and standard operating procedures, are used as a safeguard against process deviation and accidental release, consideration must be given to human factors to ensure reliability, especially if an administrative control is the sole layer of protection. Humans make mistakes; the consequences of a human error should not lead to a catastrophic release. Processes, equipment and procedures must be designed with potential for human error in mind. For manual operations, preventive measures should be considered to minimize the likelihood of human error, for example, interlocks. SOP's must be understandable, periodically reviewed, and kept up-to-date. Employees must be trained on the SOP's and mechanisms set up to ensure that SOP's are followed at all times. The consequences of deviation from SOP's must be well understood by all employees.

Temperature control - The capability of the cooling system to remove the heat generated by the reaction is critical to the safe operation of an exothermic process. Facilities should evaluate capacity of cooling system with respect to controlling unexpected exotherms. Condensation cooling of reflux is commonly used to cool exothermic reactions that generate vapor as a byproduct, but has several limitations to control unexpected exotherms. Reflux cooling is limited until the reaction mass reaches the boiling point of the liquid and cannot control exotherms that begin while the reaction temperature is below the liquid's boiling point. As a runaway reaction proceeds, the increased generation rate of vapor increases the vapor velocity, the mass flow rate, and the inlet temperature in the overhead condenser. The increased heat load on the condenser results in only partial condensation and reflux of water.

Addition of raw materials - Frequently, the reaction rate is controlled by the addition rate of one reactant or the catalyst and should be determined based on chemistry studies. Facilities must pay attention to the order of ingredients, the addition rates, under- or over-charging, and loss of agitation.

Emergency relief - Runaway reactions may lead to the rapid generation of gas or water vapor. Under certain conditions, the vapor generation rate may be large enough to cause the vapor-liquid mixture to swell to the top of the vessel, resulting in two-phase flow in the relief venting system. Relief system capacity should be evaluated in conjunction with the hazard analysis to ensure that sizing is based on an appropriate worst case scenario.

Learning from accident history and near misses - Very few accidents occur without any warning. As Table 1 shows, a search of readily available sources found a number of incidents involving phenol-formaldehyde reactions. Accident history should be included in the information evaluated as part of the process hazard analysis. Additionally, many accidents are preceded by one or more near-miss incidents. Near misses should be analyzed to determine if operating procedures or other items need change.

Steps To Reduce Hazards

The consequences of a runaway reaction can be severe. Therefore, facilities must focus on prevention of conditions favorable to a reaction excursion through process design control, instrumentation, and interlocks to prevent recurrence of similar events.

Facilities should take the following steps to prevent runaway reactions:

Modify processes to improve inherent safety. Consider inherently safer processes to reduce reliance on administrative controls. (See CCPS, 1996)

Minimize the potential for human error. Anticipate possible human errors and carefully evaluate scenarios where an error could have catastrophic results. Managers should implement various protective measures, such as temperature control, instrumentation, and interlocks to eliminate opportunities for human error, especially in critical manual operations.

Understand events that may lead to an overpressure and eventually to vessel rupture.
Ensure that all chemical and process hazards and consequences are understood, evaluated, and appropriately addressed. Examine scenarios that include the failure of engineering and/or administrative controls. Evaluating these hazards may require detailed process hazard assessments. Use techniques and available information to minimize the chance of missing an important potential accident scenario.

Use lessons learned. Go beyond issues of quality control and operator error and identify true root causes. Learn from near misses and similar incidents and foster an environment where any deviation, no matter how small, is raised and addressed. Identify root causes and recommend changes to prevent recurrence. Share your expertise with all facilities in the corporate structure and share your experience through regular participation in safety forums sponsored by trade associations or professional organizations.

Evaluate SOPs. SOP's should include critical operating parameters and why they are important. Each numbered step in the SOP should include only one action. Evaluate SOP's and modify when necessary to minimize the likelihood of an undetected human error. Supervisors should audit SOPs regularly, including the direct observation of employees and conducting employee interviews to ensure the SOPs are fully understood. This information will help supervisors identify deviations from SOP's and will help supervisors recommend and ensure revision of SOPs.

Evaluate employee training and oversight. Ensure that operators are adequately trained and supervised before assignment to critical manual operations. Be aware that a limitation of on-the-job training is that trainees are prepared to handle only a limited number of problems, primarily those encountered before. To offset this limitation, trainees should work alongside an experienced operator and be supervised when using new procedures. Operator training can frequently be improved by showing operators how to respond to upset conditions or process deviations.

Evaluate measures to inhibit a runaway reaction. A runaway reaction, if caught early, can sometimes be halted by adding chemicals to cancel the effect of the catalyst. Common measures include neutralization, quenching with water or other diluent, or dumping the contents into another vessel which contains a quench liquid. Carefully select the inhibitor or quench material, determine the appropriate concentration and rate of addition of inhibitor and understand the inhibition reaction.

Evaluate the effectiveness of the emergency relief system. Proper vent sizing for potential runaway exothermic reactions is complex and requires data on the heat and pressure generation that may occur during a runaway. The most recent procedures used to calculate vent size were developed by the Design for Emergency Relief Systems (DIERS) program, a consortium of companies chartered by the American Institute of Chemical Engineers (AIChE). For certain reaction systems, the pressure rise due to a runaway may be so quick that the calculated vent size will be impractical and the only safety options are to prevent or inhibit a runaway reaction.

Related Statutes and Regulations

EPA

! General Duty Clause [Section 112(r) of the Clean Air Act (CAA)]- Facilities have a general duty to prevent and mitigate accidental releases of extremely hazardous substances.

! Risk Management Program (RMP) Rule [40 CFR 68]- Facilities with listed substances in quantities greater than the threshold planning quantity must develop a hazard assessment, a prevention program, and an emergency response program

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OSHA

! Process Safety Management (PSM) Standard [29 CFR 1910.119] - Facilities with listed substances at or above the threshold planning quantity are subject to a number of requirements for management of hazards, including performing a process hazards analysis and maintaining mechanical integrity of equipment.

Information Resources

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