

Learning from reactive chemistry incidents

The general lessons from an incident are often more important for preventing future occurrences than the details of what actually happened in that particular event. An incident is always a specific example of a more general category of potential incidents. If the investigation and follow up consider the more general lessons, you can prevent other similar events. Several specific reactive chemistry incidents will be discussed, with an emphasis on general lessons which can be applied to a broad range of processes.

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INTRODUCTION

In the past several years there has been a renewed focus on reactive chemistry incidents by the chemical industry, and from government and regulatory agencies. The US Environmental Protection Agency issued case studies related to runaway reactions¹ and reactive chemical explosions² in 1999 and 2000. The United States Chemical Safety and Hazard Investigation Board (CSB) issued a report³ describing the results of a study of reactive chemistry incidents. The Center for Chemical Process Safety (CCPS) has published an alert⁴ which introduces basic tools for understanding and managing reactive chemistry hazards, and a book with more extensive guidance for managing reactive chemical risks.⁵

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Understanding the causes of past reactive chemistry incidents is an important tool for preventing future incidents. The details of a particular incident are specific to the process and chemistry in which the incident occurred. However, all incidents provide general lessons which are useful for preventing future events, regardless of the technology and chemistry. This paper will review three reactive chemistry incidents, focusing on general lessons which are applicable to a wide range of processes and technologies:

1. An unexpected runaway reaction during decomposition of an organic peroxide dissolved in an organic solvent
2. A decomposition reaction while blending two organic compounds, a process in which no chemical reaction was intended
3. An uncontrolled release from a neutralization vessel caused by insufficient solvent during the reaction

We will also discuss tools which can be used to understand the potential for reactive chemistry incidents, and to avoid them in the future.

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INCIDENT 1—ORGANIC PEROXIDE DECOMPOSITION

Process Description

The plant equipment involved in this incident consisted of a batch solution polymerization reactor, which was protected by a rupture disk which discharged to a catch tank, and then to atmosphere, as shown in Figure 1.

The rupture disk was properly designed to protect the reactor from overpressure in case of a runaway polymerization reaction for the worst case of many polymer products which were manufactured in the reactor. The catch tank was a flat top vessel not rated for any pressure, which had been in place for a number of years. This catch tank had been identified as potentially inadequate, and an upgrade project was in the design stage at the time of the incident.

Incident Description

Because of an instrument failure, a batch of polymerization initiator, a dilute solution of 2-amyl-peroxy-2-ethylhexanoate (CAS 686-31-7) dissolved in a mixture of common solvents

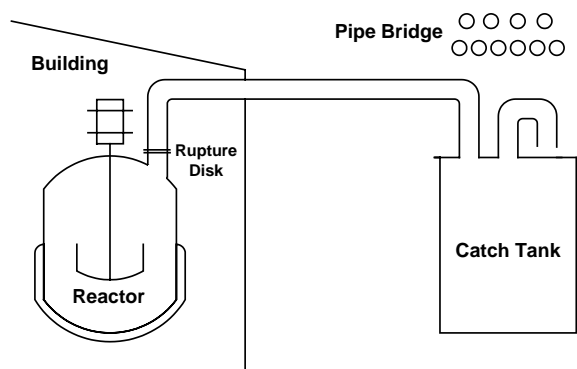


Figure 1. Polymerization reactor equipment layout.

including ketones and aromatic hydrocarbons, was improperly prepared. It was not possible to re-work the initiator solution so that it could be used for production. Because of the difficulty of disposing of the peroxide solution, the plant decided to use a laboratory procedure to decompose the peroxide in the solution, allowing the remaining solvent to be burned as normal waste solvent. The procedure was as follows:

- charge the off grade peroxide solution to the reactor
- add sufficient additional solvent so that the batch level reaches the agitator blades
- turn on the agitator and heat the batch to a specified temperature (~100 °C)
- hold for a specified time at that temperature
- cool and discharge the material for disposal as solvent waste

The temperature and time for the peroxide decomposition were determined by the laboratory based on the peroxide half-life to ensure complete decomposition of the peroxide. Supplier literature reported the half-life for 2-amyl-peroxy-2-ethylhexanoate as about 6 min at about 100 °C, although the half-life can vary depending on factors such as the solvent and concentration. This peroxide decomposition procedure had been used many times in the laboratory without incident. Unfortunately, the half-life of a peroxide only provides information about the rate of the decomposition reaction. To ensure a safe scale up of the decomposition “process,” additional information is needed, including:

- heat of reaction (decomposition)
- decomposition products (particularly non-condensable gases)
- maximum adiabatic temperature and pressure from the decomposition reaction

In the plant, the operators had difficulty in heating the batch—not surprising because it just barely reached the agitator blades and only a small portion of the reactor heating jacket was actually in contact with the small batch. The operators increased the heating, and the temperature began to rise more rapidly. As the batch temperature approached 90 °C, the operators reduced the heating, but the temperature continued to rise rapidly. Pressure was observed on the reactor pressure gage, and cooling was applied, but it had little effect—not much of the jacket area was exposed to the batch and available for cooling either. The batch temperature continued to rise, and pressure began to build up in the reactor. Eventually the pressure reached the rupture disk burst pressure of 135 psig, and the disk opened, discharging to the catch tank.

The rupture disk size was adequate to prevent overpressurization of the reactor, and there was no damage inside the building. However, this was by good luck, not by design. The rupture disk was sized based on a runaway polymerization reaction for a normal production batch, not for a peroxide decomposition reaction. Outside the building, the catch tank was overpressurized, and its top was blown off. The catch tank top was propelled into the pipe bridge above the tank, and it damaged or ruptured several

pipes in the pipe bridge. Fortunately, the spilled material was contained in a paved area. Some flammable materials were released, but did not ignite. The catch tank top did not hit anybody, and there were no injuries.

Causes

- *Inadequate understanding of reactive chemistry hazards.* The peroxide half-life provides some information about the rate of decomposition, but no information about the heat of reaction, the decomposition products, or the potential maximum temperature and pressure from the reaction.
- *Insufficient understanding of the effects of scale up on the behavior of the reaction.* This decomposition had been carried out numerous times in the laboratory on a small scale with no problem. But this is not an indication that the reaction can be done safely on a large scale. The relatively large heat removal capability, and even heat leakage to the surrounding environment, allows a reaction to be controlled in the laboratory when it is not possible to control the same reaction in plant scale equipment.
- *This batch process contained all of the possible chemical reaction energy at the start of the reaction.* The process depended on control of the batch temperature to limit the rate of reaction. Once that temperature control was lost, the runaway could not be prevented. A better process would have been to gradually add the peroxide solution to a reactor containing hot solvent, at a temperature high enough that the peroxide would have decomposed immediately. If there were any problems with temperature or pressure control, the feed of peroxide solution could be stopped, and there is no potential chemical reaction energy present in the batch.
- *Inadequate catch tank design.* While the catch tank had been recognized as inadequate, it was not recognized that it could fail as badly as it did when the incident occurred. A new catch tank was designed using current methodologies as developed by DIERS (Design Institute for Emergency Relief Systems).

- *Other causes not directly related to reactive chemistry hazards.* This unusual operation was not captured by the plant Management of Change (MOC) process, because the MOC system was directed toward normal production changes. Also, there were no detailed operating instructions for this operation.

General Lessons

- Treat all chemical reaction processes the same, whether they are part of the main production process or not. Make sure that Management of Change procedures, process hazard analysis programs, and operating instructions cover all reaction processes.
- Understand the maximum adiabatic temperature and pressure of all reaction processes, and make sure vessel pressure relief systems (including all equipment downstream of the emergency relief device) are adequate.
- Good experience in the laboratory does not mean that a reaction can be safely run on a large scale. You must understand the reaction kinetics and thermodynamics, and the heat removal capabilities of the plant reactor.
- Gradual addition, or “semi-batch” processes are usually preferable to batch reactions for exothermic reactions, or reactions which produce gaseous products. Gradual addition to a reactor, at a temperature high enough to ensure immediate or rapid reaction, limits the available chemical energy in the reactor if something

goes wrong. If the process deviates from intended conditions, the feed of the limiting reactant can be stopped, and the reaction will stop because the reactor contains little or no unreacted material.

INCIDENT 2—DECOMPOSITION DURING A BLENDING OPERATION

Process Description

The process involved in this incident required mixing two compounds and heating them in a mixing vessel to make a solution. The exact chemicals involved in the incident are not relevant to the major lesson—that reactive chemistry incidents are possible even when the process is a simple physical mixing operation with no intended chemical reaction. The mixing vessel was equipped for heating only, no cooling was available on the vessel jacket. The solution was normally fed from the mixing vessel to a heat exchanger for cooling and final product pack out, as shown in Figure 2a. No chemical reactions were intended in this process—the product was a physical mixture of the two components. This was an existing product and process that had been run twenty years without issue.

Incident Description

During the incident, the product was run in a new mixing vessel. In the new vessel, the mixture was heated to a temperature 35 °C higher than the mixing temperature in the old equipment. This was done so that the feed tempera-

ture where the solution entered the downstream heat exchanger, which was further away, would be the same (Figure 2b). At the higher mixing temperature an unexpected reaction occurred, generated an exotherm, and blew the rupture disk on the vessel.

The rupture disk was designed for a fire case (material vapor pressure and boiling), not an exothermic reaction. Fortunately, the rupture disk was large enough to prevent overpressure from the decomposition reaction, and the vessel did not rupture. The discharged material was carried up to 0.7 km away from the plant, and deposited on plant buildings, neighboring buildings, and a soccer field (which, fortunately, was not being used at the time).

Incident Causes

The reaction was caused by the decomposition of the two organic raw materials in the vessel. The manufacturer’s Material Safety Data Sheet (MSDS) for one of the materials indicated that decomposition of the compound could occur above 180 °C. Although a Management of Change process was followed before running the product on the new equipment, decomposition or side reactions of the materials were not considered an issue because the process temperature was significantly below the decomposition temperature.

After the incident, the reaction was reproduced in a laboratory using retained samples of the same raw materials. An Accelerated Rate Calorimetry (ARC) test was run to determine the decomposition temperature of the mixture. The more reactive of the two raw

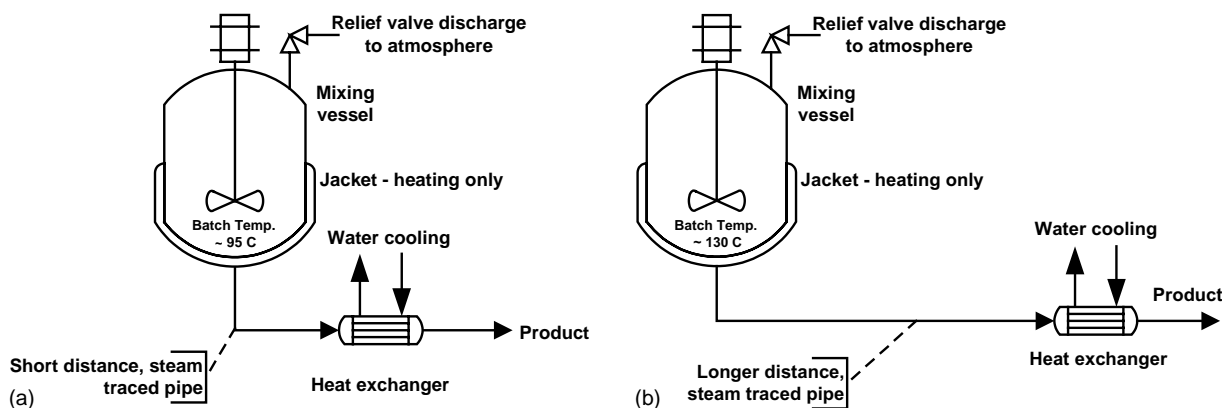


Figure 2. (a) Original mixing vessel configuration, (b) modified mixing vessel configuration.

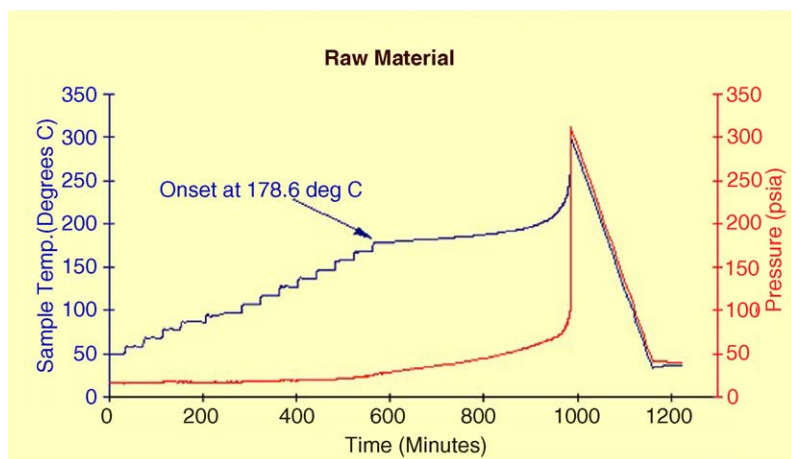


Figure 3. ARC test results for the more reactive component of the mixture.

materials was also run separately in the ARC test. The pure component decomposition temperature was about the same as the temperature indicated in the vendor's MSDS—the vendor's information was accurate with respect to the decomposition temperature (Figure 3). However, the mixture of components underwent a reaction at a temperature of about 130 °C, or 50 °C less than the decomposition temperature of the more reactive component (Figure 4). The solution was less stable than either of the pure components.

General Lessons

When considering decomposition reactions, a mixture may react or decompose at a lower temperature than any of the pure components. Stability mea-

surements on the actual solution provide the best information for determining a safe operating temperature.

Reactive chemistry incidents can occur even when there is no intentional chemistry in the process. This process was a simple physical blending operation, no chemical reaction was intended.

INCIDENT 3—VESSEL OVERPRESSURIZED DURING NEUTRALIZATION

Process Description

The process involved dissolving solid sodium hydroxide (NaOH) in deionized water, followed by neutralization with a strong aqueous acid to

form the desired product. In this case, the acid was methane sulfonic acid, but a similar incident could have occurred during neutralization of any strong acid with a base. The neutralization reaction occurred in a plastic vessel with a loose fitting top and no relief system. It was not rated for pressure and had no temperature control.

Incident Description

A power failure delayed production for several days and shut down the deionized (DI) water unit. When production resumed, there was urgent demand for product due to the unscheduled downtime, and DI water was not available to dilute the NaOH. The production team decided to add pure, undiluted NaOH directly to the vessel containing the aqueous acid. They thought that DI water would be available later, and the product could be diluted after the neutralization was complete. A sudden, severe exothermic reaction occurred, boiling the mixture and the vapors overpressurized and cracked the mixing vessel. The operators were sprayed with the released solution. Minor injuries were incurred, but everyone involved was able to return to work the same day.

Incident Causes

The more severe exothermic reaction was a direct result of not diluting the NaOH with DI water. The production team failed to recognize the potential

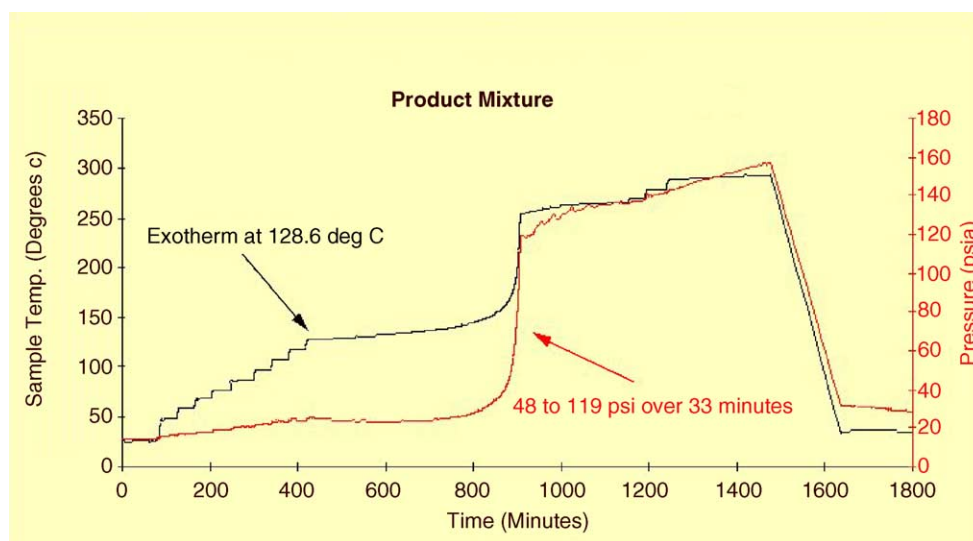


Figure 4. ARC test results for the two component mixture.

hazard of the exothermic reaction with smaller quantities of water present. Not knowing the reaction thermodynamics, their decision to proceed without DI water eliminated part of the heat sink for the heat of reaction and mixing. The heat of neutralization and mixing of the acid and base was sufficient to raise the mixture temperature above its boiling point without the additional dilution water present.

Additionally, there was no Management of Change (MOC) process carried out. The production team did not follow standard operating procedure (SOP) when they charged undiluted NaOH to the vessel. Also, the operators were not wearing the appropriate Personal Protective Equipment (PPE).

General Lessons

- Make sure that personnel at ALL levels have an awareness of the potential reactive chemical hazards. This includes the chemists, engineers, operators, shift foremen and production supervisors, and anybody else involved with operations.
- Know the heat of reaction and the maximum adiabatic temperature for any reaction or exothermic dilution process.
- Recognize the impact of changes in concentration on maximum adiabatic temperature.
- If the presence of a diluent or solvent is critical to maintaining temperature control in an exothermic reaction process, consider using one or more of the reactants already dissolved in the diluent or solvent. In this case, aqueous NaOH is an inherently safer reactant, because dilution with DI water is not necessary. Using aqueous reactant eliminates the dilution step and would have avoided this incident.
- Do not compromise process safety or quality to meet short term production demands, or demands for increased productivity. This culture must exist at all levels in the organization. In this incident, the operators were trying to do a good job—the customer wanted the product quickly and they thought they knew how they could satisfy the need. They did not understand the impact

that their deviation from the SOP would have on the batch temperature, and they did not seek advice or approval from technical management.

- Strictly follow the SOP at all times. If changes are needed, conduct MOC reviews, develop modified procedures, and train personnel on the new procedure. Consult with the appropriate expertise about these process changes—make sure that the participants in the MOC review have the necessary knowledge to understand the potential hazards.
- Protect vessel integrity with a properly designed overpressure relief system.
- Wear proper PPE at all times during the process.

HOW CAN REACTIVE CHEMISTRY INCIDENTS SUCH AS THESE BE AVOIDED?

There are a number of available tools and resources which can help to avoid reactive chemistry incidents such as those described.

Review of Material Safety Data Sheets

A key follow up action in Incident 2 was to review all raw material combinations for other undesirable reactive situations. In order to quickly narrow down the hundreds of raw material mixtures used in the plant, we reviewed the “Stability and Reactivity” section of each vendor’s MSDS. In particular, we were looking for chemical incompatibilities with other categories of materials (such as acids, bases, oxidizing agents, reducing agents, and other material types) which might be present in formulations using the material being reviewed, or which might come into contact with the material through use of shared equipment or nearby storage. Decomposition temperatures, if reported in the MSDS, were compared to maximum temperatures attainable in storage or processing. In addition, the review of chemical mixtures by knowledgeable chemists who could identify potential reactions was critical—remember that the individual material MSD Sheets for the materials involved in the incident did not suggest a reactivity pro-

blem. Using this information, the original group of raw materials could be reduced to a smaller set of materials and mixtures with potential reactivity hazards, which received a more detailed review and testing.

Other information was used to determine whether undesired reactions were possible with the reduced set of raw materials. Raw material vendors were contacted to determine whether stability testing of their material had been performed. Processes and equipment which used the reactive materials were reviewed, to determine likelihood of a reaction. In situations where no information existed, stability testing of the raw material or raw material mixture was performed to determine decomposition temperature of the compound or mixture. By analyzing the raw materials using existing information we avoided the time and expense of testing hundreds of mixture combinations in the laboratory.

“Suspect” Chemical Structures

Many chemical structures are known to be particularly energetic or reactive. Certain functional groups indicate instability or a tendency to polymerize. For example, many chemicals with strained rings, double bonds, or heterogeneous ring structures are known to be unstable or reactive. Figure 5 lists some examples of highly reactive functional groups. This table is not a complete list of unstable or reactive functional groups and should only be used as an example of the types of materials which should be subject to additional review. Processes using materials with energetic structures should be thoroughly evaluated for potential reactivity hazards, even if there is no chemical reaction intended in the process.

Literature Resources, Hazard Analysis Tools, and Computer Tools

There are many published resources and tools to help in understanding and managing chemical reactivity hazards. Some particularly useful sources are listed below.

- Center for Chemical Process Safety publications


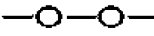


Reactive Chemical Structure Identification	
Any chemical with strained rings, double bonds, or heterogeneous ring structures in addition to the following:	
$C \equiv C$	$N = N$
$-N^*$	$-O^*$
$-NO_x$	$N=O$
$-N_3$	$-O_3$
	$C = N$
	CN_2
	
* Potentially unstable unless attached to C or H	
** N-sided rings potentially unstable unless N = 6	
*** Heterogeneous ring structures - those containing elements other than carbon	

Figure 5. Some potentially unstable or reactive chemical structures (compiled based on information in References 6,8,10,11).

- o *Safety Alert: Reactive Material Hazards*⁴ (2001)
- o *Guidelines for Safe Storage and Handling of Reactive Materials*⁶ (1995)
- o *Guidelines for Chemical Reactivity Evaluation and Application to Process Design*⁷ (1995)
- o *Essential Practices for Managing Chemical Reactivity Hazards*⁵ (2003)
- *Bretherick's Handbook of Reactive Chemical Hazards*⁸ (1999)
- *Chemical Reactivity Worksheet*,⁹ U.S. National Oceanic and Atmospheric Administration, <http://response.restoration.noaa.gov/chemaids/react.html>
- United Kingdom Health and Safety Executive, *Designing and Operating*

*Safe Chemical Reaction Processes*¹⁰ (2000)

- Barton and Rogers, *Chemical Reaction Hazards: A Guide to Safety*¹¹ (1997)
- Descriptions and examples on the application of process hazard analysis (PHA) tools such as HAZOP, interaction matrices, and checklists to reactive chemistry hazard management.^{12,13}

Hazard Awareness

The three incidents detailed in this paper all could have been prevented with knowledge of the chemistry, process, and the potential hazards. So who is responsible for knowing these aspects of production? Everybody, from office management to engineers,

chemists, and plant operators. Different levels of understanding, however, are required at each level.

- *Managers* must implement safety programs to maintain awareness or chemical reactivity hazards, including everybody involved in manufacturing—engineers, chemists, and operators. They must maintain a safety culture which includes rigorously following written operating procedures and management of change of any deviations.
- *Engineers and chemists* are responsible for the chemistry and process understanding. They must look for suspect chemical structures, and train operators to report any unexpected reaction behavior, such as temperature and pressure excursions. They must review the reactivity and incompatibility sections of all MSD Sheets to confirm that they are handling the material correctly. If still unsure, they should solicit the material's thermal stability data from the manufacturer and confirm the process conditions will not cause reactivity issues, or conduct appropriate calorimetry testing to obtain the needed information.
- *Operators and other production personnel* should know the steps to maintain control of the reaction and the consequences of losing control of the reaction. Operators must follow written procedures without deviation, and be aware of the hazards of the materials they are using. If the process involves reactive materials or operations, operators should feel free to question handling procedures and seek safety information from the engineers and chemists. They must report any unusual behavior of the process, particularly regarding temperature and pressure control.

To summarize, safeguard procedures must be coordinated for all potential hazards and open communication between all levels of the organization is crucial to the safety and success of production. *Reactive chemistry hazard management is everybody's business.*

SUMMARY

Incidents which have occurred in the past are an important source of the knowledge required to prevent future incidents. In this paper, we have shared three reactive chemistry incidents, and, more importantly, the general lessons from them which can be applied to many chemical processing operations. We have also shared some tools and techniques which we have used to avoid this kind of incident in the future. We hope that this information will be helpful to others in preventing reactive chemistry events, and encourage others to also share incidents in an effort to improve the overall safety of the chemical industry.

Acknowledgements

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without which we would not have been able to share the lessons learned.

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