Pilot Plant Reactive Chemistry Incidents: Case Studies and Prevention

Dennis C. Hendershot[*]
Albert I. Ness

Rohm and Haas Company
Engineering Division
Croydon, PA, USA

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ABSTRACT

Reactive chemistry incidents in manufacturing plants have received a lot of attention from industry, government, and the public in recent years, following a number of serious incidents and a major study by the United States Chemical Safety and Hazard Investigation Board. But reactive chemistry incidents can also occur in the laboratory and in pilot plant facilities. Several reactive chemistry incidents which occurred in pilot plants will be reviewed. In these examples, the chemical reaction which occurred was not anticipated by the people managing and operating the pilot plant. But, the reactions were not unknown, and they could have been anticipated with the aid of readily available process safety tools. Reactivity hazard awareness and recognition was a major contributor to these incidents, and education of process development and pilot plant operating personnel on these hazards can reduce their likelihood of occurrence. It is also essential to recognize these hazards as early in process development as possible so that the appropriate hazard management systems can be developed for the commercial process and plant. Tools, checklists, and resources for recognizing and managing reactive chemical hazards, applicable at all scales of operation, will be reviewed.

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[*] Corresponding author, Rohm and Haas Company, retired, 534 Norris Drive, Furlong, PA 18925, dchendershot@member.aiche.org

I. Introduction

Reactive chemistry incidents continue to occur in industry throughout the world, and these incidents have resulted in increased attention to reactive chemistry issues by industry, government, and other stakeholders. In the United States, the Environmental Protection Agency issued case studies related to runaway reactions[1] and reactive chemical explosions[2] in 1999 and 2000. The United States Chemical Safety and Hazard Investigation Board (CSB) recently issued a report[3] describing the results of its study of reactive chemistry incidents. In October 2001, the Center for Chemical Process Safety (CCPS) published a Reactive Chemistry Alert[4] which introduces some basic tools for understanding and managing reactive chemistry hazards. In 2003, CCPS published *Essential Practices for Managing Chemical Reactivity Hazards*[5], which provides more extensive guidance for managing reactive chemical risks.

Good process safety management systems, including consideration of reactive chemistry issues and the handling and storage of individual reactive chemicals, are important to operating a safe chemical process. In many cases, reactive chemistry hazards are not thoroughly considered in a process safety management program because the process does not involve any intentional chemical reaction – it may consist only of blending or physical processing operations such as drying or distillation. However, the molecules are not aware of the intention of the plant designers and operators, and they will react, perhaps in a hazardous manner, if their chemical properties allow them to do so. This paper will describe three incidents where the chemical reaction which occurred was unexpected, or unexpectedly fast, and potentially hazardous.

To help prevent future reactive chemistry incidents, we will summarize some checklist questions to help develop procedures for safe operation of chemical processes from the viewpoint of potential hazards from intended or unintended chemical reactions. Consideration of these principles will aid in the development of inherently safer processes. The discussion will focus on the technical aspects of safety, rather than on process safety management systems, although we recognize that these management systems are also essential to reactive hazard management.

Reactive chemistry hazards can result from any chemical reaction with the potential to release heat and/or pressure in quantities too high to be absorbed or contained by the environment and equipment which holds the reacting mixture. It is important to distinguish between reactive chemicals and hazardous chemical reactions. The chemical substances in the process might not be considered to be reactive chemicals, but this does not mean that the process does not have reactivity hazards. Interactions of chemical substances may be more important for understanding process hazards than the reactivity of individual chemicals. Materials which are not considered to be “reactive chemicals” may give rise to significant reactivity hazards when they are mixed with other, incompatible materials.

II. Reactive chemistry incidents in laboratories and pilot plants

We will discuss four reactive chemistry case studies which occurred in the laboratory, pilot plant, or during the first scale up to a plant facility. While none of these incidents resulted in any injury, all had the potential to cause a serious injury. In all four cases, the chemical reaction which occurred was unexpected by the operators of the facility.

Incident 1 – Decomposition during a blending operation

Description

This incident occurred in a small manufacturing plant in the first batch of a modified process. The incident was originally described by Carpenter, et al.[6] The process mixed two compounds and heated them in a stirred tank to make a solution. The specific chemicals 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. However, it is important to note that the solvent was an organic material containing several chemical species with one or more carbon-carbon double bonds, and the other compound was a substituted aromatic material with energetic, oxygen containing substituent groups. For this simple mixing operation with no chemical reaction or heat of mixing, the mixing tank was provided with steam heating to heat the mixture to the required dissolution temperature, and no cooling. Following mixing, the solution was pumped to downstream operations through a heat exchanger which cooled it to a specified temperature (Figure 2a).

The plant was modified, and the product solution was manufactured in a new mixing vessel. The mixing temperature was 130ºC in the new mixing tank, compared to a typical temperature of about 95ºC in the original mixing tank. The higher temperature was implemented so that the feed temperature at the inlet of the downstream heat exchanger, which was further away, would be the same (Figure 2b). A management of change review was held, and the review team did not identify any potential hazards as a result of the higher operating temperature.

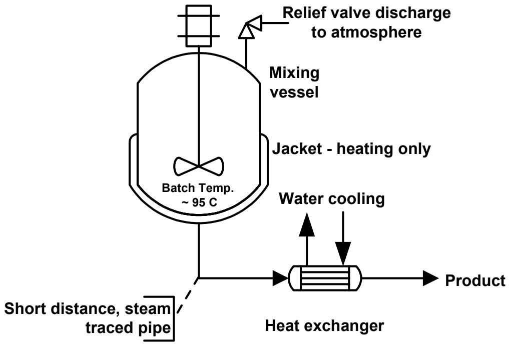

Figure 2a: Original mixing vessel configuration

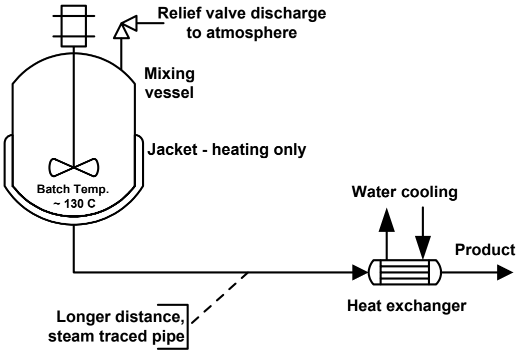

Figure 2b: Modified mixing vessel configuration

When the plant was started up, an unexpected exothermic decomposition reaction occurred at the higher operating temperature, and the resulting pressure burst the rupture disk on the vessel. The rupture disk was not designed for the unknown reaction, but fortunately it was large enough to prevent a vessel rupture, although there was some vessel damage and deformation. The effluent from the rupture disk was released to atmosphere and caused local, short term environmental damage, but there were no injuries.

Findings

The reaction was caused by the decomposition of the mixture of the materials in the vessel. The Material Safety Data Sheets (MSDS) for the two materials indicated that both were stable at the intended operating temperatures in both the new and old mixing tank. In fact, the less stable of the materials was stable up to a temperature of about 180ºC. Therefore, the management of change review did not anticipate a decomposition hazard from the increased temperature.

After the incident, the decomposition reaction was reproduced in a laboratory using retained samples of the raw materials. An Accelerated Rate Calorimetry (ARC) test was run to determine the decomposition temperature of the mixture. These tests revealed that the mixture of components decomposed exothermically at a temperature of about 130ºC, essentially the same as the intended operating temperature in the new equipment (Figure 3). The solution was less stable than either of the pure components. In fact, based on this information, the original operating temperature of 90ºC may be considered to be too close to the decomposition temperature of 130ºC, even though there had not been an incident in many years of operation.

Actions

In this case, manufacture of the solution was discontinued. However, if production were to be resumed, it would be necessary to re-evaluate the design of the mixing vessel. A lower operating normal operating temperature would likely be appropriate. A safe normal operating temperature could be determined by an evaluation of the thermodynamics and kinetics of the decomposition reaction, and evaluation of the heat generation and removal capabilities of the mixing vessel. High temperature alarms should be provided, and cooling capability for the vessel jacket should also be considered. Also, the vessel rupture disk should be evaluated to confirm that it is adequate for the runaway reaction under all operating conditions – while it was adequate for this particular batch, other credible vessel conditions (mixture composition, vessel fill level, etc.) should also be evaluated.

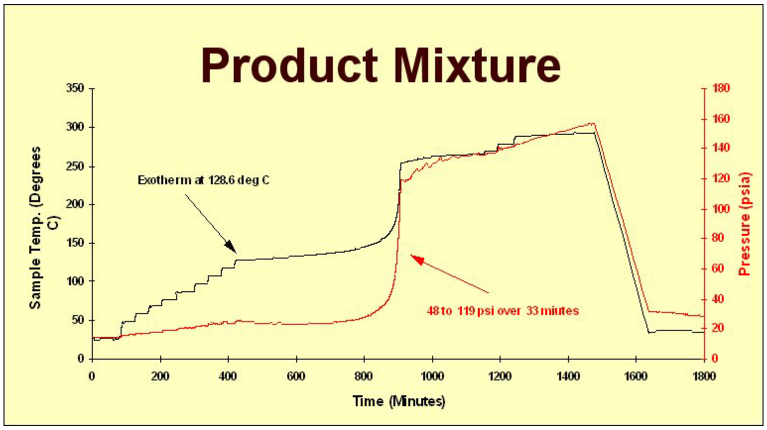

Figure 3: ARC test results for the Incident 2 solution

Also, the facility reviewed all other blending and mixing operations to identify other situations in which a similar type of incident might occur in a different process. Attention was focused on materials with energetic chemical structures, and also operations conducted at higher temperatures.

A number of mixtures were identified where it was possible that a similar incident could occur, thermal stability testing was conducted on these mixtures, and modifications to equipment and procedures were made where appropriate.

Comments

Remember that a mixture may react or decompose at a lower temperature than any of the pure components. Stability measurements on the actual solution provide the best information for determining a safe operating temperature. Also, 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. But, nobody told the molecules that they were not supposed to react, and they did what their chemistry told them to do. When dealing with mixtures of chemicals containing energetic structures (for example, double or triple bonds, nitro groups, peroxides, ethers, strained ring structures, heterogeneous ring structures, etc.), be aware that reactions and decompositions may occur in mixtures at lower temperatures than might be expected based on the stability characteristics of the pure materials. Thermal stability testing may be the only way to recognize stability problems in many cases.

Incident 2 – Unexpected reaction caused by overcharging a raw material

Description

This incident occurred in a batch pilot plant facility, in a 300 gallon general purpose batch reactor. The reaction was an intermediate step in a complex organic synthesis process. A substituted aromatic compound was being reacted with sodium hydroxide (to form a sodium salt form of the molecule) and another organic material. The intent was to charge one mole of sodium hydroxide per mole of reactant. During one batch, the charge of sodium hydroxide was inadvertently doubled. This is actually an easy mistake to make in a batch process. For example, an operator might charge the correct amount of material right before the shift change, and forget to write it down on the batch record. The operator on the next shift, seeing no record of the charge, might make the same charge again. In this case, the extra mole of sodium hydroxide per mole of reactant reacted with another substituent group on the molecule and formed a by-product which readily polymerized. When the batch was heated up for the expected reaction, the highly exothermic polymerization occurred, overpressurizing the reactor and bursting the reactor rupture disk. Fortunately the rupture disk was large enough to prevent a reactor rupture – primarily because the general purpose batch reactor was sometimes used for process development for some specialty acrylic monomers.

Discussion

In the post-incident investigation, it turned out that the side reaction with excess caustic was well known to the chemists working on the process. However, the information was not passed on to the pilot plant personnel. While this incident occurred many years ago, before process hazard analysis techniques such as Hazard and Operability (HAZOP) studies were in common use in the chemical industry. A HAZOP meeting, with both pilot plant engineers and process chemists present, would surely have identified the unexpected reaction from the HAZOP deviation "More sodium hydroxide". The engineers could then have provided additional safeguards to protect against excess sodium hydroxide (a simple batch test would show the presence of excess sodium hydroxide). Also, the thermodynamics and kinetics of the reaction could have been investigated so that the reactor emergency relief system could be properly sized for an uncontrolled runaway reaction if the safeguards failed. In fact, these actions were taken after the pilot plant incident, and no similar incidents occurred in the production facility.

This incident could also have been identified through use of a Chemistry Hazard Analysis – a procedure based on the application of the HAZOP guide words to the chemical reaction. This is much simpler than a complete HAZOP, and can be very useful at a research or pilot plant stage of process development. Simply write down the intended chemical reaction, and apply the HAZOP guide words (no, more, less, as well as, reverse, other) to the chemical reaction.

Incident 3 – Vapor phase reaction of an organic solvent with chlorine

Description

A batch pilot plant reactor was being used for process development of a chlorination process. An organic substrate was charged to the reactor containing solvent, and chlorine was gradually added to the batch to produce the chlorinated product. In the normal reaction process, the vapor space of the reactor contained little or no chlorine – the chlorine was rapidly consumed by reaction in the batch and the vapor space contained primarily HCl by-product from the reaction. In one batch, the organic substrate was left out because of an operating error, and chlorine was fed to the reactor which contained only the organic solvent. The solvent did not react rapidly with chlorine, and the reactor vapor space composition was primarily chlorine, with solvent vapor at a concentration determined by the solvent vapor pressure. The solvent concentration was such that it formed a reactive mixture in the vapor space – this is equivalent to a flammable vapor mixture of fuel in air or oxygen except that the oxidant is chlorine. The mixture was initiated and "burned", bursting the reactor rupture disk from the vapor phase reaction[7].

Discussion

Following the incident, the "combustion" of the organic solvent in a chlorine atmosphere was studied, and properties analogous to lower flammable limit, upper flammable limit, and ignition energy for a fuel in air were determined. Additional safeguards to confirm that the required reaction mixture was present in the reactor before beginning addition of chlorine were added.

Once again, this incident could have been prevented through the application of HAZOP or a Chemistry Hazard Analysis (CHA). The HAZOP or CHA guide word "no" would have lead the engineer and chemist to ask what would happen if no organic substrate was charged to the reactor. Knowledge of the chemistry would have identified the known fact that the solvent did not react rapidly with chlorine, and the result would be a mixture of solvent fuel in a chlorine oxidant in the reactor vapor space.

Incident 4 – Unexpectedly fast reaction in a laboratory reactor

Description

A laboratory reactor was being used for an oxidation process which required mixing of an organic material, hydrogen peroxide solution, and sodium hydroxide. In one batch, the sodium hydroxide was left out or significantly undercharged. At the lower pH, the oxidation reaction was much faster than under the normal conditions. The reaction was uncontrollable, and the laboratory reactor was overpressurized and ruptured. Fortunately, it was in a hood and nobody was injured.

Discussion

Subsequent laboratory calorimeter testing reproduced the uncontrolled oxidation reaction. In this case, the reaction was known, but the impact of pH on the rate of reaction was not known. The faster reaction at lower pH generated gas and heat much more rapidly than the laboratory reactor could remove it. Once again, this reaction might have been anticipated by a HAZOP or CHA – "no sodium hydroxide" or "less sodium hydroxide". The impact of pH on reaction rate was known to chemists in the facility, but not to the people running this laboratory reactor.

A common theme

There is a common root cause which is associated with all of the incidents described – a lack of awareness of the chemical reaction or decomposition hazard by those operating the laboratory, pilot plant, or plant facility. Other experts in the facility were aware of the hazard associated with the materials involved, or with similar materials. But this expert knowledge was not readily available to those operating the facility. There are a number of tools which can be used to help recognize potential chemical reactivity and decomposition hazards, and to identify process operations and conditions where unexpected or uncontrolled chemical reactions may present an important hazard. The remainder of this paper will discuss some of these tools and methods. The focus is on hazard recognition and process design rather than on thermal stability test methods and techniques. It should be recognized that there are a wide variety of chemical reaction hazard evaluation methodologies and tools available and described in the literature. The focus of this discussion is to help a process chemist or engineer to identify situations where there are potential reaction hazards, so that the appropriate analytical tools can be applied to understand the hazards and to develop appropriate hazard management systems.

III. Recognizing chemical reaction hazards

The Center for Chemical Process Safety (CCPS) has published an excellent book[5] on reactive chemistry hazards. A primary objective of this book is to provide tools to aid in determining if a chemical reactivity hazard is likely in a given chemical handling operation. A process is provided, consisting of a series of questions in a logic diagram format. If this logic process indicates that a reactivity hazard may be present, further investigation, and perhaps laboratory testing, may be required. The testing can confirm the potential hazard, assess its magnitude, and help to define appropriate risk management measures to be implemented. Table 1 is a checklist and logic diagram based on the CCPS methodology with some modifications based on the authors' experience which can be used to help answer the question “Is there a potential chemical reactivity hazard in my chemical handling operation?”

In addition to the CCPS logic process for identifying chemical reaction hazards, a series of questions may also be applied to a chemical process to determine if there are potential reactivity hazards. The following checklist, taken from Hendershot[8], provides some specific suggestions for consideration in understanding reactivity hazards.

1. **Know the heat of reaction for the intended and other potential chemical reactions.** There are a number of techniques for measuring or estimating heat of reaction, including various calorimeters, plant heat and energy balances for processes already in operation, analogy with similar chemistry (confirmed by a chemist who is familiar with the chemistry), literature resources, supplier contacts, and thermodynamic estimation techniques. You should identify all potential reactions that could occur in the reaction mixture and understand the heat of reaction of these reactions.

2. **Calculate the maximum adiabatic temperature for the reaction mixture**. Use the measured or estimated heat of reaction, assume no heat removal, and that 100% of the reactants actually react. Compare this temperature to the boiling point of the reaction mixture. If the maximum adiabatic reaction temperature exceeds the reaction mixture boiling point, the reaction is capable of generating pressure in a closed vessel and you will have to evaluate safeguards to prevent uncontrolled reaction and consider the need for emergency pressure relief systems.

3. **Determine the stability of all individual components of the reaction mixture at the maximum adiabatic reaction temperature.** This might be done through literature searching, supplier contacts, or experimentation. Note that this does not ensure the stability of the reaction mixture because it does not account for any reaction among components, or decomposition promoted by combinations of components. It will tell you if any of the individual components of the reaction mixture can decompose at temperatures which are theoretically attainable. If any components can decompose at the maximum adiabatic reaction temperature, you will have to understand the nature of this decomposition and evaluate the need for safeguards including emergency pressure relief systems.

4. **Understand the stability of the reaction mixture at the maximum adiabatic reaction temperature**. Are there any chemical reactions, other than the intended reaction, which can occur at the maximum adiabatic reaction temperature? Consider possible decomposition reactions, particularly those which generate gaseous products. These are a particular concern because a small mass of reacting condensed liquid can generate a very large volume of gas from the reaction products, resulting in rapid pressure generation in a closed vessel. Again, if this is possible, you will have to understand how these reactions will impact the need for safeguards, including emergency pressure relief systems. Understanding the stability of a mixture of components may require laboratory testing.

5. **Determine the heat addition and heat removal capabilities of the pilot plant or production reactor.** Don’t forget to consider the reactor agitator as a source of energy – about 2550 Btu/hour/horsepower. Understand the impact of variation in conditions on heat transfer capability. Consider factors such as reactor fill level, agitation, fouling of in-

ternal and external heat transfer surfaces, variation in the temperature of heating and cooling media, variation in flow rate of heating and cooling fluids.

6. **Identify potential reaction contaminants.** In particular, consider possible contaminants which are ubiquitous in a plant environment, such as air, water, rust, oil and grease. Think about possible catalytic effects of trace metal ions such as sodium, calcium, and others commonly present in process water. These may also be left behind from cleaning operations, such as cleaning equipment with aqueous sodium hydroxide. Determine if these materials will catalyze any decomposition or other reactions, either at normal conditions or at the maximum adiabatic reaction temperature.

7. **Consider the impact of possible deviations from intended reactant charges and operating conditions.** For example, is a double charge of one of the reactants a possible deviation, and, if so, what is the impact? This kind of deviation might affect the chemistry which occurs in the reactor – for example, the excess material charged may react with the product of the intended reaction or with a reaction solvent. The resulting unanticipated chemical reactions could be energetic, generate gases, or produce unstable products. Consider the impact of loss of cooling, agitation, and temperature control, insufficient solvent or fluidizing media, and reverse flow into feed piping or storage tanks.

8. **Identify all heat sources connected to the reaction vessel and determine their maximum temperature.** Assume all control systems on the reactor heating systems fail to the maximum temperature. If this temperature is higher than the maximum adiabatic reaction temperature, review the stability and reactivity information with respect to the maximum temperature to which the reactor contents could be heated by the vessel heat sources.

9. **Determine the minimum temperature to which the reactor cooling sources could cool the reaction mixture.** Consider potential hazards resulting from too much cooling, such as freezing of reaction mixture components, fouling of heat transfer surfaces, increase in reaction mixture viscosity reducing mixing and heat transfer, precipitation of dissolved solids from the reaction mixture, and a reduced rate of reaction resulting in a hazardous accumulation of unreacted material.

10. **Consider the impact of higher temperature gradients in plant scale equipment compared to a laboratory or pilot plant reactor**. Agitation is almost certain to be less effective in a plant reactor, and the temperature of the reaction mixture near heat transfer surfaces may be higher (for systems being heated) or lower (for systems being cooled) than the bulk mixture temperature. For exothermic reactions, the temperature may also be higher near the point of introduction of reactants because of poor mixing and localized reaction at the point of reactant contact. The location of the reactor temperature sensor relative to the agitator, and to heating and cooling surfaces may impact its ability to provide good information about the actual average reactor temperature. These problems will be more severe for very viscous systems, or if the reaction mixture includes solids which can foul temperature measurement devices or heat transfer surfaces. Either a local high temperature or a local low temperature could cause a problem. A high temperature, for example, near a heating surface, could result in a different chemical reaction or decomposition at the higher temperature. A low temperature near a cooling coil could result in slower reaction and a buildup of unreacted material, increasing the potential chemical en-

ergy of reaction available in the reactor. If this material is subsequently reacted because of an increase in temperature or other change in reactor conditions, there is a possibility of an uncontrolled reaction due to the unexpectedly high quantity of unreacted material available.

11. **Understand the rate of all chemical reactions.** It is not necessary to develop complete kinetic models with rate constants and other details, but you should understand how fast reactants are consumed and generally how the rate of reaction increases with temperature. Thermal hazard calorimetry testing can provide useful kinetic data.

12. **Consider possible vapor phase reactions.** These might include combustion reactions, other vapor phase reactions such as the reaction of organic vapors with a chlorine atmosphere, and vapor phase decomposition of materials such as ethylene oxide or organic peroxide.

13. **Understand the hazards of the products of both intended and unintended reactions.** For example, does the intended reaction, or a possible unintended reaction, form viscous materials, solids, gases, corrosive products, highly toxic products, or materials which will swell or degrade gaskets, pipe linings, or other polymer components of a system? If you find an unexpected material in reaction equipment, determine what it is and what impact it might have on system hazards. For example, in an oxidation reactor, solids were known to be present, but nobody knew what they were. It turned out that the solids were pyrophoric, and they caused a fire in the reactor.

14. **Consider doing a Chemical Interaction Matrix and/or a Chemistry Hazard Analysis**. These techniques can be applied at any stage in the process life cycle, from early research through an operating plant[9]. They are intended to provide a systematic method to identify chemical interaction hazards and hazards resulting from deviations from intended operating conditions.

IV. Summary

We have shared several reactive chemistry incidents which have occurred in the laboratory, pilot plant, or on initial scale up to plant facilities. These incidents were the result of unanticipated chemical reactions. We have also provided a checklist of considerations to help in identifying potential reactive chemical hazards before an incident occurs, and to assist in obtaining the information required to safely manage those hazards. Like any checklists, these suggestions are based on the experience of the authors and their colleagues, are inevitably not complete, and cannot cover all possible hazards. Users should incorporate their own experience and background into any review of a chemical process to ensure a more complete understanding of the chemical reactivity hazards.

Table 1: Reactive Chemistry Hazard Identification Checklist
(Derived from the logic diagram in Johnson, Rudy, and Unwin (2003), page 32[5])

Question	Answer	Actions	Comments
1. From the MSD Sheets, are any of the materials which are used: • spontaneously combustible • peroxide forming • water reactive • oxidizers • self reactive (polymerize, decompose, etc.) • other specific reactivity hazards	Yes	• Handle individual materials in compliance with all requirements identified for the specific reactivity hazard. • Go to Question 2.	
	No	• Go to Question 2.	
2. Are any materials handled in ways which could result in contact with incompatible materials listed on the MSD Sheet (including common industrial contaminants such as rust, water, air, nitrogen, oil and grease, etc.)?	Yes	• There is a potential for a reactive chemistry incident in this process. The consequences of accidental contact with incompatible materials should be evaluated using a chemical interaction matrix (References 7 and 10). Potential incident scenarios should be identified and safeguards evaluated using an appropriate process hazard analysis (PHA) technique such as HAZOP. Layer of Protection Analysis (LOPA) may be an appropriate tool to evaluate the adequacy of safeguards. • Go to Question 3.	
	No	• Go to Question 3.	
3. Does the facility perform intentional chemistry (other than burning fuels such as natural gas or gasoline)?	Yes	• Go to Question 8.	
	No	• Go to Question 4.	
4. Does the facility mix or combine different substances?	Yes	• Go to Question 5.	
	No	• Go to Question 6.	
5. Does the mixing or combining operation generate any heat?	Yes	• Go to Question 8.	
	No	• Go to Question 6.	
6. Does the facility conduct any other physical processing operations which require the addition of energy, including agitation, distillation, grinding, heating, thawing, etc.?	Yes	• Go to Question 7.	

Table 1: Reactive Chemistry Hazard Identification Checklist
(Derived from the logic diagram in Johnson, Rudy, and Unwin (2003), page 32[5])

Question	Answer	Actions	Comments
	No	• A reactive chemistry incident is unlikely. Ensure that all materials are handled in accordance with applicable standards and procedures.	
7. Do these physical processing operations generate any heat, or require the addition of heat?	Yes	• Go to Question 10.	
	No	• A reactive chemistry incident is unlikely. Ensure that all materials are handled in accordance with applicable standards and procedures.	
8. What is the heat of reaction or the heat of mixing for the intended reaction or physical operation?		• Use the heat of reaction to answer Question 9.	
9. What is the maximum temperature which the process can reach if the heat of reaction or mixing is released with ***no cooling or heat loss***?		• Use result to answer Questions 11 and 12.	
10. What is the maximum temperature to which the materials can be heated from physical processing operations or external heat sources, ***assuming all temperature control systems fail***?		• Use result to answer Questions 11 and 12.	
11. Are all individual materials in the mixture stable at the higher of the temperatures identified in Questions 9 and 10?	Yes	• Go to Question 12.	
	No	• There is a potential for a reactive chemistry incident in this process. Potential incident scenarios should be identified and safeguards evaluated using an appropriate process hazard analysis (PHA) technique such as HAZOP. Layer of Protection Analysis (LOPA) may be an appropriate tool to evaluate the adequacy of safeguards. • Go to Question 12.	

Table 1: Reactive Chemistry Hazard Identification Checklist

(Derived from the logic diagram in Johnson, Rudy, and Unwin (2003), page 32[5])

Question	Answer	Actions	Comments
12. Is the mixture of components stable at the higher of the temperatures identified in Questions 9 and 10?	Yes	• Go to Question 13.	
	No	• There is a potential for a reactive chemistry incident in this process. Potential incident scenarios should be identified and safeguards evaluated using an appropriate process hazard analysis (PHA) technique such as HAZOP. Layer of Protection Analysis (LOPA) may be an appropriate tool to evaluate the adequacy of safeguards. • Go to Question 13	
13. What is the minimum temperature which can be reached in the processing equipment, assuming failure of all temperature control systems to minimum temperature (also consider low ambient temperatures in winter)?		• Use result to answer Question 14.	
14. If the process is cooled to the temperature identified in Question 13, can this cause any reactivity hazards (for example, freezing and segregation of polymerization inhibitors, loss of reaction with buildup of reactants, freezing or thickening and loss of mixing, freezing on heat transfer surfaces, etc.)?	Yes	• There is a potential for a reactive chemistry incident in this process. Potential incident scenarios should be identified and safeguards evaluated using an appropriate process hazard analysis (PHA) technique such as HAZOP. Layer of Protection Analysis (LOPA) may be an appropriate tool to evaluate the adequacy of safeguards. • Go to Question 15	
	No	• Go to Question 15	

Table 1: Reactive Chemistry Hazard Identification Checklist
(Derived from the logic diagram in Johnson, Rudy, and Unwin (2003), page 32[5])

Question	Answer	Actions	Comments
15. Can accidental variations in operating parameters (pressure, temperature, ratio of ingredients, concentration, etc.) result in an unexpected reaction?	Yes	• There is a potential for a reactive chemistry incident in this process. Potential incident scenarios should be identified and safeguards evaluated using an appropriate process hazard analysis (PHA) technique such as HAZOP. Layer of Protection Analysis (LOPA) may be an appropriate tool to evaluate the adequacy of safeguards.	
	No	• No additional action required.	
	Not sure	• Consider a Chemistry Hazard Analysis (Reference 10) to identify potential variations in operating conditions and understand their consequences.	

Notes:

- This checklist is derived from the "Preliminary Screening Method for Chemical Reactivity Hazards" described in Chapter 3 of Reference 5 (pages 31-64) and from Reference 9.

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