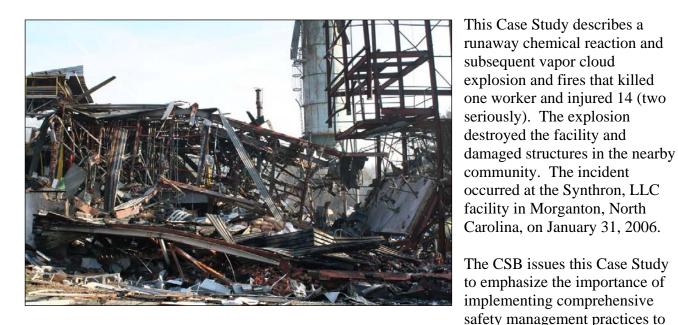
CASE STUDY



Runaway Chemical Reaction and Vapor Cloud Explosion

No. 2006-04-I-NC July 31, 2007

Worker Killed, 14 Injured



Synthron, LLC

Morganton, NC January 31, 2006

KEY ISSUES:

- Reactive Hazards and Safeguards
- Corporate Oversight
- Safe Operating Limits
- Evacuation Planning and Drills

INSIDE ...

control reactive hazards.

Incident Description Synthron Operations Incident Analysis Lessons Learned Recommendations References

1.0 Incident Summary

This incident occurred at Synthron, LLC's Morganton, North Carolina, facility. The company manufactured a variety of powder coating and paint additives by polymerizing acrylic monomers in a 1,500 gallon reactor.

The company had received an order for slightly more of an additive than the normal size recipe would produce. Plant managers scaled up the recipe to produce the required larger amount of polymer, and added all of the additional monomer needed into the initial charge to the reactor. This more than doubled the rate of energy release in the reactor, exceeding the cooling capacity of the reactor condenser and causing a runaway reaction.

The reactor pressure increased rapidly. Solvent vapors vented from the reactor's manway, forming a flammable cloud inside the building. The vapors found an ignition source, and the resulting explosion killed one worker and injured 14. The blast destroyed the facility (Figure 1) and damaged off-site structures.

The U.S. Chemical Safety Board (CSB) found that the reactor lacked basic safeguards to prevent, detect, and mitigate runaway reactions, and that essential safety management practices were not in place.

1.1 The Incident

The production department began preparing a 6,080 pound acrylic polymer batch the day before the incident, approximately 12 percent more material than would normally be made in a single batch. The plant superintendent determined the quantities of solvent, monomer, and initiator needed for the batch.¹ The day shift operators then blended the solvents and used some of the blend to prepare the initiator solution. They added the balance to the 1,500 gallon reactor. The second shift operators, in accordance with written instructions, added some of the monomer to the reactor and held back the remainder for use later in the reaction sequence.

The day shift arrived on the morning of January 31 and added steam to the reactor jacket (Figure 2) to heat the reactor to the temperature specified on the batch sheet, then shut off the steam.

The senior operator took the final step to start the reaction by pumping initiator solution into the reactor. He then visually checked the flow of condensed solvent through the condenser sight glass to monitor the rate of reaction. While the reaction initially did not proceed as vigorously as he expected, the condensed solvent flow later increased and appeared to be in the normal range.

Several minutes later, the senior operator heard a loud hissing and saw vapor venting from the reactor manway. The irritating vapor forced him out of the building.

Three other employees were also forced from the building by the release. Joined by the plant superintendent and the plant manager, the employees gathered outside an upper level doorway (Figure 3). The senior operator re-entered the building wearing a respirator, and was able to start emergency cooling water flow to the reactor jacket. However, the building exploded less than 30 seconds after he exited.

¹ Refer to section 2.2 for an explanation of the chemistry involved.



Photo courtesy of Morganton Department of Public Safety

Figure 1. Synthron facility after the explosion

The blast knocked down the personnel gathered outside the doorway. All were injured, and one required helicopter transport to hospital. Administrative personnel working in an onsite trailer also suffered minor injuries.

The maintenance supervisor was near the lab on the lower level when the explosion occurred (Figure 3). He was severely burned over most of his body and was transported by helicopter to a regional burn center, where he died five days later.

The blast damaged structures in the nearby community. Two church buildings and a house were condemned, and glass was broken up to one-third of a mile from the site. Two citizens driving by the site were slightly injured.

The Environmental Protection Agency (EPA) federalized the site under the CERCLA (Superfund) regulation, remediated the site and eventually razed the heavily damaged structures at Synthron's facility.

1.2 Community Emergency Response

The Morganton Department of Public Safety responded rapidly and called in mutual aid support from Burke County and nearby municipalities. Employees and Public Safety officers assisted injured employees.

The fires following the explosion generated thick smoke, and local residents were asked to shelter-in-place for several hours.² The fires were extinguished the next day.

² Shelter-in-place can protect people in emergencies by reducing their exposure to toxic substances. People should take refuge in a small interior room, close windows, seal openings, and shut off heating and air conditioning systems.

2.0 Synthron Operations

2.1 Company Overview

Protex International has owned a controlling interest in Synthron since 1972, and Protex' president is also president of Synthron. Protex, based in Paris, France, is a privately held company with over \$100 million a year in sales, and operations in Europe, Asia, and North and South America. In addition to the Synthron facility, Protex operates chemicalrelated businesses in Massachusetts, New Jersey, and Florida.

Synthron's single U.S. facility was located in Morganton, North Carolina, approximately 70 miles northwest of Charlotte. The 17 Morganton employees included the company's vice president, who was responsible for day-to-day operations. Synthron had 2004 sales of approximately \$3 million.

Following the explosion, Synthron, LLC filed for bankruptcy under Chapter 7 of the bankruptcy laws.

2.2 Reaction Overview

Synthron produced acrylic polymers,³ primarily additives for the powder coating and paint industries.⁴ The polymers were produced by the free-radical polymerization of acrylic monomers in various flammable solvents.⁵ Synthron converted many of its

liquid products into free-flowing powders by adsorbing them onto silica.

The product being manufactured on the day of the incident, Modarez MFP-BH, was a liquid acrylic polymer. It was produced using acrylic monomer purchased through a national chemical distributor. The batch was intended to fill an order for a major diversified chemical manufacturer.

Polymerization was performed in a 1,500 gallon reactor, rated at 75 psig maximum operating pressure and designated as reactor "M1" (Figure 2). The reactor was located in a manufacturing area adjacent to the warehouse (Figure 3).

In a typical reaction sequence, operators added a mixture of solvents and monomers to the reactor. They then injected steam into the reactor's jacket to heat the reaction mixture to a specified temperature, usually the expected mixture boiling point. The steam was turned off and initiator solution metered into the reactor to start polymerization.

The heat given off by the reaction boiled the solvent and monomer mixture, causing hot vapors to flow to an overhead water-cooled heat exchanger where they were totally condensed.

³ Acrylic polymers are produced from monomers based on acrylic acid or related esters, known as acrylates. Synthron used a variety of acrylic monomers to produce polymer resin additives for paint and powder coating manufacturers.

⁴ Powder coatings are mixtures of resins and pigments that are applied to goods, such as appliances, and then baked at high temperature to fuse the powder into a smooth polymer surface.

⁵ Free radical polymerization uses thermally unstable initiators, typically peroxides, persulfates, or azo

compounds, to promote controlled polymerization and obtain desired product properties. Manufacturers can customize product properties by selecting appropriate monomers and initiators and by controlling reaction conditions such as monomer concentration and temperature. Unlike catalysts, which promote reactions but are not consumed or modified by them, initiators are consumed in the polymerization reaction.

Liquid solvent drained from the bottom of the condenser back into the reactor.⁶ The outlet of the condenser vented to the atmosphere through a small pipe, keeping the pressure in the reactor very near atmospheric under normal operation. In an emergency, water could be manually directed through the reactor's jacket to increase cooling.

A complete manufacturing cycle could include several reaction steps. The finished liquid polymer was stripped of solvent, cooled, and packaged into drums for shipment to customers.

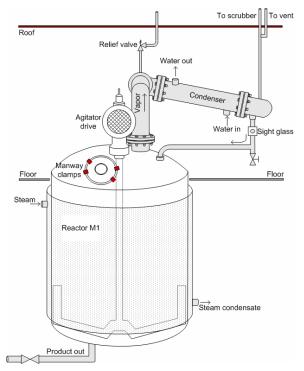


Figure 2. Reactor M1

3.0 Incident Analysis

The CSB investigators determined that the key factors leading to this incident included

- ➤ a lack of hazard recognition,
- poorly documented process safety information,
- ineffective control of product recipe changes,
- a lack of automatic safeguards to prevent or mitigate the effects of loss of control over the reaction,
- improper manway bolting practices,
- poor operator training,
- inadequate emergency plans drills, and
- inadequate corporate oversight of process safety.

3.1 Hazard Identification

When performing reactive chemistry, companies should maintain a high degree of awareness of the hazards involved. Synthron combined monomers and reaction initiators in the presence of flammable solvent to produce polymer products, but failed to identify the hazards associated with this type of chemistry.

Texts such as Loss Prevention in the Process Industries (Mannan, 2005) and Bretherick's Chemical Reaction Hazards (Urban, 2000) describe appropriate means characterizing industrial for chemical reactions. These include determining the heat generation rate as a function of temperature, the available heat removal capacity, and the potential for excessive monomer or initiator accumulation in the Failure to control these critical reactor. characteristics can lead to severe upsets, including runaway reactions.

Managers can detect hazards by asking "What can go wrong?" to identify the

⁶ Operators could monitor the condensed solvent flow, known as "reflux," through a sight glass (Figure 2).

potential consequences of inappropriate mixing, recipe changes, greater- and lowerthan-normal heating, lack of mixing, etc. The answers can be used to develop improvements or changes that can prevent reactive upsets or mitigate their consequences.

Synthron had not identified the hazards of its reactive chemical operations. No formal hazard review (also known as a process hazard analysis, or PHA) was conducted to address "What could go wrong?" during reactor operations.⁷

Furthermore, most of the management and operations personnel at Synthron had been on the job for less than a year, in some cases much less (Table 1), and lacked previous polymer manufacturing experience.⁸ In addition, Synthron's training program was informal and did not include reactive hazards training.

Employee	Time at Synthron	Polymer Experience?
Manager	9 months	No
Superintendent	8 months	No
Vice President	5 months	No
2 nd Shift Op-1	3 months	No
2 nd Shift Opt-2	3 months	No
Chemist	3 weeks	No

Table 1: Management and operations personnel tenure at Synthron

Personnel, including site managers, were thus poorly prepared to recognize potentially hazardous changes to product recipes, or to respond to an incipient runaway reaction.

Additionally, Synthron had no chemical or other engineers on staff, and none had been contracted to evaluate the hazards associated with reactive operations at the site.

3.2 Lack of Process Safety Information and Training

Synthron had minimal safety information on its polymerization process, even though this was the core of its manufacturing business. Synthron optimized product formulations to meet customer specifications. However, reaction characterization and calorimetry⁹ were not performed to establish process equipment performance requirements and operating limits for safe operations.

When scaling-up new products from the laboratory, the previous Synthron plant manager had typically estimated initial production batch sizes based on past experience. He then gradually increased batch quantities until the sight glass in the condensate return line showed that the condenser was close to flooding,¹⁰ or that another performance limit was being approached (e.g., the reactor pressure

⁷ Guidance on conducting hazard assessments is available from the Center for Chemical Process Safety (CCPS):, "Guidelines for Hazard Evaluation Procedures," 2nd ed., and other CCPS publications.

⁸ Synthron's president had replaced the management team in an attempt to increase sales. A variety of causes had simultaneously contributed to high operator turnover. The senior operator had been brought back from retirement to provide a degree of continuity.

⁹ Reaction calorimetry uses specialized instruments to measure heat flow from a laboratory-scale reacting mixture under controlled conditions. Calorimetry results can be extrapolated to full-scale processes.

¹⁰ Condensers flood when vapors condense faster than the liquid produced can flow back to the reactor. Liquid begins to fill the condenser, blocking off the heat transfer area. The resulting loss of cooling can result in a sharp increase in pressure and possible loss of reaction temperature control. The M1 condenser was located only slightly above the reactor, which made it prone to flooding.

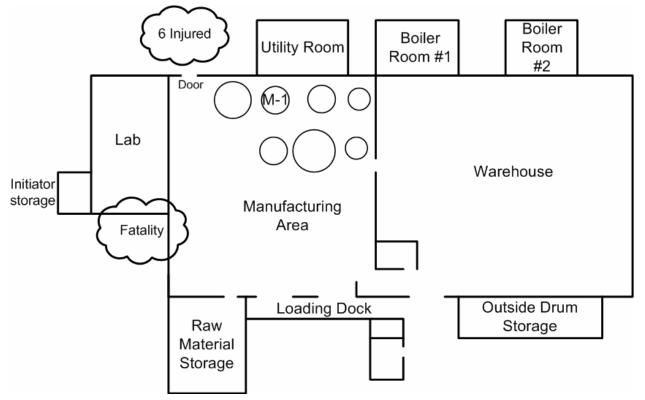


Figure 3. Synthron facility layout

increased). Polymerization scale-up to their standard batch sizes had historically been done by simple trial-and-error. The condenser's cooling capacity was not documented, nor could the cooling load placed on the condenser be determined with the available instrumentation. As a result, information essential to the safe operation of available. the reactor was not Polymerization reactors can runaway with disastrous consequences if they are not carefully controlled.¹¹

Based on interviews the CSB conducted, Synthron employees and managers had little or no understanding of reactive hazards. They had not been trained on,¹² and did not understand, the margin of safety needed or available in their polymerization operations. Furthermore, they had little knowledge of the sensitivity of the reactor to changes in product recipes, batch sizes, or reaction conditions.

Synthron's employees were thus unprepared to recognize and respond to the reactive hazards they faced the day of the incident.

3.3 Batch Recipe Changes

In planning the MFP-BH batch, Synthron managers made several changes that greatly increased the heat released by the reaction in reactor M1 and the potential for a runaway

¹¹ In a runaway reaction, the pressure, and thus the boiling temperature, in the reactor increases, further increasing the rate of reaction, and leading to higher pressures and heating rates.

¹² Synthron's training program was informal, relying on unstructured on-the-job training. Testimony indicated that reactive hazards were not systematically addressed.

reaction. However, the changes were not effectively reviewed and the hazards went unrecognized. Synthron:

- increased the total amount of monomer to be charged to the reactor by 12 percent. The additional monomer, with a Normal Boiling Point Temperature (NBPT¹³) of 147°C (297°F), was placed in the initial reactor charge.
- reduced the amount of aliphatic solvent, with an NBPT of 81°C (178°F), charged to the reactor by 12 percent.
- increased the amount of aromatic solvent, with an NBPT of 111°C (234°F), by 6 percent.

The customer had ordered 12 percent more MFP-BH than a standard batch would produce. To avoid the additional time and effort of running two half-size batches, the superintendent scaled up the recipe to produce the order in a single batch.

MFP-BH was produced in two stages. In the first, an initial charge of acrylic monomer and solvent was loaded into reactor M1, heated, and then reacted by adding an initiator over a brief period. In the second, the remaining monomer and initiator were co-fed into the reactor over an extended period. Unfortunately, the superintendent placed almost all of the additional monomer for the larger batch into the initial charge of chemicals loaded into the reactor.

According to the batch sheet, roughly equal amounts of aromatic and aliphatic solvent should have been added to the reactor. However, there was not enough of the lower boiling temperature aliphatic solvent available in storage. To compensate, the superintendent and manager decided to make up half the shortfall using the higher boiling aromatic solvent, and to run the batch with slightly less total solvent than specified in the recipe.

Together, these changes:

- increased the total amount of monomer in the reactor by 45 percent,
- increased the concentration of monomer by 27 percent, and
- increased the atmospheric boiling point temperature of the mixture by almost 5°C (9°F).¹⁴

Each of these changes would be expected to increase the rate of heat release in the reactor. When asked to review the changes in the solvent quantities, the plant chemist estimated that the boiling point of the solvent mixture would increase about 1° C (1.8° F). However, the chemist, manager, and superintendent did not recognize or address the potential impact of the increased monomer amount and concentration on the mixture boiling point, reaction rate, or total rate of heat release.

The combined effect of the changes was to increase the maximum heat output from the reaction to at least 2.3 times that of the standard recipe. Figure 4 illustrates the results of reaction calorimetry performed to simulate the early stages of the incident.

¹³ NBPT is the boiling temperature at 1 atmosphere absolute pressure.

¹⁴ The CSB measured the boiling points of laboratory mixtures with the same compositions.

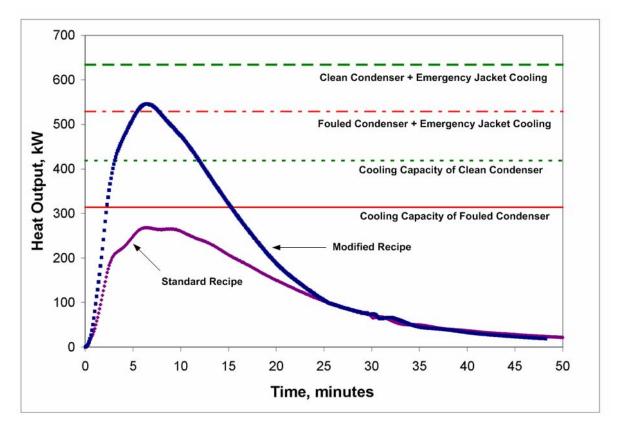


Figure 4. Reaction calorimetry heating curves for standard (lower) and modified (upper) recipes

The lower curve shows the heat release rate (thermal power) versus time for the standard recipe, while the upper curve shows the heat release rate for the modified recipe.¹⁵ The lower solid horizontal line is the estimated cooling capacity of the reactor condenser on the day of the incident (see section 3.6 for a discussion of condenser fouling). Once the heating curve exceeded the condenser cooling line, control of the reaction was lost, resulting in a runaway reaction.

3.4 Chemical Process Safeguards

The incident occurred before the second, continuous feed phase of the manufacturing process could begin.

Synthron relied primarily on a procedural safeguard to prevent loss of reactor control: the batch sheet, which was used as an operating procedure at the site. Procedures are essential for safety in chemical processing operation, but are the least reliable form of safeguard for preventing process incidents (CCPS, 2004).

Failures with potentially severe consequences, such as runaway reactions, should have multiple independent safeguards.

¹⁵ Each curve was generated isothermally at the NBPT of the mixture, closely simulating the operation of the reactor up to the time when control was lost. Heat generation rates during the subsequent runway reaction were higher.

Examples of safeguards that could have prevented or mitigated this incident, but were not installed at Synthron, include:

- high pressure alarms to notify operators of problems early in the incident when action to control the reaction might still be possible,
- automatic emergency cooling water flow to the reactor jacket,
- automatic shut-off of initiator feed,
- automatic or remotely operated injection of "short stop" solution to stop the polymerization reaction,¹⁶ and
- automatic or remotely operated venting or dumping of the reactor to a safe location.

Good practice is to review the adequacy of safeguards on chemical reactors using a structured method such as Layers of Protection Analysis (CCPS, 2001). Such reviews can help ensure that runaway reactions are prevented or are rapidly and reliably detected and controlled.

3.5 Manway Bolting Practice

Operators opened the reactor manway after every batch cycle to clean the reactor. Long-standing practice at the facility was to then close the manway and secure it using only four of the 18 clamps specified by the manufacturer (Figure 5).¹⁷ The risk posed by this practice had not been recognized because the reactor normally ran at nearatmospheric pressure, for which four clamps were thought to be adequate.

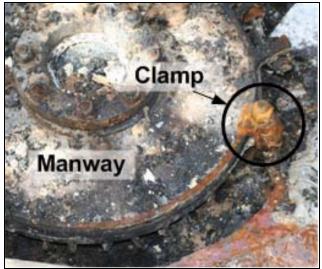


Photo courtesy of Morganton Department of Public Safety

Figure 5. One of four installed manway clamps

The CSB investigators calculated that, with only four clamps installed, the manway began to leak flammable solvent vapors when the reactor pressure reached approximately 23 psig, well below the reactor's maximum allowable working pressure (and likely relief valve set point) of 75 psig.¹⁸ The vapor leak path is clearly visible in Figure 6 (arrow).

¹⁶ Chemicals, such as phenothiazine, can be injected into a reactor to slow or stop free-radical polymerizations such as the reaction at Synthron.

¹⁷ The reactor manufacturer specified 18 clamps to maintain a tight seal at the reactor maximum working pressure of 75 psig. The clamps were not permanently attached to the manway, and no markings on the manway indicated the required number of clamps.

¹⁸ The reactor M1 relief valve could not be recovered from the debris, and the relief valve records were destroyed in the explosion and subsequent fires. Other relief valves examined were set at the rated operating pressure of the vessels they protected.



Figure 6. Damaged manway gasket, showing vapor release path

3.6 Process Equipment Fouling

Synthron failed to establish procedures to maintain the performance of the M1 condenser, an inclined shell-and-tube heat exchanger essential to safe operation of the reactor.

In the condenser, solvent vapors flow inside the tubes and are cooled and condensed by cooling water flowing through the shell (Figure 2). Inspection of the cooling water side of the condenser after the incident revealed that it was badly fouled, likely reducing condenser capacity at least 25 percent (Figure 7).

The condenser's design, with the tubes permanently bonded to plates at both ends of the condenser, made inspecting or cleaning the water side difficult.¹⁹ Furthermore, the

company had no program to systematically monitor and control water side fouling.²⁰ The CSB found no evidence that the water side of the condenser had ever been inspected or cleaned to remove the scale, rust, and sediment that had accumulated during 30 years of service. Synthron's employees lacked the expertise and experience to recognize the risk posed by water side fouling of the condenser.

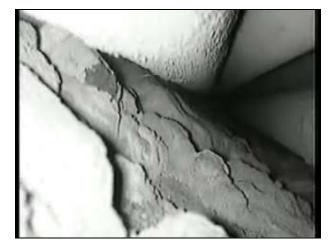


Figure 7. Deposits fouling the water side of the M1 reactor's condenser.

A clean condenser, combined with automatic emergency jacket cooling (Figure 4, upper dashed line), would likely have prevented the runaway reaction and subsequent explosion.

3.7 Emergency Evacuation Procedures and Training

Effective evacuation plans are important for minimizing injuries and fatalities in chemical emergencies.

During this incident, none of the production employees evacuated to a safe location. At the time of the explosion, six employees,

¹⁹ The condenser was a Tubular Exchanger Manufacturer's Association (TEMA) type BEM, fixed tubesheet exchanger with the process fluid on the tube side and cooling water on the shell side. The tubes could not be removed for inspection or cleaning. This design may require periodic chemical cleaning of the shell side to maintain good thermal performance.

²⁰ Chemical treatment of the cooling water is almost always required to prevent biological growth, fouling, and/or corrosion. The cooling water at Synthron was not treated.

including the manager and superintendent, gathered outside a doorway on the upper level while a seventh was on the lower level by the lab. The employee on the lower level was killed, while all the employees outside the doorway were injured, two seriously.

Synthron was unprepared for an emergency; specifically,

- The facility Emergency Action Plan did not list events or describe situations that might necessitate a plant evacuation.
- Operating procedure did not specify employees' actions in the event of a chemical release or loss of reactor control.
- Employees were not trained on the Emergency Action Plan and evacuation drills were not conducted.
- The facility was not equipped with an emergency alarm system.

In this incident, there was sufficient time after the release began to evacuate employees to a safe location. Adequate emergency response planning by Synthron could have prevented the death and serious injuries caused by the explosion.

3.8 Corporate Oversight

Synthron was part of Protex International, a much larger organization. However, the parent company provided little safety oversight or support to Synthron.

While Synthron performed quality control testing and limited product development work in Morganton, the procedures, equipment, and trained personnel needed to characterize reactive hazards were not in place.

However, Protex had the ability to perform detailed reaction characterization work,

including reaction calorimetry, at its European facilities. It is good practice (CCPS, 2003) to ensure that reactive safety programs at small facilities are adequately supported by technically qualified resources. Protex did not provide adequate reactive safety support to Synthron.

Furthermore, in the summer and fall of 2005. Synthron's president (also the president of Protex) hired a new vice president, plant manager, and plant superintendent for the Morganton site. While two of these key management employees had degrees in chemistry, they had no previous polymerization experience and were not trained on the parent company's process safety procedures or its testing capabilities. Having little reactive chemistry background or training, they did not recognize the reactive hazards at the Morganton site.

CCPS (1995) stresses that expertise in managing process safety must be ensured when making staffing changes. Synthron's president failed to ensure that the new team he installed at the Morganton site had the requisite training, knowledge, and experience to operate the facility safely.

Finally, Protex did not comprehensively audit or review Synthron's safety program. Such a review should have identified the absence of an effective reactive hazard control program.

4.0 Regulatory Analysis

Synthron had not implemented a Process Management Safety (PSM) system consistent with the requirements of the Occupational Safety and Health Administration's (OSHA) PSM regulation (29 CFR 1910.119).²¹ The site had last been inspected by North Carolina OSHA (NC-OSH) in 1996. No PSM citations were issued following that inspection. Following the explosion, NC-OSH proposed numerous PSM citations, which Synthron contested.

The batch being processed at the time of the explosion, had it been completed, would have contained in excess of the OSHA PSM threshold of 10,000 pounds of flammable liquid. However, only 4,500 pounds of material were in the reactor at the time of the incident, well below the PSM threshold quantity. Nonetheless, a catastrophic incident occurred. Synthron's experience demonstrates that companies working with reactive chemical quantities less than the PSM flammables' threshold still need to consider and guard against potentially catastrophic accidents.

5.0 The CSB Reactives Study

In its comprehensive 2002 report. "Improving Reactive Hazard Management" (CSB, 2002), the CSB found that reactive incidents are a serious problem in the United States, and that both management system and regulatory improvements are needed to help facilities control reactive hazards. This report studied reactive incidents, causal factors, and preventive measures,²² and outlined the screening, hazard identification, hazard review, operating procedures, and training needed to prevent reactive incidents.

The report documented 167 serious reactive incidents in the United States between January 1980 and June 2001 that resulted in 108 deaths, hundreds of injuries, and significant public impacts. Ongoing monitoring by the CSB indicates that reactive incidents, such as the Synthron explosion, continue to occur.

The CSB report also found that 70 percent of reactive incidents occurred in the chemical manufacturing industry, with 35 percent due to runaway reactions, such as that which occurred at Synthron.²³ While 42 percent of reactive incidents resulted in fires and explosions, another 37 percent caused toxic emissions. Many reactive incidents occurred at small manufacturing sites such as Synthron.

More than 50 percent of the 167 incidents documented in the CSB report involved chemicals not covered by existing OSHA PSM (29 CFR 1910.119) or EPA Risk Management Program (40 CFR Part 68) regulations. The CSB recommended better

²¹ OSHA Process Safety Management regulation, 29 CFR 1910.119, is a performance-based processsafety regulation requiring manufacturers to implement certain management practices on processes containing greater than threshold quantities of toxic or flammable chemicals.

²² Available for download at <u>http://www.csb.gov</u>.

²³ Of reactive incidents, 25 percent originate in reactors, with the rest occurring in a wide range of equipment.

coverage of reactive hazards by these regulations. EPA now requires reporting of reactive chemical incidents under RMP reporting rules. OSHA has taken steps to increase industry awareness of reactive hazards, but has not fully implemented the CSB recommendations.

The CSB report identified many valuable sources of good practices for managing reactive hazards. Since the report's publication, additional guidance has become available. The Center for Chemical Process Safety (CCPS) published *Essential Practices for Managing Chemical Reactivity Hazards* (CCPS, 2003), which can be downloaded at no cost from <u>http://info.knovel.com/ccps/</u> (January 2007). This book lays out the basic steps manufacturers should take to protect against reactive hazards.

Other valuable sources of guidance are available. The EPA's Chemical Emergency Preparedness and Prevention web page <u>http://yosemite.epa.gov/oswer/ceppoweb.nsf</u> /content/ap-book.htm (May 2007) contains useful links. The United Kingdom's Health and Safety Executive also offers an informative web page, <u>http://www.hse.gov.uk/pubns/indg254.htm</u> (May 2007) and the comprehensive booklet, "Designing and Operating Safe Chemical Reaction Processes" (HSE Books, 2000).

6.0 Lessons Learned

This incident provides important lessons for manufacturers with operations involving reactive chemistry.

6.1 Identify and Control Reactive Hazards

Manufacturers should take a comprehensive approach, and:

- identify and characterize reactive hazards;
- systematically evaluate what can go wrong, including mis-charging of reagents, loss of cooling, instrument malfunction, and other credible failure scenarios; and
- implement, document, and maintain adequate safeguards against the identified failure scenarios. Multiple, independent safeguards may be needed to reliably ensure the safety of the reactive process.

6.2 Control Change

Chemical manufacturers and others with reactive chemistry operations should control changes to batch recipes, including key operating conditions, such as:

- the quantities, proportions, and sequencing of reactor feeds,
- reaction temperature,
- conditions that could cause initiator or monomer accumulation, and
- conditions that could affect the deactivation of monomer inhibitors or stabilizers.

6.3 Maintain Process Equipment Capability

Manufacturers with reactive chemistry operations should:

- document the performance requirements and capabilities of process equipment, such as the reactor condenser at Synthron; and
- periodically inspect and service process equipment, including the water side of heat exchangers, to maintain appropriate safety margins.

6.4 Train Personnel on Hazards and Procedures

Manufacturers should ensure that worker training includes:

- the nature of the reactive hazards, including process safety margins; and
- operating procedures, \geq including appropriate cautions and warnings, the consequences of deviations, recognition deviations of and abnormal operations, and the appropriate responses to control or mitigate their effects.

6.5 Prepare for Emergencies

Manufacturers should:

- implement an effective emergency plan,
- train employees on the plan,
- install an evacuation alarm system that is audible and/or visible throughout the facility,
- conduct regular exercises to help ensure rapid evacuation to a safe location in an emergency, and
- coordinate their emergency planning with offsite response organizations

and the Local Emergency Planning Committee (LEPC).

7.0 Recommendation

Protex International 2006-04-I-NC-R1

Establish a program to ensure that reactive hazards at Protex' U.S. facilities are managed in accordance with good industry practices.

At a minimum, the program should:

- identify and characterize reactive hazards;
- implement, document, and maintain appropriate safeguards;
- manage changes to recipes;
- document and maintain safetycritical process equipment capabilities;
- train personnel on reactive hazards, safe operating limits, and the consequences of and responses to deviations;
- train personnel on emergency evacuation alarms and procedures, and conduct emergency drills; and,
- conduct periodic audits of program implementation to identify and address weaknesses.

8.0 References

Health and Safety Executive (HSE) [Online], 2007. Chemical Reaction Hazards and the Risk of Thermal Runaway, <u>www.hse.gov.uk/pubns/indg254.htm</u>, London, UK: HSE.

HSE. Designing and Operating Safe Chemical Reaction Processes, Rugby, UK: HSE Books, 2000.

Center for Chemical Process Safety (CCPS). *Guidelines for Hazard Evaluation Procedures - With Worked Examples*, 2nd ed, New York: American Institute of Chemical Engineers (AIChE), 1992.

CCPS. Plant Guidelines for Technical Management of Chemical Process Safety (Revised Edition), New York: AIChE, 1995.

CCPS. Layer of Protection Analysis - Simplified Process Risk Assessment, New York: AIChE, 2001.

CCPS. Essential Practices for Managing Chemical Reactivity Hazards, New York: AIChE, 2003.

CCPS. Inherently Safer Chemical Processes, A Life Cycle Approach, New York: AIChE, 2004.

Mannan, S., *Lees' Loss Prevention in the Process Industries*, 3rd ed., Burlington, MA: Elsevier Butterworth-Heinemann, 2005.

Urban, P. G., Ed. *Bretherick's Handbook of Reactive Chemical Hazards*, 6th ed., St. Louis, MO: Elsevier Science and Technology Books, 2000.

The United States Chemical Safety and Hazard Investigation Board (CSB). *Improving Reactive Hazard Management*, Washington, DC: CSB, 2002.

The U.S. Chemical Safety and Hazard Investigation Board (CSB) is an independent Federal agency whose mission is to ensure the safety of workers, the public, and the environment by investigating and preventing chemical incidents. The CSB is a scientific investigative organization; it is not an enforcement or regulatory body. Established by the Clean Air Act Amendments of 1990, the CSB is responsible for determining the root and contributing causes of accidents, issuing safety recommendations, studying chemical safety issues, and evaluating the effectiveness of other government agencies involved in chemical safety.

No part of the conclusions, findings, or recommendations of the CSB relating to any chemical accident may be admitted as evidence or used in any action or suit for damages. See 42 U.S.C. § 7412(r)(6)(G). The CSB makes public its actions and decisions through investigation reports, summary reports, safety bulletins, safety recommendations, case studies, incident digests, special technical publications, and statistical reviews. More information about the CSB is available at www.csb.gov.

CSB publications can be downloaded at www.csb.gov or obtained by contacting:

U.S. Chemical Safety and Hazard Investigation Board Office of Congressional, Public, and Board Affairs 2175 K Street NW, Suite 400 Washington, DC 20037-1848

(202) 261-7600

