Case Study

U.S. CHEMICAL SAFETY AND HAZARD INVESTIGATION BOARD

FIRE AND EXPLOSION: HAZARDS OF BENZOYL PEROXIDE

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CATALYST SYSTEMS, INC.
Gnadenhutten, Ohio
January 2, 2003

INSIDE . . .

KEY ISSUES:

- Hazards of Benzoyl Peroxide
- Reactive Chemical Hazards
- Process Safety Management Systems

Introduction

This Case Study describes a benzoyl peroxide (BPO) explosion and fire that occurred at the Catalyst Systems, Inc., production facility in Gnadenhutten, Ohio. At 11:55 am on January 2, 2003, a vacuum dryer holding nearly 200 pounds of BPO exploded. Employees were drying granular 75 percent BPO to make 98 percent BPO when the material explosively decomposed. One employee was slightly injured, and the BPO processing building was significantly damaged.

1.0 Benzoyl Peroxide Properties and Applications

Organic peroxides may be thermally unstable and sensitive to shock, impact, and friction. A peroxide is any compound with an oxygen-to-oxygen bond[1] (-O-O-) in its chemical structure. An organic peroxide has an organic (or carbon-containing) molecule attached to at least one side of the oxygen-to-oxygen bond.

The thermal instability of organic peroxides is caused by the weak oxygen-to-oxygen bond, leading to a tendency for spontaneous change toward more stable substances. Although their potential energy is low compared to that of conventional explosives, these compounds can be very destructive when stored energy is released. The degree of hazard is reduced by dilution, either in a suitable solvent or in water.

The National Fire Protection Association (NFPA)[2] divides organic peroxides and their solutions into hazard classes based on reactivity and destructive effects. Table 1 lists the NFPA hazard classifications for selected concentrations of BPO.

[1]The oxygen-to-oxygen bond is also referred to as a peroxy bond.

[2]NFPA Standard 432, *Code for the Storage of Organic Peroxide Formulations*, 2002.

BPO—also known as "dibenzoyl peroxide"—is represented by the chemical formula $(C_6H_5CO)_2O_2$. Its chemical structural formula shows the unstable oxygen-to-oxygen bond:

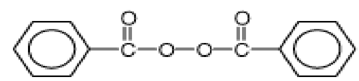

Table 2 lists the characteristic properties of BPO, which is available in several forms. Dry BPO is a granular solid and usually contains less than 5 percent water. Wet BPO is also a granular solid; common formulations contain between 66 to 85 percent BPO and 34 to 15 percent water. BPO pastes usually contain 50 percent BPO, with the remainder being water and some type of plasticizer.

Ninety-eight percent granular BPO is classified as a strong oxidizer susceptible to explosive decomposition[3] by excessive heat, friction, or sudden shock; NFPA lists it as a Class I organic peroxide. In contrast, 50 percent BPO paste is listed as a Class IV organic peroxide.

[3]Decomposition is a chemical reaction that leads to the breakdown of a chemical into smaller molecules or elements, often with liberation of energy and gases.

CSB Case Studies summarize incident investigation data and present conclusions based on CSB analyses. They do not discuss root and contributing causes or make safety recommendations—unlike the more comprehensive CSB Investigation Reports.

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Table 1

NFPA Peroxide Classifications

Peroxide Hazard Class	Characteristics	BPO Concentrations
I	Capable of deflagration but not detonation (a)	98% granular
II	Burns very rapidly, presents a moderate reactivity hazard	78% granular
III	Burns in the same manner as ordinary combustibles, presents a minimal reactivity hazard	75% granular
IV	Burns with less intensity than ordinary combustibles or does not sustain combustion, presents no reactivity hazard	50% paste

(a) A deflagration is a reaction that propagates at less than the speed of sound and, with confinement, can result in an explosion. By comparison, a detonation is a reaction that propagates at greater than the speed of sound and results in an explosion regardless of confinement. Detonations have a much greater destructive potential than deflagrations.

Table 2

Characteristic Properties of 98 Percent Granular BPO

Appearance	White rhombic crystalline solid
Stability	Becomes unstable and may spontaneously decompose if exposed to temperatures of 75 to 80 degrees Celsius (°C) for prolonged periods; decomposes explosively if subjected to friction or sudden shock
Decomposition products	Dense white smoke consisting of benzoic acid, phenyl benzoate, terphenyls, biphenyls, benzene, and carbon dioxide
Reactivity	Reacts violently with various organic and inorganic acids, amines, alcohols, metallic naphthanates, polymerization accelerators, and other chemicals that are easily oxidized

SOURCE: NIOSH, 1977.

What is a reactive incident?

A reactive incident is a sudden event involving an uncontrolled chemical reaction—with significant increases in temperature, pressure, or gas evolution—that has caused, or has the potential to cause, serious harm to people, property, or the environment. The January 2003 incident at Catalyst Systems was a reactive incident.

In September 2002, CSB completed its major hazard investigation, entitled *Improving Reactive Hazard Management*. This investigation concluded that better management of reactive hazards is necessary to prevent reactive incidents.

At Catalyst Systems, BPO is manufactured by reacting benzoyl chloride, sodium hydroxide, and hydrogen peroxide. Because the reactions between these chemicals are exothermic (i.e., generating heat), crushed ice is added for cooling. A centrifuge removes excess water to obtain the desired concentration, normally 50 to 78 percent BPO.

BPO is used in a number of industrial processes, particularly in manufacturing plastics. Some common applications are dental resin cement, automobile body putty, mine roof bolt systems, flour and cheese bleaches, acne medication, and silicone rubber and polyvinyl chloride (PVC) manufacturing.

2.0 Catalyst Systems Operations

Catalyst Systems is a wholly owned subsidiary of U.S. Chemical and Plastics, Inc., a privately owned corporation headquartered in Massillon, Ohio, which is a subsidiary company of Alco Industries. U.S. Chemical and Plastics formulates and manufactures repair, appearance, and maintenance products for the marine and aviation industries and the automobile aftermarket. These products include a variety of putties, fillers, waxes, compounds, paints, coatings, catalysts, and adhesives.

Twenty-five people are employed at the facility in Gnadenhutten, Ohio. A portion of this staff supports Catalyst Systems operations, while the remainder is dedicated to other activities of U.S. Chemicals and Plastics.

The plant site has two buildings (Figure 1). Building 1 contains offices, a quality control laboratory, a shop, storage areas, and a paste filling and packaging area. Building 2 was constructed in 1977 and is used solely for BPO production. It is divided into a manufacturing area and a paste room.

In the manufacturing area, raw materials are added to a reactor to produce 20 percent BPO—which is then sent through a centrifuge, where water is removed. The resulting product is 78 percent granular BPO. Some of this material is packaged in drums for sale or further processing. In the paste room, the 78 percent BPO, a plasticizer, water, pigments, and surfactants are mixed to create 50 percent BPO paste.

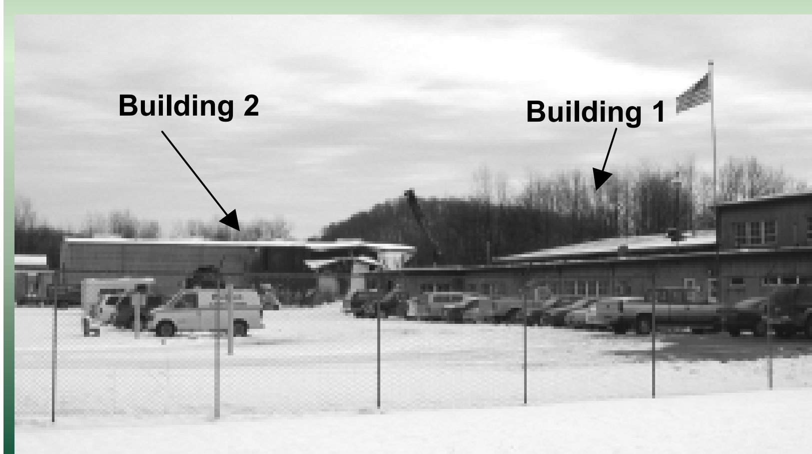
A 98 percent granular BPO product is also made in the paste room by drying batches of purchased 75 percent granular BPO using a spherical rotating vacuum dryer. The 98 percent product is packaged into 1-pound bags.

Catalyst Systems began producing 98 percent granular BPO 5 years ago for the rubber, marine, and printed circuit board industries. This product was initially manufactured by air-drying 75 or 78 percent BPO granular products in open metal pans in an oven over several days. Because the process

Catalyst Systems began producing 98 percent granular BPO 5 years ago for the rubber, marine, and printed circuit board industries.

Figure 1

Catalyst Systems, Inc., plant site



In June 2001, Catalyst Systems purchased a used double-cone vacuum dryer, which was jacketed and glass-lined.

was both time consuming and subject to quality problems (i.e., the metal pans rusted and contaminated the finished product), Catalyst Systems determined that vacuum drying was more economical and maintained the required quality control.[4]

In June 2001, Catalyst Systems purchased a used double-cone vacuum dryer, which was jacketed and glass-lined (Figure 2). Maintenance personnel installed the equipment and placed it in the northwest corner of the paste room (Figure 3).

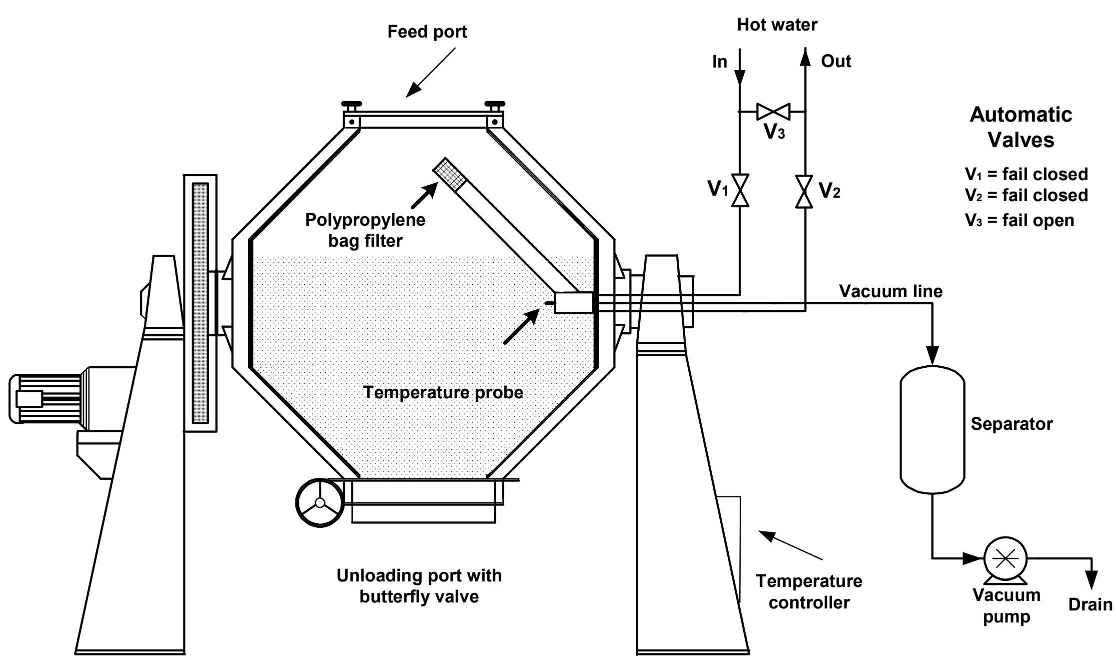
The vacuum dryer was loaded through a feed port with 200 pounds of 75 percent BPO. Hot water (approximately 82°C) was circulated through the dryer's jacket to indirectly heat the BPO. The dryer rotated slowly, causing the BPO to tumble and evenly heat, minimizing the production of hot spots.

The atmosphere in the dryer was placed under vacuum. As the BPO was heated, the vacuum system pulled air and water vapor from inside the dryer through a polypropylene bag filter, then a separator, and

[4]When a system is dried under vacuum, the temperature at which water evaporates is lower—which allows the material to be dried at a lower and usually safer temperature.

Figure 2

Catalyst Systems vacuum drying system
(8.7-ft^3 working capacity dryer and associated piping/equipment)



finally to a water suction vacuum pump.

Hot water from the building's heating system circulated through the dryer's jacket. As shown in Figure 2, there were three automatic valves in the hot water piping. When operating normally, valves V_1 and V_2 are open and V_3 is closed.

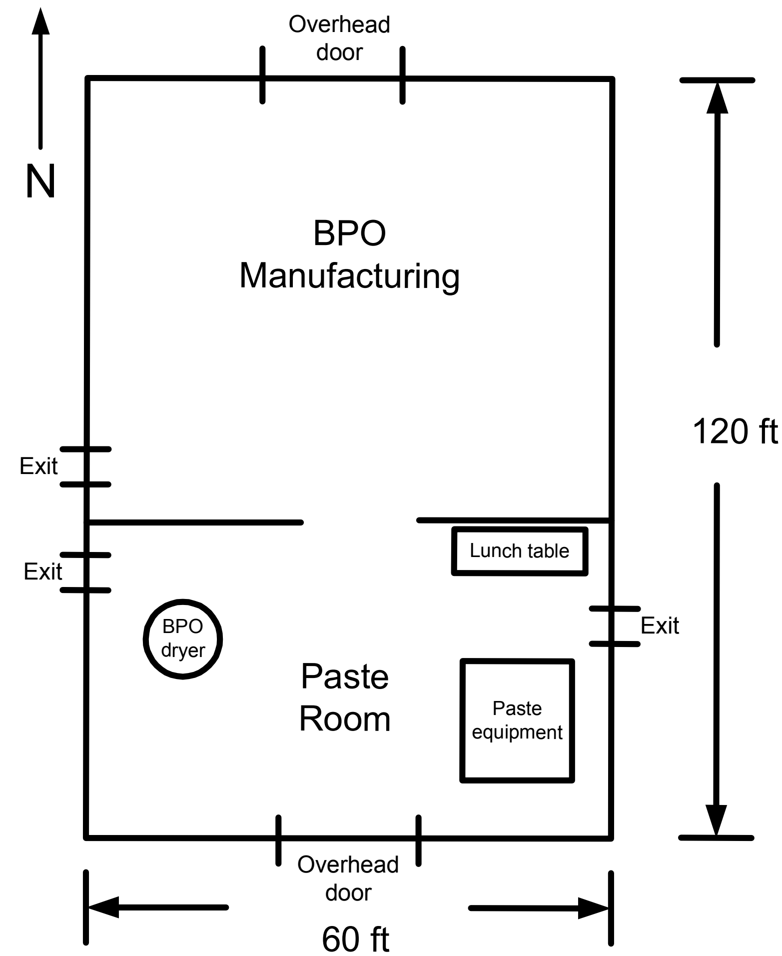
A temperature control system used a probe located inside the vacuum dryer to determine when to open and close the hot water valves. When the thermocouple reached 42°C,[5] the inlet and outlet valves on the jacket lines closed and the bypass line opened, which stopped hot water from circulating through the jacket.

A typical batch took 2 to 2.5 working days to dry from 75 to 98 percent BPO. The drying system was started in the morning and ran until about 2:00 pm, when the hot water was shut off; however, the dryer continued to rotate under vacuum until 3:30 pm, when the entire system was shut down for the evening. The same procedure was followed on the second day. On the morning of the third day, the cover was removed and a sample taken for analysis. If the concentration was at 98 percent, the dryer was unloaded; otherwise, the BPO was subjected to additional heating cycles.

[5]Employees interviewed stated that the temperature was 42°C. CSB was unable to independently verify this temperature because of damage following the explosion.

Figure 3

Building 2 layout



The 98 percent BPO was emptied through the bottom butterfly valve discharge opening into fiber drums. BPO from the drums was then packaged in 1-pound plastic bags—20 bags to a box—for shipping. The dryer was cleaned after every second batch by rinsing with water and allowing it to air-dry with the doors open.

Because it typically took 2.5 days to dry 75 percent material to 98 percent, operators anticipated that the batch would be ready after completing one drying cycle [on] the morning [of January 2].

At 11:55 am, the vacuum dryer suddenly exploded . . .

3.0 Incident Description

3.1 Pre-Incident Activities

On Friday morning, December 27—6 days before the incident—Catalyst Systems employees began normal procedures to prepare a batch of 98 percent BPO. The vacuum dryer was loaded with 200 pounds of granular 75 percent BPO and started. As per practice, hot water to the dryer was shut off at about 2:00 pm to allow the material to cool. At approximately 3:30 pm, the entire drying system was shut down for the day. Because the plant did not operate over the weekend, the drying system remained off and sealed on Saturday and Sunday.

On Monday morning, December 30, operators followed normal procedure to restart the drying system. The drying process described above was repeated. On the following 2 days—plant holidays—the drying system was not operated, and the dryer remained sealed.

Plant personnel returned to work on January 2, 2003. Because it typically took 2.5 days to dry 75 percent material to 98 percent, operators anticipated that the batch would be ready after completing one drying cycle in the morning. The dryer was opened and sampled at approximately 8:00 am. The plant laboratory determined the concentration to be 97 percent BPO, which was within the range expected. The drying system was started.

At about 8:50 am, operators heard the hot water valve close, indicating that the temperature inside the dryer had reached 42°C. They then closed a manual valve on the hot water line to ensure that the hot water did not automatically restart. The dryer continued to rotate under vacuum to allow the material to cool. Operators planned to resample the material after lunch to determine if it had reached the desired concentration of 98 percent.

3.2 The Explosion

At 11:30 am on January 2, the operators took their lunch break at a table located in the Building 2 paste room (Figure 3). One of the operators noted an unusual noise coming from the vacuum pump, which he planned to check after lunch. At 11:55 am, the vacuum dryer suddenly exploded while the operators were still seated at the lunch table.

The employees described thick black smoke with rolling flames and a loud boom. They quickly exited the building and went to the designated evacuation area. One of the employees received a minor puncture wound on his shoulder, possibly from flying debris.

The automatic building sprinkler system activated. The Gnadenhutten Police and Fire Departments responded immediately; they extinguished a small fire in the southwest corner of the paste room. The Tuscarawas County Hazardous Materials Team and several other nearby fire departments were called to assist.

Following the advice on the material safety data sheet (MSDS) for BPO, the fire department continued to put water on the building and its contents. Runoff water leaving the property was tested at several locations and determined to be nonhazardous.[6]

Figures 4, 5, and 6 show some of the damage caused by the explosion. The dryer was propelled through the corrugated steel dividing wall, shown in Figure 4, and through several pallets of filled fiber drums (Figure 5). It landed approximately 35 feet from its original location.

The siding and siding supports on the south side of the building, as well as the dividing wall, were extensively damaged (Figure 6). The building's primary structural frames were intact, though the roof decking and supports in the southwest corner were badly damaged.

[6]Tests were performed to determine pH as well as the presence of oxidizers, fluoride, petroleum products, organic solvents, iodine, bromine, and chlorine.

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Figure 4

Damage to Catalyst Systems BPO production building

Figure 5

Filled fiber drums damaged by dryer

Figure 6

Building damage, southwest side

4.0 Potential Initiating Scenarios

The Catalyst Systems BPO drying system had no indicators or recording devices for temperature or pressure; it was primarily manually controlled. Because the drying system was extensively damaged and there was little recorded information, it was not possible to determine exactly what initiated the explosion. However, CSB identified several potential scenarios by examining and testing physical evidence, interviewing employees, and reviewing system documentation.

BPO may decompose violently when exposed to excessive heat, shock, or friction. Contaminants may initiate the decomposition reaction, which produces a large volume of gas. Each of these hazardous conditions was potentially present in the BPO drying system.

The drying system was designed to use 82°C water to heat the material in the dryer to approximately 42°C, at which point the water was shut off by closing the valve that supplied the dryer's jacket. However, the jacket was not designed to be drained; the water remained in the jacket at 82°C until it was cooled by heat losses to the surrounding environment.

The self-accelerating decomposition temperature (SADT)[7] for a 1-pound bag of 98 percent BPO is 68°C.[8] Because SADT is dependent on the size and type of package, it would be lower for the 200-pound batch that was being processed in the dryer.

Half-life data suggest that half of the 98 percent BPO in the dryer would have decomposed in about 3 hours at 82°C.[9] To maintain an appropriate factor of safety below SADT, another manufacturer's literature suggests that 1-pound bags of 98 percent BPO should not be stored at temperatures higher than 38°C.[10] Clearly, the BPO drying system at Catalyst Systems was running very close to the thermal decomposition temperature for 98 percent BPO, which was the likely cause of the explosion.

[7]SADT is the temperature at which a peroxide undergoes a rapid and violent decomposition, and may self ignite.

[8]The SADT for a 1-pound bag of 98 percent BPO is listed in various manufacturers' MSDSs.

[9]Degussa Corporation general technical information. Half-life indicates the time in which half of the original quantity of peroxide will decompose at a given temperature. Under adiabatic conditions, where no heat is lost from the vessel, the half-life time is decreased.

[10]Atofina, *Organic Peroxides—Their Safe Handling and Use*, 2001.

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. . . The probable and possible events . . . all point to inadequacies in system design due to insufficient management systems.

CSB identified several probable/ possible initiating events and other factors that could have led to a thermal decomposition, as listed in Table 3.

Although CSB was unable to conclusively determine the initiating event that led to the January 2 incident, the probable and possible events listed below all point to inadequacies in system design due to insufficient management systems.

Table 3

Potential Initiating Scenarios Leading to Thermal Decomposition

Probable Initiating Events	Possible Initiating Events
Failure of the temperature probe	Contamination in the dryer from foreign material
Hot spot in the dryer	Contamination in the dryer from exposure to metal surface
BPO remaining in the dryer too long	Generation of heat energy from friction
Failure of the vacuum pump, loss of evaporative cooling	Generation of a spark due to static electricity

5.0 Standards and Guidance

Numerous standards and guidance documents describe the hazards of organic peroxides and recommended practices for storage and handling. Some of these documents also contain specifics on BPO. In addition, a number of trade groups, insurance companies, and government agencies have published books, research reports, and technical papers, as listed in Section 9.0, Annotated References.

A review of standards and guidance suggests that several commonly accepted practices would have significantly reduced the likelihood of the explosion at Catalyst Systems, as noted below:

- Safeguards should be in place to avoid overheating BPO. The SADT is reported as 68°C for 1-pound plastic bags. Manufacturers and users should recognize that these data are specific to the package size and characteristics, which are determined by testing. It is not possible to suggest an exact temperature at which BPO will decompose; however, at higher temperatures, the decomposition reaction takes less time to start and proceeds more rapidly. Safe temperatures should be chosen for specific systems, and temperature controls and alarms should be installed accordingly.
- Equipment used to heat organic peroxides should be isolated from storage areas, other equipment, and work areas. Buildings that house manufacturing equipment should be built with fire- and explosion-resistant walls with adequate capabilities to vent pressure.
- Safeguards should be in place to protect against the possibility of exposing BPO to ignition sources, friction, and shock. Electrical equipment in areas with open containers of BPO should be classified according to Class I, Division 1, of Article 500 of the National Electric Code; and all equipment should be adequately grounded.
- BPO generates large volumes of gases during decomposition and should not be confined. Additionally, precautions should be taken to avoid contamination, which may initiate the decomposition reaction.

These good practices—discussed throughout the standards and guidance documents—do not represent a complete set of practices for BPO handling. However, if they had been in place, they may have reduced the potential for the explosion.

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. . . The development, understanding, and application of process safety information during process design was inadequate for managing the explosive decomposition hazard of 98 percent BPO.

6.0 Management of Chemical Process Safety

Process safety management is the application of management systems to control hazards to ensure the safety of a process and prevent catastrophic incidents. It is considered to be good practice in operations that handle and process hazardous materials. In *Guidelines for Technical Management of Chemical Process Safety*, the American Institute of Chemical Engineers (AIChE) Center for Chemical Process Safety (CCPS) describes 12 core elements of a good process safety management system.

Catalyst Systems did not have a process safety management program in place, nor were employees trained in the use of these management systems. Deficiencies in certain elements, as discussed below, significantly contributed to the January 2 incident.

6.1 Process Knowledge and Documentation

A process safety management system for chemical manufacturing is only as good as the foundation upon which it is built—the actual research, development, design, construction, and operational data. Basic process safety information includes the following:

- Chemical, physical, and reactive properties of materials.
- Health and toxicity data for reactants and products.
- Thermal and chemical stability data for reactants and products.
- Process chemistry and technology information.
- Equipment design temperature and pressure.
- Range of process temperature and pressure.
- Equipment and materials of construction specifications.
- Material and energy balances of the chemical process.
- Safety systems (e.g., interlocks, pressure relief systems, detection or suppression systems).
- Operating procedures and training information.
- Design codes and regulatory standards.

All of this information should be compiled, analyzed, and updated before beginning design and construction, and then kept up to date. The information should be readily available to employees.

At Catalyst Systems, the development, understanding, and application of process safety information during process design was inadequate for managing the explosive decomposition hazard of 98 percent BPO. Although Catalyst Systems was aware of the SADT for a 1-pound package of BPO, this information was inappropriately used to determine the high temperature limit for the much larger amount in the dryer.

Further evaluation of thermal and chemical stability would likely have taken into account the differences between 1 pound of BPO in a plastic shipping container and 200 pounds in a closed metal dryer.[11] Such an evaluation would have allowed Catalyst Systems to adequately design its drying system.

Test information on the resistivity of 98 percent BPO would have prompted the design of a drying system to prevent static accumulation and to assess the hazard posed by static sparks. For example:

- The vacuum dryer was set to rotate slowly enough to prevent the buildup of static charges and frictional heating, yet still allow BPO to tumble (e.g., two revolutions per minute). However, little consideration was given to adequately grounding the dryer to dissipate static charges that might accumulate while the material tumbled. Likewise, there was no consideration of whether the polypropylene bag filter over the vacuum inlet might be a source of static electricity inside the dryer.
- Although the electric motor attached to the frame of the dryer was grounded through its electrical wiring, it is unknown whether the grease in the sealed bearings—where the dryer rotated on its frame—was conductive.[12] If nonconductive grease was used, the rotating dryer shell might have been totally isolated from the frame, allowing static charges to accumulate on and inside the dryer.

The only information that Catalyst Systems had on the vacuum dryer was an item description on a purchase order. There was no wiring diagram. There were no sketches or basic process flow diagrams, and there were no engineering drawings for major system components. This basic system information is necessary to properly review the design, maintain the equipment, and manage changes.

There were no written operating procedures for drying BPO using the vacuum dryer; management provided only verbal instructions to the operators. Catalyst Systems has written procedures for other operations. For example, for the previous drying process, which used an oven, written procedures included warnings and other information on the sensitivity and instability of 98 percent BPO.

Although Catalyst Systems was aware of the SADT for a 1-pound package of BPO, this information was inappropriately used to determine the high temperature limit for the much larger amount in the dryer.

. . . Little consideration was given to adequately grounding the dryer to dissipate static charges . . .

[11] An increase in volume changes the ability of the substance to cool because of differences in surface area.

[12] Catalyst Systems had no documentation describing the type of grease used in the sealed bearing.

. . . Procedures should have included safety precautions during operation . . . and how to handle upset conditions . . .

Basic reactive hazard testing and evaluation procedures should have been used to determine the magnitude of potential hazards.

Process flow diagrams, engineering drawings, and detailed operating procedures should have been a key component of operations and maintenance training at Catalyst Systems. Operating procedures should have been prepared for operator tasks, instrument readings, sampling, and normal operating conditions (e.g., temperature, pressure, concentration, reaction rate). These procedures should have included safety precautions during operation; safe operating limits for critical operating parameters; and how to handle upset conditions, such as what to do if the vacuum pump malfunctions.

6.2 Capital Project Review and Design Procedures

Capital projects add or significantly modify processes or equipment. Safety reviews are normally completed during the various stages of implementation. These reviews may include hazard reviews, reactive hazard evaluations, siting reviews, process design reviews, and prestartup safety reviews.

A reactive hazard evaluation is designed to identify, evaluate, and control hazardous chemical reactivity in a chemical process. Catalyst Systems did not conduct such an evaluation. After collecting relevant reactive hazard data for BPO, Catalyst Systems should have identified process parameters for further evaluation. Basic reactive hazard testing and evaluation procedures should have been used to determine the magnitude of potential hazards.

The results of this testing and evaluation could then have been translated into control measures and safeguards. For example, safe temperature limits could have been developed based on the SADT for the specific processing conditions; and the testing data could have been used to determine if pressure relief was necessary to eliminate confinement hazards.

Catalyst Systems did not complete any formal hazard reviews during design and installation of the BPO drying system. A formal process hazard analysis (PHA) would have systematically evaluated the hazards of the drying process and reviewed the following questions:

- What scenarios could cause the temperature in the dryer to go beyond an established safe level (e.g., valves fail to isolate hot water)? What warnings alert operators to a high temperature? What control systems are in place to prevent the temperature from getting too high?
- What happens if a decomposition reaction starts in the dryer? How fast and with what force does it occur? Is venting adequate to alleviate pressure buildup?

- What are potential sources of static electricity or friction? What are potential sources of contamination?
- Are employees adequately protected and able to safely evacuate?

Catalyst Systems did not complete a prestartup safety review, as is customary prior to startup of a new process. This safety review looks at differences between the intended design and the system as actually installed to ensure that there is no compromise on safe operation. During its design process, Catalyst Systems planned to include redundancy in the control of valves in the heated water piping to protect against the failure of a single valve; however, this safety feature was removed due to wiring problems during installation.

A proper prestartup safety review would have ensured that if an intended safety feature was removed, it would be replaced with a suitable alternative. Catalyst Systems did not have a management system in place that mandated these reviews.

If Catalyst Systems had completed a formal PHA and reactive hazard evaluation, it likely would have discovered that the drying system did not include adequate measures to protect against thermal decomposition or its consequences. Measures should have been taken to prevent the temperature from getting too high; to eliminate potential sources of contamination, static charges, electrical charges, and friction; and to avoid confinement.

6.3 Process and Equipment Integrity

Equipment used to handle or process hazardous materials should be maintained to control the risk of fires, explosions, releases, and other accidents. Even well designed equipment cannot ensure process safety if it fails prematurely, or if its components do not operate in an emergency.

Preventive maintenance is a program of inspections and tests to ensure that equipment operates satisfactorily. A preventive maintenance program consists of the following activities:

- Identification of equipment and instrumentation critical to process safety.
- Determination of required inspections or tests, their frequency, and acceptable limits or criteria for passing.
- Establishment of maintenance procedures.
- Training of maintenance personnel.
- Documentation and analysis of results.

Catalyst Systems had no established preventive maintenance program for the BPO drying system.

If Catalyst Systems had completed a formal PHA and reactive hazard evaluation, it likely would have discovered that the drying system did not include adequate measures to protect against thermal decomposition or its consequences.

Catalyst Systems had no established preventive maintenance program for the BPO drying system.

Although the operators appeared to have good knowledge of normal operation, there were no written procedures and no structured training.

Because the temperature controller was critical to safe operation of the system, it should have been included in such a program. Catalyst Systems should have developed test methods to ensure that the thermocouple was working properly, and that the high temperature set point on the temperature controller was accurate and functioned as intended. The frequency of testing should be based on known failure history, manufacturer's recommendations, and operating experience.

A preventive maintenance program should also have included the glass lining inside the vacuum dryer. Interviews with operators revealed that a chip had developed in the lining. Granular BPO may have become lodged in this chip and overheated (because it was now closer to the jacket and heated to a higher temperature than the rest of the batch), creating a hot spot. Moreover, the metal under the glass lining provided a potential source of contamination. Catalyst Systems should have developed procedures for inspecting the glass lining and making repairs when necessary.

6.4 Training and Performance

To safely operate a chemical process, operators must be trained on its normal operation and hazards, in addition to deviations during abnormal situations.

At Catalyst Systems, operators received on-the-job training only. Although the operators appeared to have good knowledge of normal operation, there were no written procedures and no structured training. In addition, there were no procedures for abnormal situations. Catalyst Systems should have identified unusual scenarios and trained operators on response actions, such as what to do about finding a chip in the dryer's glass lining, hearing unusual noises from the vacuum pump, or detecting abnormal process conditions.

7.0 Regulatory Analysis

The Occupational Safety and Health Administration (OSHA) Process Safety Management (PSM)[13] Standard was established to prevent or minimize the consequences to employees from catastrophic releases of highly hazardous chemicals (HHC) in the workplace. It covers processes containing individually listed chemicals that present a range of hazards, including reactivity.

The PSM Standard lists BPO because of its reactivity. When the standard does not specify a chemical concentration, the listed chemicals are covered in pure "chemical" or "commercial" grades.[14, 15] For BPO, this concentration is 98 percent.

For a process to be covered by the PSM Standard, a minimum or threshold quantity of the listed chemical must be present. The threshold quantity for BPO is 7,500 pounds. The Catalyst Systems process was not covered because the maximum amount of 98 percent BPO onsite at a given time was 2,550 pounds.[16]

[13]See www.osha.gov.

[14]OSHA Director, Directorate of Compliance Programs, letter re HHCs as applied to how high the percentage of a chemical must be to require compliance, April 14, 1993.

[15]OSHA Deputy Director, Directorate of Compliance Programs, letter re HHCs as applied to threshold quantity, April 24, 1994.

[16]The approximate amount of 98 percent BPO onsite on the day of the explosion was 2,140 pounds.

In determining the appropriate threshold quantities for PSM-listed chemicals that pose reactivity hazards, OSHA chose the quantity of material that would cause a 2.3-pound-per-square-inch (psi) overpressure at 100 meters[17] based on the following:

- Blast waves with pressures greater than 2.3 psi cause serious physical damage to buildings and structures, and cause fragments to fly at speeds that could seriously injure workers.
- An explosion that produces an overpressure of 2.3 psi or greater at a distance of 100 meters from the blast origination represents a catastrophic incident rather than a local incident. This is the same distance used by the State of Delaware in developing its Extremely Hazardous Substances Risk Management Act[18] prior to the PSM Standard. One hundred meters was also supported by public comments received by OSHA during its rulemaking process.

[17]The rationale for OSHA threshold quantities is discussed in a 1996 memo prepared by Thomas H. Seymour, Directorate of Safety Standards Programs, "Rationale for Preamble, Appendix A, Chemical List."

[18]In its regulation, the State's objective was to protect people in the vicinity of a catastrophic release beyond a facility boundary.

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. . . Explosions such as the one at Catalyst Systems can be very hazardous to workers who may be closer than 100 meters to the origin.

Catalyst Systems should have reviewed consensus standards and guidance documents on the handling, storage, and manufacture of BPO, and implemented their recommended practices.

- The amount of material necessary to cause a 2.3-psi overpressure at 100 meters from the blast origination is determined using an empirically derived function method based on equivalent mass of trinitrotoluene (TNT).

Although there were no serious injuries on January 2, explosions such as the one at Catalyst Systems can be very hazardous to workers who may be closer than 100 meters to the origin. Because of the potential hazard, good practices must be followed even when handling small amounts of a hazardous chemical such as BPO.

OSHA investigated the Gnadenhutten plant following the January 2 incident. For violation of the General Duty Clause (Section 5(a)(1) of the Occupational Health and Safety Act of 1970), OSHA issued a citation with willful violation to Catalyst Systems for not following the good practices outlined by the principles of process safety management.

8.0 Conclusion

The January 2 explosion at Catalyst Systems was most likely caused by a thermal decomposition of 98 percent BPO. Other possible causes or contributors include contamination, static electricity, or friction.

The hazards of BPO are well known and documented. Catalyst Systems should have reviewed consensus standards and guidance documents on the handling, storage, and manufacture of BPO, and implemented their recommended practices.

Dry BPO is hazardous in any quantity. Regardless of OSHA PSM coverage, companies should implement good engineering practices when working with BPO, such as gathering relevant hazard information, reviewing reactive hazards, developing a preventive maintenance program, and developing and conducting training on operating procedures for normal and abnormal situations.

If Catalyst Systems had reviewed and followed industry standards and guidance documents, and implemented good engineering practices to manage the hazards, it is likely that this incident would not have occurred.

9.0 Annotated References

Code for the Storage of Organic Peroxide Formulations, NFPA 432

The National Fire Protection Association (NFPA) began developing codes for the storage of organic peroxides in 1969; the current standard was published in 2002. NFPA 432 applies to storage only and excludes manufacturing. The standard defines hazard classifications for organic peroxides based on the characteristics of available peroxide formulations and a limited number of full-scale fire tests.

Fire, Explosion, and Health Hazards of Organic Peroxides, American Insurance Association

Research Report No. 11 discusses problems associated with the use of concentrated organic peroxides, classification and evaluation, fire and explosion hazards, and typical fires and explosions; and includes precautionary recommendations. This 1966 report reviews case histories of eight BPO explosions and fires in transportation, laboratory, and manufacturing environments.

Guidelines for Technical Management of Chemical Process Safety, American Institute of Chemical Engineers (AIChE) Center for Chemical Process Safety (CCPS)

The CCPS chemical process safety management system focuses on management systems, along with technological advances, as essential to prevent catastrophic incidents. This book, published in 1989, describes the 12 core elements necessary for a complete process safety management program. These practices are recognized throughout the chemical industry.

"Hazard Evaluation of Dibenzoylperoxide (BPO)," *Proceedings, 17th International Pyrotechnics Seminar–2nd Beijing International Symposium on Pyrotechnics and Explosives*

In this scientific technical paper, from Volume 2 of the 1991 proceedings (pp. 993-998), authors Tadao Yoshida and others describe an explosion in a manufacturing factory in Tokyo in 1990, including the results of several experiments on the hazards of dry and 75 percent water-wetted BPO. The authors conclude that—unlike dry BPO—75 percent BPO diluted with water is rather safe under ordinary handling conditions but displays some potential hazards under confinement.

"Hazard Evaluation of Organic Peroxides," *Journal of Hazardous Materials*, Elsevier Scientific Publishing

This scientific technical paper was authored by V. K. Mohan, K. R. Becker, and J. E. Hay—and published jointly by IDL Chemicals Ltd. (India) and the Pittsburgh Research Center, U.S. Bureau of Mines, in 1982 (Volume 5; pp. 197-220). It contains detonability, thermal stability explosion, and energy release test data for a number of organic peroxides, including BPO. These tests compare BPO to results obtained with conventional explosives, such as TNT. For example, in a ballistic mortar test, BPO had a weight strength of 15.5 percent of TNT; the relative underwater bubble energy for dry BPO (98 percent pure) relative to the bubble energy for an equivalent mass of TNT was 42.7 percent. In contrast, the relative bubble energy of wet BPO (22 percent water) was only 28.8 percent.

Hazardous Substance Fact Sheet: Benzoyl Peroxide, New Jersey Department of Health and Senior Services

This fact sheet, revised in 1998, summarizes the hazards of BPO and includes information on determining exposure. It provides workplace exposure limits as defined by OSHA, NIOSH, and the American Conference of Governmental Industrial Hygienists. Guidelines on reducing exposure are also included.

Occupational Exposure to Benzoyl Peroxide, National Institute for Occupational Safety and Health

NIOSH published this recommended standard (77-166) in 1977, recognizing that the most significant concern with BPO is its hazards due to instability, flammability, and explosive properties. The standard includes a discussion of BPO hazards and provides general recommendations for storage and handling.

"Organic Peroxides: Evaluation and Management of Hazards," *Organic Peroxides*, Wiley-Interscience

In Chapter V of Volume III, published in 1972, author E. S. Shanley discusses the storage stability of organic peroxides; hazards from rapid decomposition, including tests for evaluation of hazardous behavior; hazard classification schemes; health hazards; and safe handling practices in both the laboratory and plant environment. The author advocates separating organic peroxide storage and manufacturing areas.

Organic Peroxides, Factory Mutual (FM) Global Property Loss Prevention Data Sheet 7-80

FM Insurance Company develops engineering guidelines to help prevent property losses. FM Data Sheet 7-80, revised in September 2000, makes recommendations on the safe storage and handling of organic peroxides. It applies to both storage and manufacturing.

Properties and Essential Information for Safe Handling and Use of Benzoyl Peroxide, Manufacturing Chemists Association

MCA has split into several different organizations since the publication of this guidance in 1960. Although the new organizations no longer support this document, it provides a thorough evaluation of the hazards of BPO; and recommends procedures for handling, storing, and manufacturing the product.

Safety and Handling of Organic Peroxides: A Guide, Society of Plastics Industry Inc.

The Organic Peroxide Producers Safety Division published this guidance (Publication AS-109) in 1999. This document covers characteristic properties of organic peroxides, types of organic peroxides, and rules for safe handling—including temperature control, contamination control, confinement control, quality control, disposal of wastes, and fire protection.

"Thermal Hazards: How to Identify and Minimize Them in Your Drying Process," *Powder and Bulk Engineering*

This technical article from the April 1977 issue describes potential thermal hazards involved in drying processes and explains how to evaluate powders to minimize these hazards. Authors V. Ebadat and J. C. Mulligan discuss heating and cooling during the drying process, the onset temperature for exothermic decomposition, and how powders can self-heat. Smoldering, charring, and other factors that affect the self-heating rate are also explained. For example, the authors state that increasing residence time in the dryer (inadvertently or otherwise) may cause a powder to decompose to a stage that leads to a fire or explosion.

Incident Investigation Process

The U.S. Chemical Safety and Hazard Investigation Board (CSB) examined and tested physical evidence at the site, interviewed employees, and reviewed relevant plant documents. CSB contracted with Hazards Research Corporation for assistance in evaluating benzoyl peroxide (BPO) chemistry and processing. CSB also met with the Organic Peroxide Producers Safety Division of the Society for Plastics Industry (SPI) regarding the hazards, safe handling, and manufacture of BPO.

Salus Populi Est Lex Suprema

People's Safety is the Highest Law

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. CSB is a scientific investigative organization; it is not an enforcement or regulatory body. Established by the Clean Air Act Amendments of 1990, 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.

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