

**For Review Purposes Only
Not for Publication**

**HYDROGEN PEROXIDE ACCIDENTS AND INCIDENTS:
WHAT WE CAN LEARN FROM HISTORY ***

Ben Greene
Honeywell Technology Solutions, Inc.
NASA Johnson Space Center White Sands Test Facility
Las Cruces, New Mexico

David L. Baker
NASA Johnson Space Center White Sands Test Facility
Las Cruces, New Mexico

Wayne Frazier
NASA Headquarters
Washington, D.C.

ABSTRACT

Historical accidents and incidents involving hydrogen peroxide are reviewed and presented. These hydrogen peroxide events are associated with storage, transportation, handling, and disposal and they include exposures, fires, and explosions. Understanding the causes and effects of these accident and incident examples may aid personnel currently working with hydrogen peroxide to mitigate and perhaps avoid similar situations. Lessons learned, best practices, and regulatory compliance information related to the cited accidents and incidents are also discussed.

BACKGROUND

Accidents and injuries associated with liquid propellant storage, handling, and use are typically mitigated through hazard assessments and the resultant administrative controls, engineering controls, and personal protective equipment that are employed. Hydrogen peroxide has a rich history and hazard assessments can benefit from its study. In addition to its use as a propellant, hydrogen peroxide has been used as a multi-purpose laboratory and industrial chemical for many years, thus a number of accidents, incidents, close calls, and lessons learned have been documented. The NASA White Sands Test Facility (WSTF) *Fire, Explosion, Compatibility and Safety Hazards of Hydrogen Peroxide* summarizes a number of these events from a variety of sources.

Recent experiences at a NASA facility have been reported elsewhere and will not be addressed in this paper, although they are essential to the understanding of hydrogen peroxide hazards.¹

INTRODUCTION

Hydrogen peroxide hazards have been extensively documented.^{†, 2} The properties of hydrogen peroxide that contribute to most accidents include the following:

- Sensitivity to contamination: hydrogen peroxide will decompose if contaminated and the decomposition reaction may be rapid and produce water, oxygen and heat. The pressure generated can have deleterious effects on containment systems resulting in explosions that produce shrapnel capable of destroying structures and injuring personnel.
- Reactivity with organic materials: hydrogen peroxide will react with a variety of organic materials and can form explosive mixtures, shock sensitive compounds, and initiate fire.

* Approved for public release, distribution is unlimited.

• In-house document. WSTF-RD-0972-001-03. *Fire, Explosion, Compatibility and Safety Hazards of Hydrogen Peroxide*. 2004.

† Ibid, WSTF-RD-0972-001-03.

- **Reactivity with inorganic materials:** hydrogen peroxide will react with a variety of inorganic materials. The reaction may be catalytic or may be an oxidation-reduction reaction. The reactions with common inorganic materials in bulk, as trace contaminants, or on surfaces typically produce oxygen. The heat released from hydrogen peroxide decomposition may be sufficient to initiate combustion of flammable or combustible materials.
- **Reactivity with fuels:** hydrogen peroxide will react with a variety of fuels including organic amines, catalytically-enhanced fuels, and hydrocarbon-based fuels. This is one reason why hydrogen peroxide is used a propellant. The reactions may be rapid and are exothermic. Exhaust products and propellant residues with some fuels can be toxic to personnel and harmful to the environment.
- **Corrosivity to the skin and eyes:** hydrogen peroxide may cause chemical burns and blindness upon exposure to the skin and eyes when adequate first aid and medical attention is not provided in a timely manner.
- **Physical hazards:** heat, pressure, shrapnel, and fire resulting from explosive and exothermic events can be injurious and sometimes fatal to personnel.
- **Decomposition in the body:** ingestion and injection of hydrogen peroxide can result in embolisms, damage to internal organs, and other medical complications that, if not treated aggressively, cause severe internal injuries that are sometimes fatal.

OBJECTIVE

The objective of this work is to provide examples and a brief analysis of accidents, close calls, incidents, and lessons learned from selected hydrogen peroxide events. The events and corresponding analyses are intended to increase awareness of hydrogen peroxide hazards, the need for appropriate training, and rigorous controls.

APPROACH

A literature survey was performed to establish a reference collection of adverse events involving hydrogen peroxide. Information was also obtained from journal articles, reports, the Chemical Propulsion Information Agency (CPIA), the National Transportation Safety Board (NTSB) and the Occupational Safety and Health Administration (OSHA). Approximately 70 events were located and the applicable supporting documentation was summarized. Example events were selected for this paper to cover topics including storage, transportation, contamination, laboratory accidents and explosions, and exposures.

Two laboratory experiments were conducted to provide further insight and illustration of selected events.

EXPERIMENTAL

Simulated Failure of a Class 1 Protective Liner in Contact with a Class 4 Metal

The test specimen was a mild carbon steel, approximately 6-cm long with a 0.25-cm outer diameter, and was shrink-wrapped in fluorinated ethylene propylene (Teflon[®] FEP). The Teflon[®] FEP sheath exposed portions of the carbon steel surface and is shown in Figure 1. A 150-mL beaker was charged with 50 mL of 98 percent hydrogen peroxide (FMC), and a sheathed thermocouple was immersed in the fluid until the temperature equilibrated. The test specimen was then immersed in the fluid and the reaction and temperature were monitored periodically for 24 h.

* Teflon[®] is the registered trademark of E.I. DuPont de Nemours and Company, Wilmington, Delaware.

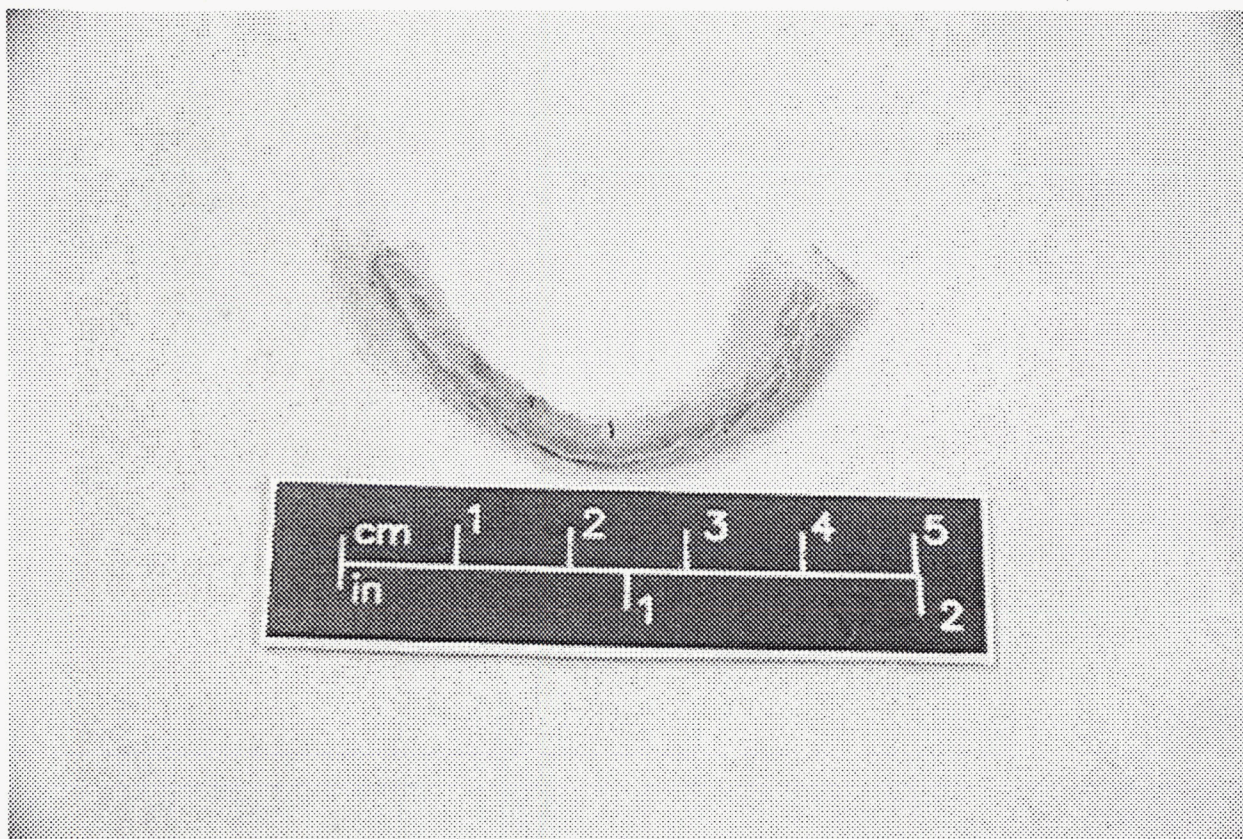


Figure 1. Carbon Steel Shrink-Wrapped Test Specimen

Reaction of Hydrogen Peroxide with a Mixed Amine Fuel

A mixture of unsymmetrical dimethylhydrazine (UDMH) and diethylenetriamine (DETA), both obtained from Aldrich, was prepared as follows: in a nitrogen-purged glove bag containing an analytical balance, the propellants were weighed in an amber glass bottle to yield a mixed amine fuel (MAF) containing 60 percent UDMH and 40 percent DETA by weight. This product is referred to as MAF-4, U-DETA, and Hydyne.³ A lead coupon, approximately 1 cm², was obtained from laboratory stock. Propellant-grade hydrogen peroxide (98 percent) was obtained from FMC.

The test apparatus was assembled as follows: An aluminum tray was placed behind a safety shield in a fume hood. One end of a piece of borosilicate glass tubing was tapered using a flame and the glass tubing was bent over a flame to allow liquid to be dispensed to the reaction vessel without reaching behind the safety shield. The other end of the glass tubing was fitted with a Pasteur pipet bulb to complete the propellant delivery tube. Glass 10-mL beakers, cleaned with nitric acid (Aldrich), 35 percent hydrogen peroxide (Mallinckrodt), and deionized water were used as reaction vessels. A clean glass reaction vessel and the test materials were placed in the aluminum tray immediately prior to each of three experiments.

In the first experiment, 0.25 mL of U-DETA was added by syringe to the reaction vessel. Approximately 1 mL of hydrogen peroxide was added dropwise to the reaction vessel through the propellant delivery tube. In the second experiment, the lead coupon was placed in the reaction vessel. Approximately 1 mL of hydrogen peroxide was added dropwise to the reaction vessel through the propellant delivery tube. In the third experiment, the lead coupon was first placed in the reaction vessel. 0.25 mL of U-DETA was added by syringe to the reaction vessel ensuring liquid contact with the upper surface of the lead coupon. Approximately 1 mL of hydrogen peroxide was added dropwise to the reaction vessel through the propellant delivery tube.

EXAMPLE ACCIDENTS AND INCIDENTS

STORAGE

Failure of a Class 1 Protective Liner in Contact with a Class 4 Metal

The failure of a Class 1 protective liner in contact with a Class 4 metal has been reported elsewhere.¹ Our experimental results from the simulated failed liner test showed that hydrogen peroxide in contact with a carbon-steel gradually decomposed. Figure 2 is a photograph of the reaction mixture after the 24-h period. Although oxygen was evolved, there was no significant temperature rise over the 24-h period because the reaction was mild and gradual in the open beaker in the constant air stream of the fume hood. Had this occurred in a storage vessel or in a system without adequate pressure relief, severe consequences as a result of accelerated hydrogen peroxide decomposition, such as expulsion of liquid through a vent or an explosion, could have occurred.

Analysis

While best practices dictate that hydrogen peroxide systems, including pumps, should be constructed of highly compatible materials, similar considerations should apply to the safe packaging and transportation of hydrogen peroxide. The packaging requirements for shipping hydrogen peroxide were clearly spelled out in paragraph 5 of MIL-P-16005E,⁴ and exceeded those required by the Department of Transportation (DOT). However, when MIL-P-16005E was cancelled, responsibility for the selection of suitable DOT-approved packagings became that of the user and the shipping organization. There are several issues associated with the selection of packagings, but one of the most important is that DOT-allowed combination packaging may create unsafe conditions. Thorough discussions of some of the concerns and problems associated with the shipping of propellant HP have been reported.^{5, 6, 7, 8} As they pertain to the failed protective liner experiment and events reported elsewhere, decades of knowledge and experience that had been put into the very clearly stated transportation requirements of MIL-P-16005E may be lost. By conforming only to the DOT requirements, a threat to safe transportation and use may be created. An example of a DOT-allowable non-bulk combination packaging is a stainless steel drum and a Teflon[®] liner.⁸ Such a combination is a potential hazard for reasons that include failure of the Teflon[®] liner. This could permit prolonged contact of hydrogen peroxide with the stainless steel, resulting in leaching of iron, nickel, and chromium into the hydrogen peroxide. The contaminated hydrogen peroxide could then begin to decompose and pressurize the drum. If the contamination is sufficient, over-pressurization may cause structural failure of the drum even if a vent is provided.

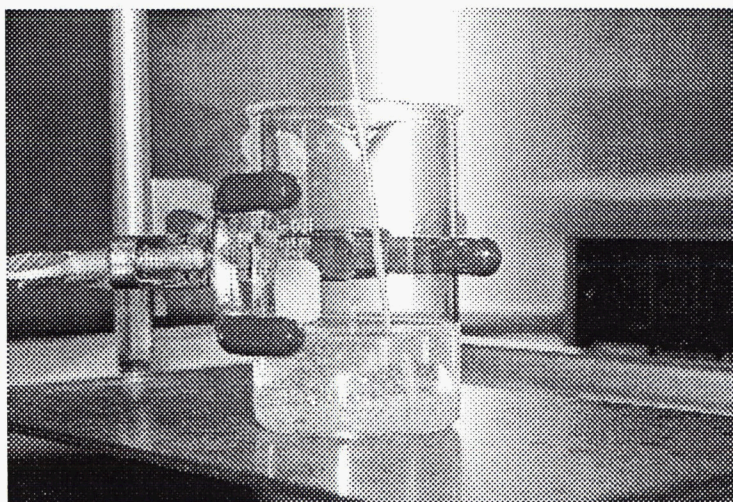


Figure 2. Reaction Mixture after 24-h Period

Our experiment illustrates this possibility. These above examples further demonstrate the need to understand the history of the development of safe packagings for hydrogen peroxide.

Fire in a Storage Yard

A chemical storage facility contained various service buildings and hydrogen peroxide in concentrations from 35 to 70 percent.⁹ An employee discovered a fire in the outside of the storage yard where the drums of 35 percent hydrogen peroxide were stored on wood pallets. The fire department was called, but the fire spread rapidly after it involved drums of nitrocellulose. When the fire fighters arrived chemicals were burning, drums were exploding, and potentially hazardous smoke was threatening exposures. Using water and foam streams, fire fighters were able to limit damage to outside storage areas and a section of the warehouse. Investigators believed the fire ignited spontaneously when hydrogen peroxide either spilled or leaked onto the wood pallets. The fire then spread to the nitrocellulose, which is highly flammable, causing the fire to spread rapidly. One fire fighter was injured in the event. A section of the warehouse roof collapsed as a result of the fire. Damage to the structure and the contents were estimated at \$1,193,000.

Analysis

A leaking drum or spilled hydrogen peroxide was believed to come into contact with a wooden pallet. Wood can ignite after exposure to hydrogen peroxide. Ignition can be accelerated if the material is impregnated or coated with certain preservatives, some of which can be hydrocarbon-based (creosote) or metal-containing (lead, chromated copper arsenate). Other components of wood pallets, such as nails, or contaminants of various types (metals, oils, dirt) can also accelerate ignition. The resultant fire spread to drums of highly flammable nitrocellulose, and causing them to burn and explode. The fire also spread to the structure causing further damage. There was apparently no fire alarm or fire extinguishing system to provide early warning or mitigation of the event, and the nature of the injury was not reported.

Hydrogen peroxide should be stored on compatible pallets with secondary containment and away from flammable and combustible materials. Drums should be monitored periodically for signs of leaks or temperature increase. There should be an emergency plan in place. Storage areas should also be equipped with fire detection and fire extinguishing systems. Fire fighters must be aware of the hazards of fires in areas that contain fuels, hydrogen peroxide, and combustible materials including structures.

TRANSPORTATION

Aircraft Incident (1)

The National Transportation Safety Board reported a hazardous materials incident brief (Accident No. DCA-99-MZ-001) that occurred on October 28, 1998.¹⁰ Briefly, 2 gal of a 35-percent hydrogen peroxide solution in water spilled in a cargo compartment of a passenger airplane flying from Orlando, Florida, to Memphis, Tennessee. The solution leaked from two undeclared 1-gal plastic bottles. The bottles were in an ice chest that belonged to a passenger on the flight and had not been properly checked as baggage (a skycap had been "tipped" by the owner and bypassed the normal baggage check-in routine). The leaking hydrogen peroxide contaminated three mail sacks and an undetermined number of bags. The leak was not discovered until cargo handlers in Memphis began to unload the baggage. Thinking that the spilled liquid was water, the cargo handlers ignored it and transferred some of the baggage to another passenger-carrying flight departing for Seattle, Washington. When the flight arrived in Seattle, two bags in a cargo compartment were smoldering. One handler said the smoke was "like someone blowing on a good cigar." As a result of the spill, several people required treatment. In Memphis, 11 employees were treated at the airport's first aid station because their hands (that were tingling and turning white) had been exposed to the hydrogen peroxide, and two more employees went to a local clinic where they were treated and released. In Seattle, the employee who removed the smoldering bags from the cargo compartment was exposed to fumes and went to a hospital for treatment.

Analysis

Hydrogen peroxide, in a quantity that exceeded the DOT quantity limitation of 1 L for 35 percent hydrogen peroxide for passenger aircraft transportation, was shipped undeclared.¹¹ Although the inner packaging material (plastic) was allowable by DOT,¹² the outer packaging (an ice chest) was not allowable and did not contain the spilled fluid. The spilled fluid came into contact with and contaminated combustible material (paper). Paper may catch on fire after exposure to hydrogen peroxide. Personnel unloading the baggage did not recognize a hazardous material release despite being exposed to the fluid, and sent the contaminated baggage ahead on another flight. Sufficient contact time allowed the contaminated baggage to begin to smolder and employees who unloaded that baggage were exposed to fumes. A fire on the aircraft could have had further and potentially disastrous consequences.

Hazardous materials transportation requirements with respect to quantity, labeling, and packaging must always be followed. Transportation personnel, in this case baggage checking employees must follow procedures. Baggage handling personnel must be trained to recognize hazardous materials spills (hydrogen peroxide may look like water). Information regarding potentially contaminated baggage must be communicated as soon as possible along with appropriate precautions and instructions for spill response.

Aircraft Incident (2)

An earlier aircraft transportation incident involving hydrogen peroxide occurred in 1988.¹³ A passenger aircraft had to make an emergency landing after smoke, odor, and a softening of the cabin floor was detected. 120 passengers, 4 flight attendants, and two flightcrew members followed emergency evacuation procedures. Nine passengers, two firefighters and three airline employees suffered minor injuries. Total repair costs for the airplane were \$228,823. In this incident, 5 gal of undeclared and improperly packaged 50 percent hydrogen peroxide was transported in a fiberboard drum that also contained a 35-percent hydrogen peroxide solution and a sodium orthosilicate-based material ($\text{SiO}_2 \cdot 2\text{Na}_2\text{O}$). These goods were used in the laundering industry and had been offered for transport as "Laundry Equipment" rather than as chemicals. The drum was not affixed with directional arrows and was stowed on its side. The 50-percent hydrogen peroxide was packaged in a 5-gal, non-vented DOT-34 polyethylene drum. The sodium orthosilicate material was packaged in a plastic bag. The investigation concluded that the hydrogen peroxide leaked, coming into contact with the fiberboard and the sodium orthosilicate, resulting in a fire.

Analysis

Shipment of 50 percent hydrogen peroxide is not allowable in any quantity on passenger aircraft. Hydrogen peroxide is not compatible with sodium orthosilicate, which is a base and will destabilize hydrogen peroxide.¹¹ Laboratory tests conducted by the NTSB showed that fiberboard drum material ignited when exposed to a mixture of 50 percent hydrogen peroxide and sodium orthosilicate.

Very specific regulations for the safe transportation of hydrogen peroxide are defined by DOT. Illegal shipments of hydrogen peroxide must be avoided. Approved packagings must not leak, and leakage must not be allowed to contact incompatible and combustible materials. Do not ship basic materials in the proximity of hydrogen peroxide and combustible materials, as a base will destabilize hydrogen peroxide and increase its ability to cause ignition. Fire fighting personnel must follow appropriate procedures and use respiratory protection to prevent smoke inhalation.

Railcar Incident

A runaway train in Helena, Montana, collided with a helper train and derailed in 1989.¹⁴ Approximately 26,250 gal of 70 percent hydrogen peroxide in two tank cars, and approximately 12,136 gal of isopropyl alcohol from another tank car were released. Fire and explosions resulted. About 3500 residents of Helena, Montana were evacuated. Two crewmembers were slightly injured. The NTSB believed the hydrogen peroxide combined with contaminants on the ground following the

derailment and puncture of the tank. A chemical reaction resulted in a fire; the fire heated 91 tons of polyethylene pellets in a hopper car causing the release of volatile organic vapors, which exploded with sufficient energy to initiate a second explosion. Seven individuals were treated for minor injuries associated with smoke inhalation, headaches, dizziness, sore throats, lacerations, anxiety, and fainting. The estimated damage (including clean-up and lading) exceeded \$6 million.¹⁴ In this report, the NTSB briefly discussed a previous hydrogen peroxide release in which spilled hydrogen peroxide ignited several rail crossties.

Analysis

Crew error resulted in a runaway train that derailed, spilling a large quantity of hydrogen peroxide. Fuels that were also spilled were exposed to hydrogen peroxide which resulted in explosion and fire.

Transportation safety regulations when operating trains and transporting hazardous materials must be adhered to. The DOT regulations do not prohibit the transport of hydrogen peroxide and reactive materials on different railcars on the same train.¹⁵

CONTAMINATION

Mixture of Hydrogen Peroxide with Incompatible Materials

An incident occurred at Rocky Flats that was reported in 1993, where leaking 35 percent hydrogen peroxide in a glove box containing plutonium was vacuumed into a pickup vessel that contained a solution high in iron, copper, and nickel.¹⁶ The hydrogen peroxide began to foam in the pickup vessel. Within a few minutes, a stream of liquid ejected from the 1-in. pressure relief valve on top of the pickup vessel and the glove box was pressurized sufficiently to cause its walls to flex outward and eject radioactive plutonium into the room.

Analysis

Mixing hydrogen peroxide with catalytic materials resulted in an explosion that was exacerbated by concurrent release of radioactive plutonium into the laboratory.

Avoid mixing hydrogen peroxide with catalytic impurities. Ensure that vacuum systems will not pick up hydrogen peroxide in a manner that will expose the fluid to impurities. Ensure that appropriate spill containment is in use and that equipment used in the clean-up of hydrogen peroxide spills is clean.

Incompatible Waste Mixture

In 1978 a very violent explosion occurred in a university chemistry laboratory, apparently due to the formation of explosive peroxides in a mixed organic waste/30 percent hydrogen peroxide solution that had been accumulating in a fume hood for three to four weeks.¹⁷ The waste solution was generated by the combination of polyacrylamide gels, toluene, and 2-ethoxyethanol (a glycol ether). The explosion caused complete destruction of the hood and moved a cinder-block wall located 30 ft from the blast. Kick-out panels and glass were blown out of the laboratory and chemicals on shelves in the adjacent laboratory were knocked to the floor. Fortunately, the explosion occurred when the labs were vacant, avoiding injury to personnel. It was suggested that addition of hydrogen peroxide to the gels to solubilize them could result in the formation of peracids, azo- and nitro-compounds, and that excess hydrogen peroxide could react with the ether to form an organic peroxide. It was recommended that either alternate methods be used for solubilization of the gels or that the peroxides be immediately destroyed.

Analysis

Hydrogen peroxide was added to a mixture of organic wastes that contained grossly incompatible materials. Complex chemical reactions may have occurred, resulting in the formation of unstable species and ultimately an explosion.

Avoid mixing hydrogen peroxide with any wastes, including grossly incompatible organic waste mixtures. Ensure that all waste containers are labeled as to contents and the limitations of what can be added to the waste container, and provide training on chemical reactivity hazards of hydrogen peroxide. Do not allow waste mixtures to sit for a prolonged time period. In the case of ether-containing wastes, these should be monitored periodically for the formation of peroxide species and should be dealt with accordingly if peroxides are detected. However, a thorough hazard assessment must be undertaken by trained chemists and hazardous materials experts in dealing with such a mixture; for example, the addition of ferrous ammonium sulfate to reduce organic peroxides might concurrently catalyze the decomposition of residual hydrogen peroxide with potential catastrophic consequences such as fire or explosion.

EXPLOSIONS

Mixture of Mixed Amine Fuel and Hydrogen Peroxide

A chemist was killed when he inadvertently poured hydrogen peroxide into a laboratory sink.¹⁸ The hydrogen peroxide reacted violently with some U-DETA (a mixed amine fuel consisting of UDMH and DETA) remaining in the trap underneath the sink and the trap exploded. No other details were reported. U-DETA fuel was used in small storable missiles similar to the Bullpup, as well as in other vehicles.¹⁹

Analysis

We postulate the explosion occurred because a reaction involving hydrogen peroxide was sufficiently violent to rupture the trap. This could occur if a reaction generated heat and pressure. A reaction could also be accelerated by contaminants in the trap, or if the trap was constructed of a Class 4 metal. Lead was used as a likely candidate Class 4 metal in our experiments. Our experiments showed that hydrogen peroxide gave a violent exothermic reaction with U-DETA. It also gave a violent exothermic reaction with lead (Class 4 metal), and a very violent flaming reaction with U-DETA in contact with lead. All these experimental results could explain a trap explosion. The most violent explosion could have occurred if the sink trap was composed of an incompatible material such as lead or had accumulated impurities that were catalytic to hydrogen peroxide decomposition. In contact with U-DETA, sufficient heat could be generated by the decomposition of hydrogen peroxide with the catalyst to ignite the U-DETA or promote a violent fuel/oxidizer reaction.

Hydrogen peroxide should never be mixed with U-DETA or other fuels for other than an intended purpose, such as missile propulsion. Workers must ensure plumbing is clean and compatible, and must always dilute hydrogen peroxide with water copiously prior to disposal. Propellant laboratories should have entirely separate areas for the preparation, characterization, analysis, and disposal of waste fuels and oxidizers. Facilities that are not built with physically separated fuel and oxidizer drains should have procedures in place to prevent their mixing at concentrations that could generate a hazardous reaction.

Chemist Dies in Chemical Explosion

A chemist was working with a mixture of an aminonitrofurazan (ANF), methylene chloride, hydrogen peroxide, trifluoroacetic anhydride, and diaminofurazan.²⁰ The chemicals were being mixed in a 2-L flask. When the mixing was complete, the chemist apparently was removing the flask from the mechanical stirrer when an explosion occurred. The explosion ruptured the flask, which expelled glass shards; one penetrated into the chemist's neck, cutting the carotid artery. The chemist suffered many other cuts and died. He was working alone and there were no witnesses. The chemist was wearing safety glasses, a lab coat, gloves, and safety shoes. He had been using a glass shield to protect himself from any potential explosions. He apparently removed the glass shield to prevent obstruction of his vision or to allow access while he removed the flask from the mechanical stirrer. He had graduated with a degree in chemistry and had received training on safety procedures with his job and safe operating procedures for the mixture of ANF.

Analysis

There was insufficient information provided to determine how much of each chemical was present, if the chemical mixture was the result of a validated and safe procedure, or if the quantity was appropriate for the procedure. Hydrogen peroxide can oxidize many organic chemicals and may have been used to oxidize diaminofurazan to ANF or trifluoroacetic anhydride or its acid decomposition product to trifluoroperoxyacetic acid, also a strong but unstable oxidizing agent. Removal of the flask from the mechanical stirrer may have provided enough energy to decompose potentially shock sensitive compounds, some of which may have accumulated in ground glass connections. Glassware must be clean and reagents free of metals; contamination can cause exothermic decomposition of hydrogen peroxide with release of sufficient heat to cause an explosion and ignite organic materials. It is unclear whether the "glass shield" referred to was a stationary shield that was placed in front of the apparatus (to protect against flying glass) or whether it was a face shield. However, engineering controls such as a safety shield and personal protective equipment must be used as appropriate for the task. It is possible that removal of the shield, whether it was a stationary shield or a face shield exposed the chemist's neck to the glass shards that killed him.

Use of hydrogen peroxide in organic oxidations must be performed with care, and reaction mixtures must be quenched upon completion. Use clean glassware and avoid contamination. Understand that energetic compounds may be shock and/or friction sensitive. Be aware that connecting and disconnecting vessels with threaded or ground glass joints may generate sufficient energy to initiate an event. Polytetrafluoroethylene (PTFE) sleeves are typically used in glass connections to minimize hazards due to friction. Know the hazards of mixtures of hydrogen peroxide with organic chemicals, and never remove mechanical barriers or personal protective equipment when performing a potentially hazardous activity.

Storage of Contaminated, Basic Hydrogen Peroxide

An outdoor metal tank containing up to 300 gal of high concentration hydrogen peroxide exploded at a laser-testing facility in California and was reported in 1999.²¹ No one was hurt. The hydrogen peroxide in the tank had begun to rapidly decompose, generating sufficient pressure to blow the tank into three pieces of shrapnel, which damaged the side of a nearby building. The tank had a pressure-relief system, but was not adequate to handle the situation that occurred. It was believed that the tank had accumulated basic hydrogen peroxide (BHP) over a period of three months of laser testing during which the BHP was returned to the tank after testing and recycled for additional testing. The BHP was a hydrogen peroxide solution containing potassium hydroxide, lithium hydroxide, and sodium hydroxide. The preliminary finding was that overpressure in the tank was caused by the rapid decomposition of the hydrogen peroxide due to long-term storage, reuse and consequent contamination of the hydrogen peroxide in the tank.

Analysis

The stability of BHP is inherently limited and its decomposition is accelerated by contamination, which could have occurred as a result of recycling the fluid. The pressure-relief system on the tank was not adequate to handle the resultant pressure due to hydrogen peroxide decomposition.

Avoid reuse of any hydrogen peroxide solutions and be aware that BHP is relatively unstable. Always assume that used hydrogen peroxide is contaminated and never return it to its original container. Dilute and dispose of it as soon as possible. Use tank monitoring for early warning of hazards and size the pressure relief system appropriately. Employ emergency stabilization as appropriate if it is safe to do so.

EXPOSURES

Ingestion of Hydrogen Peroxide

A near-fatal ingestion of hydrogen peroxide was reported in 1989.²² In this incident, the contents of a 1-pt bottle of 35 percent hydrogen peroxide were unintentionally ingested. The patient had stopped to obtain a drink of water, but mistakenly consumed the residual and unknown volume of a well-marked bottle of hydrogen peroxide, and within minutes vomited, collapsed, and experienced a brief tonic-clonic seizure. The patient survived, but aggressive airway management was critical.

Analysis

The label on the bottle was apparently not read or the hazards were not understood and the contents were ingested. Ingestion of hydrogen peroxide generates oxygen and over pressurizes the body.

Read labels on beverage containers before consuming contents. Never ingest hydrogen peroxide. Workers must be aware that hydrogen peroxide resembles water as a colorless liquid and must never confuse containers. Seek immediate medical attention in case of ingestion. In a press release issued by the Food and Drug Administration,²³ the agency warned against the use of hydrogen peroxide for human consumption. Thirty five percent hydrogen peroxide had been illegally promoted to treat AIDS and cancer, or had been mistaken for water and was drunk. At least one death and several injuries requiring hospitalization were reported in that press release to have occurred.

One Employee Killed, 2 Injured in Stripper Vessel Explosion

In a manufacturing process, soybean oil was used to make flexible plastic following epoxidation with hydrogen peroxide in a 1997 report.²⁴ After the main reaction process, the epoxidized oil was transferred to a vacuum vessel centrifuge then to a stripper vessel where steam removed water, acetic acid, and hydrogen peroxide product remnants. Two employees were checking steam traps on the first floor of the plant by tapping on them, but the steam traps were not removing any of the condensate. The employees readied two new traps as replacements after a batch in the vessel was processed. Condensate was drained out of the steam lines and after the drain valves were closed, the traps were apparently working and the stripper vessel's temperature began to rise to its set point. One of the two employees and a third employee went to the second floor to check the stripper. All appeared normal when suddenly the acidic water line near the ceiling, which contained water, acetic acid, and hydrogen peroxide, exploded, blowing out the second story wall. One employee was found dead on an adjacent roof area. Another employee was about 20 ft away from the stripper sight glass and was struck by flying debris and exposed to excessive noise, resulting in hospitalization. A third employee was walking 8 ft away from the bottom portion of the stripper on the first floor below, and also suffered injuries from flying debris and was hospitalized. The employer was issued citations for violations of 29 CFR 1910.119²⁵ (the Threshold Quantity (TQ) of hydrogen peroxide is ≥ 52 percent by weight is 7500 pounds) and 29 CFR 1910.120.²⁶

Analysis

A fluid transfer line containing water, hydrogen peroxide, and acetic acid exploded causing employee death and injuries. Hydrogen peroxide, when contaminated, can decompose generating heat and pressure. Employees had "tapped" the steam traps prior to the explosion; tapping may have dislodged potentially incompatible material. Peracetic acid, an oxidation product of acetic acid and hydrogen peroxide, may explode from heat or contamination.²⁷ There was insufficient information to determine if the system was adequately clean, sized with appropriate pressure relief, and designed to safely handle mixtures of hydrogen peroxide and its potentially explosive oxidation products.

Systems must be designed in compliance with applicable codes and standards, and personnel must be adequately trained to operate and to troubleshoot them, as appropriate. The OSHA Process

Safety standard contains requirements for preventing or minimizing the consequences of catastrophic releases of toxic, reactive, flammable, or explosive chemicals that may result in toxic, fire, or explosion hazards. The OSHA Hazardous Waste and Emergency Response standard requires that operations covered by the standard do not involve employee exposure or the reasonable possibility for employee exposure to safety or health hazards. The chemical reactions and their products, including wastes, must be well understood, and the materials of construction of the system must be compatible with the chemicals.

OCCUPATIONAL SAFETY & HEALTH ADMINISTRATION REPORTS

Seventeen accident reports concerning employee injury involving hydrogen peroxide, several of which involved multiple employee injuries, were found on the OSHA web site at the time of the preparation of this manuscript. These are accessed through the Statistics & Data → Accident Investigation Search feature (<http://www.osha.gov/cgi-bin/inv/inv1>). We categorized the 17 accident reports by cause and effect (type of injury) for statistical purposes as follows:

We found two major causes of injuries: reactive mixtures and explosive mixtures, as illustrated in Figure 3.

There were four accident reports in which the cause was a reactive mixture of hydrogen peroxide and other materials. Of these four reports, there were three causes of injury by exposure to gaseous products and one cause of injury due to both exposure to gaseous products and chemical burns. This is illustrated in Figure 4.

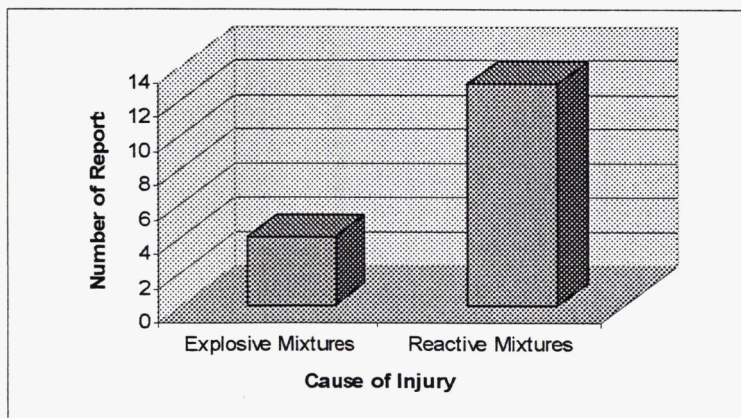


Figure 3. Major Cause of Injuries

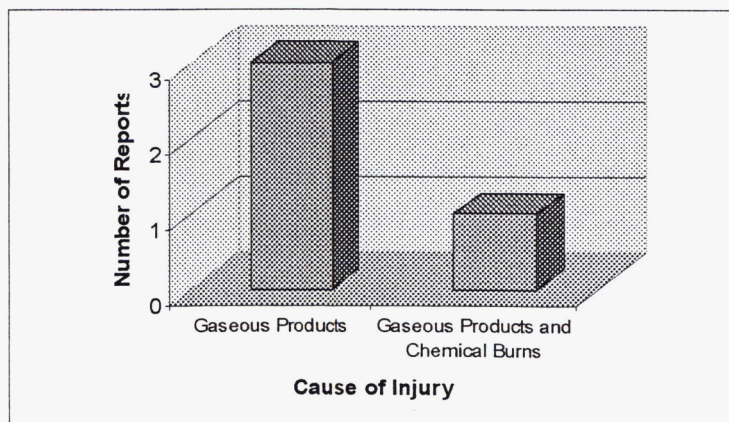


Figure 4. Effects of Reactive Mixtures

There were 13 accident reports in which the cause was an explosive mixture of hydrogen peroxide and other materials or in systems. Of these 13 reports, there were six causes of injury due to chemical burns, three causes of injury due to shrapnel, one cause of injury due to lacerations, abrasions, and internal injuries, and one cause of injury due to chemical and thermal burns. This is illustrated in Figure 5. There were two fatalities in which the causes were explosive mixtures; these fell in the cause of injury category due to shrapnel and were discussed earlier.^{20, 24}

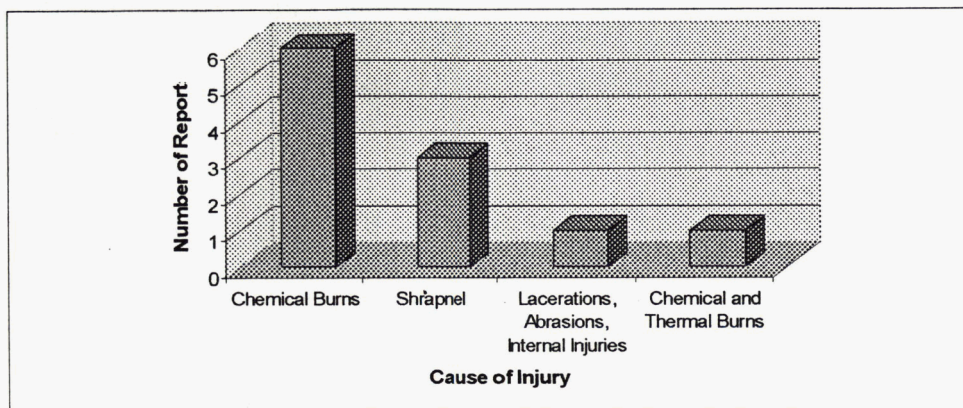


Figure 5. Effects of Explosive Mixtures

Each of the events described in these reports can be attributed directly or in part to the consequences of mixing hydrogen peroxide and reactive materials.

CONCLUSIONS

The examples provided in this paper are true and accurate to the limit of their traceability. The hazard analyses are intended to benefit anyone concerned with the hazards of working with or around hydrogen peroxide and hydrogen peroxide systems. Although the examples shown cover a wide range of applicable topics, many more examples exist.

In summary, the example accidents illustrated the effects of the following elements:

- Failure to recognize hazards
- Failure to follow established procedures
- Improper transportation and storage
- Contaminated hydrogen peroxide or mixtures of hydrogen peroxide with incompatible materials or fuels
- Failure to use appropriate engineering controls or wear appropriate personal protective equipment
- Exposure of the body to skin, eyes, and ingestion
- Injury or death from shrapnel

The lessons learned from these examples and others that have been reported should be reviewed with all personnel working with or around hydrogen peroxide and hydrogen peroxide systems.

REFERENCES

1. Bruce, R., G. Taylor, and P. Taliancich. "Rocket Propulsion Ground Testing with High Concentration Hydrogen Peroxide – Lessons Learned at the NASA John C. Stennis Space Center." Proceedings of the 5th International Hydrogen Peroxide Propulsion Conference, September 15-19, 2002, Purdue University, West Lafayette, IN.

**For Review Purposes Only
Not for Publication**

2. Schumb, W. C., C. N. Satterfield, and R. L. Wentworth. *Hydrogen Peroxide*. American Chemical Society Monograph Series, Reinhold Publishing Corporation, NY, 1955.
3. CPIA/M4, Liquid Propellant Manual. Chemical Propulsion Information Agency. Columbia, MD, 1994.
4. MIL-P-16005E. *Military Specification, Propellant, Hydrogen Peroxide*, Military Standard, United States Department of Defense, Washington D.C., 1968.
5. *Basic Hydrogen Peroxide Seminar, Version 9*. General Kinetics, LLC, Lake Forest, CA, September 2003.
6. Pinsky, M., R. Mikida, and H. Rosenhouse. "Transportation of 90 percent Hydrogen Peroxide (FMC 90 percent and 99.1 percent HTP: Process, Shipping, and Storage)." In the *3rd International Hydrogen Peroxide Propulsion Conference*. Stennis Space Center, MS, November 2000.
7. Wernimont, E., M. Ventura, G. Garboden, and P. Mullens. "Past and Present Uses of Rocket Grade Hydrogen Peroxide." In the *Second International Hydrogen Peroxide Propulsion Conference*, West Lafayette, IN, November 1999.
8. Wernimont, E. and M. Ventura. "Review of Hydrogen Peroxide Specification MIL-P-16005." *AIAA-01-3251, 37th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit*, Salt Lake City, UT, July 2001.
9. NFPA Journal. National Fire Protection Association. March/April (1992).
10. NTSB. *Hazardous Materials Incident Brief*. Accident DCA-99-MZ-001 October 28, 1998, National Transportation Safety Board, Washington D.C. www.nts.gov/publicn/2000/HZB00001.htm. Document received October 15, 2002.
11. 49 CFR 178.101. Code of Federal Regulations Title 49, Department of Transportation, Part 178.101, Subchapter C., Hazardous Materials Table. <http://www.myregs.com/dotrspa/>.
12. 49 CFR 173.202. Code of Federal Regulations Title 49, Department of Transportation, Part 173.202. *Non-bulk Packagings For Liquid Hazardous Materials in Packing Group II*. U.S. Printing Office, Washington D.C. (latest revision).
13. NTSB/HZM-88/02. *Hazardous Materials Incident Report*. In-Flight Fire, McDonnell Douglas DC-9-83, N569AA, Nashville Metropolitan Airport Nashville, Tennessee, February 3, 1988. National Transportation Safety Board, Washington D.C. September 1988.
14. NTSB/RAR-89/05. *Railroad Accident Report – Collision and Derailment of Montana Rail Link Freight Train with Locomotive Units, and Hazardous Materials Release*, Helena, Montana, February 2, 1989. National Transportation Safety Board, Washington D.C. December 1989.
15. 49 CFR 174.81. Code of Federal Regulations Title 49, Department of Transportation, Part 174.81 Subchapter C. *Segregation of Hazardous Materials*. U.S. Printing Office, Washington D.C. (latest revision).
16. Conner, W. V. "Hydrogen Peroxide Safety Issues." RFP-4599. UC-707 Health and Safety, DOE/OSTI-4500 (Rev. 75), EG and G Rocky Flats, Inc., Golden, CO, 1993.
17. Darnall, D. W. "Explosive Peroxides." *Chemical and Engineering News*, Vol. 56(47), 1978:47.
18. Wolf, S. and W. A. McNally. *Hydrogen Peroxide as a Torpedo Propellant*. Naval Underwater Ordnance Station, NUOS 360, Newport, RI (1963).

**For Review Purposes Only
Not for Publication**

19. Schmidt, E.W. *Hydrazine and Its Derivatives: Preparation, Properties, Applications, 2nd Edition*. Wiley-Interscience, NY, 2001.
20. OSHA 1993. Accident 170749618, Report ID: 0352420, Event Date: 07/02/1993, Inspection: 119559532, Thiokol Corporation.
<http://www.osha.gov/cgi-bin/inv/inv1xp?s=170749618004>.
21. Donnelly, J. "Peroxide Tank Blows Up At TRW Laser Plant, Prompting Questions." *Defense Week*, October 4, 1999.
22. Gibberson, T. P., Kern, J. D., Pettigerew III, E. W., Eaves, C. C., and Haynes, J. F. "Near- Fatal Hydrogen Peroxide Ingestion." *Annals of Emergency Medicine*, 1989, Vol. 18, p. 7.
23. *Industrial Strength Hydrogen Peroxide*, HHS News, Press Release PD89-18, U.S. Food and Drug Administration, Washington DC, April 13, 1989.
24. OSHA 1997. Accident 000999128, Report ID: 0552700, Event Date: 01/23/1997, Inspection: 126587047, Elf Atochem North America, Inc.
<http://www.osha.gov/cgi-bin/inv/inv1xp?s=000999128004>.
25. 29 CFR 1910.119. Code of Federal Regulations Title 29, Occupational Safety and Health Administration, Department of Labor, Part 1910, Occupational Safety and Health Standards, Section 119, *Process Safety Management of Highly Hazardous Chemicals*, U. S. Printing Office, Washington D.C. (latest revision).
26. 29 CFR 1910.120. Code of Federal Regulations Title 29, Occupational Safety and Health Administration, Department of Labor, Part 1910, Occupational Safety and Health Standards, Section 120, *Hazardous Waste Operations and Emergency Response*. U.S. Printing Office, Washington D.C. (latest revision).
27. ERG 2000. *2000 Emergency Response Guidebook*, U.S. Department of Transportation. Washington DC, <http://hazmat.dot.gov/guidebook.htm>.