

Safety Bulletin

U.S. Chemical Safety and Hazard Investigation Board



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REMOVAL OF HAZARDOUS MATERIAL FROM PIPING SYSTEMS

Introduction

Chemical and refinery facility personnel open piping and equipment to perform routine maintenance, add/replace components, or modify pipe routing. The piping may contain hazardous material, such as flammable hydrocarbons, toxic chemicals, or thermally reactive chemicals. Safe work practices dictate the removal or mechanical isolation of hazardous material from piping and equipment (e.g., using valves or blind flanges) before commencing work.

This Safety Bulletin identifies specific tasks that facilities should include in all work activities involving piping or equipment opening to ensure the complete removal of hazardous material. In addition, guidance is provided on implementing generic (plant-wide) procedures for nonroutine work activities.

Peroxide Explosion and Flash Fire

In January 2004, the U.S. Chemical Safety and Hazard Investigation Board (CSB) investigated an explosion and fire at a Huntsman Petrochemical Corporation facility in Port Neches, Texas. During a steam purge for a piping modification that required line opening and hot work (i.e., cutting and welding), a peroxide/alcohol mixture was heated above its thermal decomposition temperature. The mixture was trapped in a low point along a 900-foot-long, 6-inch process pipe. The resulting explosion and fire seriously injured two employees.

Plant personnel incorrectly believed that a nitrogen gas purge preceding the steam purge had removed all liquid from the pipe. However, an unknown quantity of a thermally reactive peroxide/alcohol mixture remained in an unidentified low-point trap in the pipe.

As the steam heated the trapped peroxide, it exothermically decomposed and overpressurized the pipe, causing it to rupture (Figure 1).

The venting flammable vapor then ignited, resulting in a flash fire that burned two employees and significantly damaged nearby equipment (Figure 2). The automatic deluge system and the fire brigade suppressed the fire.

Incident Causes

Incomplete Removal of Hazardous Mixture

Huntsman operating and maintenance procedures highlighted the hazards of incomplete removal of toxic, flammable, or reactive chemicals from pipes and equipment. The normal unit startup procedure required clearing the peroxide/alcohol from the line using a nitrogen gas purge.

Plant personnel were aware of the hazards associated with leaving peroxide in a closed piping system. However, the procedural steps for the nitrogen gas purge were

● Figure 1. Ruptured pipe/valve and fire damage.



- Figure 2. Floor stanchion and piping tangled in damaged overhead electrical conduits.



ineffective in removing all of the hazardous mixture from the pipe.

The modification work order for the infrequently used startup line required hot work on the pipe; it included a nitrogen purge before opening the line, similar to the normal line clearing procedure. This activity was intended to clear thermally reactive liquids from the

line prior to steam purging to remove all traces of flammable material. Steam purging was a prerequisite to performing hot work on any piping or equipment.

The pipe routing contained a low-point segment almost 300 feet long (Figure 3), with a volume in excess of 350 gallons. The pipe was routed more than 20 feet above-ground in an overhead pipe rack that obscured the long, shallow low-point section (Figure 4).

Operators were unaware that the nitrogen gas purging, required by the operating procedure, was ineffective in removing all of the peroxide/alcohol mixture in the low point. Preparing the line for hot work required an additional nitrogen purge as a precaution, then the steam purge to complete the removal of residual hydrocarbon vapor. This was the first time hot work had been specified for this line.

It was only when the pipe was purged with steam in preparation for the approved pipe modification that the peroxide overheated, causing it to decompose and over-pressurize the pipe.

Inadequate Verification of Pipe Routing

The liquid could have been safely removed before the steam purge. As shown in Figure 3, both ends of the long pipe section contained low-point drains.

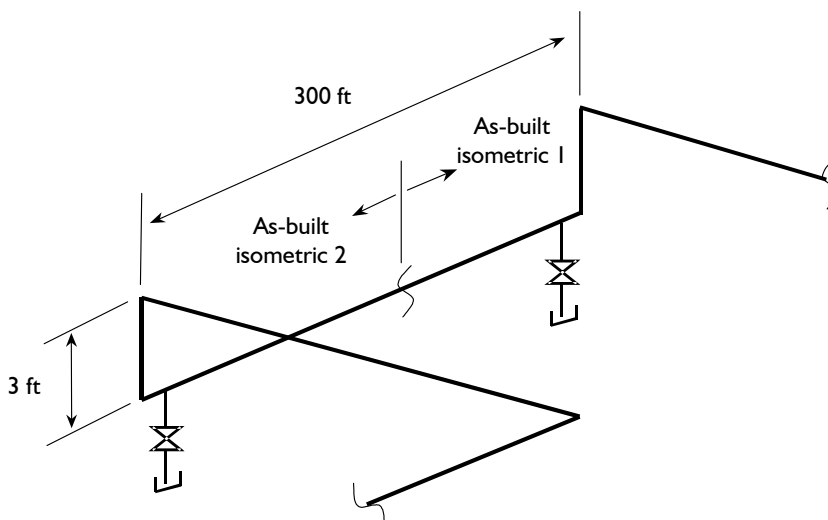
A comprehensive review of the as-built drawings, combined with a walkdown of the entire peroxide/alcohol transfer pipe – if required in the management of change (MOC) process – would have likely identified the low-point trap. Although the low-point piping segment and two available drains were shown on the as-built piping isometrics, the low point was split onto separate sheets (Figure 3),

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- Figure 3. Unused low-point drains on piping segment.



- Figure 4. Piping and electrical conduits in congested, overhead pipe rack.



making it difficult to recognize the liquid trap. Furthermore, the piping modification involved only one of the isometric drawings.

As in most large chemical manufacturing facilities, many miles of piping were routed throughout overhead pipe racks (Figure 4). There is a high probability that some low points will be overlooked unless a pipe walkdown focuses on identifying both low points and installed drains.*

Unsafe Heating of Thermally Sensitive Chemicals

Using the generic steam purging procedure on the peroxide/alcohol pipe created an unanticipated hazard. The steam temperature exceeded 380°F, which is significantly above the decomposition temperature of the peroxide.

*After the incident, Huntsman conducted a comprehensive walkdown of all peroxide piping and identified additional low-point traps. An MOC work order was implemented to eliminate each trap.

The high-temperature steam flowed through the piping system for nearly 1.5 hours, and the trapped peroxide began to decompose. Pressure buildup ultimately caused a valve gasket to fail and release flammable vapor.

At about the same time, the pipe upstream of the leaking valve burst, releasing additional flammable liquid and vapor, further spreading the fire. The pressure concussion also caused additional damage to equipment in the area.

Inadequate Hazards Review of Procedure Revision

Complex pipe routing and equipment configurations often contain low points that trap hazardous material. Flushing the pipe with water or other suitable liquid may effectively remove the material but generates a significant quantity of waste liquid. Furthermore, liquid that remains in low points or equipment may cause unsafe conditions or degrade piping.

To reduce waste volume, Huntsman revised the procedures to substitute inert gas purging for water flushing. However, purging with inert gas or steam does not necessarily remove trapped liquid.

The revised procedure:

- Failed to address the importance of identifying low points in the piping.
- Failed to require the use of low-point drains to remove trapped hazardous liquids.

Proper identification and use of drains ensures the complete removal of hazardous liquids.

The revised inert gas purging procedure was applied to process pipes containing thermally unstable liquids without adequately considering the hazards if these liquids remained in the pipe during the steam purge.

High-temperature steam — used to remove traces of flammable vapor from the pipe prior to performing hot work — may cause thermally unstable liquids to violently decompose. This is precisely what occurred with the peroxide/alcohol mixture in this incident.

Lessons Learned

Nonroutine Pipe and Equipment Opening

Opening chemical process piping and equipment can be extremely hazardous. It should never be considered routine work.

Facilities handling hazardous chemicals should:

- Perform a complete walkdown of all piping and components between the isolation devices. Update as-built drawings as necessary.

- Use as-built drawings of the affected piping to identify all branch connections, isolation valves, low-point drains, and high-point vents.
- Prepare a specific written procedure for removing, flushing, and purging hazardous material from the system. Consider the consequences if flushing liquid remains in the system after the work is complete.

Unit-Specific Procedures

Unit-specific procedures should be used to ensure the safe conduct of nonroutine activities, such as steam purging of process lines that handle thermally unstable liquids. Facilities should:

- Review planned steps against unit-specific hazards.

- Update unit-specific procedures as necessary to address unique characteristics of the activity, especially when modifications are involved.
- If a modification activity includes the use of generic safety procedures, clearly identify applicable constraints (e.g., specify additional inspection steps to verify removal of all energy sources, including thermally reactive chemicals).

For Further Reading

U.S. Chemical Safety and Hazard Investigation Board (USCSB), 2002. *Hazard Investigation, Improving Reactive Hazard Management*, Report No. 2001-01-H, December 2002.

USCSB, 2002. *Investigation Report, Steel Manufacturing Incident, Bethlehem Steel Corporation, Burns Harbor Division, Chesterton, Indiana, February 2, 2001*, Report No. 2001-02-I-IN, January 2002.

USCSB, 2002. *Investigation Report, Thermal Decomposition Incident, BP Amoco Polymers, Inc., Augusta, Georgia, March 13, 2001*, Report No. 2001-03-I-GA, June 2002.

USCSB, 2001. *Investigation Report, Refinery Fire Incident, Tosco Avon Refinery, Martinez, California, February 23, 1999*, Report No. 99-014-I-CA, March 2001.

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