

Management of Time Sensitive Chemicals (I): Misconceptions Leading to Incidents

Jim Bailey (Bechtel Jacobs, Oak Ridge), David Blair (Heritage-ETS), Lydia Boada-Clista (DOE Ohio Field Office), Dan Marsick (DOE-EH), David Quigley (Y-12), Fred Simmons (SRS), Helena Whyte (LANL-HSR-5)

Introduction

Time-sensitive chemicals are those chemicals that when stored for prolonged periods can develop hazards that were not present in the original formulation. These additional hazards develop from inappropriate and improper storage conditions as well as simply storing the chemicals too long. In the field of chemical management, unfortunately we all too often hear of incidents involving time-sensitive chemicals that occurred and their resulting injury and/or property damage. The following incidents demonstrate the very real need for safer management and better understanding of the hazards of time-sensitive chemicals.

Multi-Nitro Chemicals

In the field of time-sensitive chemicals, many have encountered those hazards associated with a multi-nitro chemical such as picric acid. Most multi-nitro chemicals are shipped with a stabilizer, usually water, to prevent them from drying out, and becoming shock sensitive over time. Additionally, some multi-nitro chemicals are not stable if permitted to come into contact with a metal, and then, over time and improper storage, allowing them to dry out.

One example of a multi-nitro chemical developing additional hazards during prolonged storage occurred in the laboratory of a large university (1). Environmental health and safety personnel discovered glass-stoppered bottles of collodion while inspecting

laboratories. Collodion, a nitrocellulose derivative, is commonly supplied in an ether and alcohol solution; however, these bottles did not have any liquid remaining. Several bottles looked like they contained what appeared to be a dry material resembling a hockey puck on the bottom. One of the bottles contained a rope of solid material that was growing from the bottom of the container up to and encapsulating the glass stopper. The manufacturer specific MSDS for this collodion formulation contained such statements as “Dangerous when dry” and “Material containing less than 25% alcohol is an explosive”. Obviously, the volatile solvent evaporated resulting in the now dry nitrocellulose material. The fact that a fairly volatile liquid was improperly stored in glass-stoppered bottles for a prolonged period created this now dangerous situation since any attempt to open these bottles could have produced an explosion.

The explosive nature of multi-nitro aromatic chemicals can be seen in this next example. Commonly, when a time-sensitive chemical such as dehydrated picric acid is discovered, a bomb squad is called to remediate the problem. In this example, a bomb squad was called to remove three containers of dried out picric acid discovered in a high school building in a densely populated area (2). The bomb squad used a robotic device to place the containers, one at a time, inside a partially covered, heavy steel, bomb containment device prepared to receive the bottles. As the third container just cleared the lid of the bomb containment device, there was an explosion. The heavy steel lid was propelled into the air and landed some distance away creating a modest crater adjacent to a highway patrol car. The cause of this incident was attributed to the slight agitation of the dried out bottle of picric acid as the robotic device moved the container into the bomb containment device. This slight agitation provided enough mechanical shock to initiate the explosion.

The third example is a warning issued (3) by the Federal Bureau of Investigation to bomb technicians on the hazards of picric acid mixtures. On November 10, 1982, in the chemistry laboratory of a manufacturing plant, a container of picric acid spontaneously exploded. The investigation revealed the bottle contained approximately two ounces of picric acid that had been mixed with an undetermined quantity of ferric chloride and the mixture was approximately four years old. The FBI warning stated, although the substance is stable in a liquid state, it gradually crystallized into iron picrate, which is an extremely sensitive, high explosive disposed to spontaneous detonation. Fortunately, no injuries were incurred as a result of the blast even though an employee of the firm was situated approximately 20 feet away from the explosion. The FBI warning advises that picric acid and its admixtures are extremely hazardous, and extreme caution should be exercised in their handling.

A hazardous waste management company was testing approximately 1500 bottles of unknown chemicals (4). Prior to conducting standard hazardous characterization tests, chemical technicians were opening each container by simply twisting off the lids. One of the containers was a small, dark green, glass bottle with a rusty metal lid. The lid could not easily be removed so a pair of channel lock pliers was obtained. As the lid began to move with the use of the pliers, there was an immediate explosion. Glass shards embedded in a nearby chair were covered with a light yellow powder; infrared analysis indicated the material was picric acid. The combination of picric acid and the metal lid resulted in the formation of metal picrates that, over time, dried out in the threads of the container. Friction from twisting the lid initiated the explosion. From a chemical management perspective, this incident is important for two reasons. First, care needs to

be exercised in safely accessing the contents of containers that have been stored for prolonged periods. Secondly, when a researcher leaves a laboratory, the chemicals should be inventoried with a particular emphasis on safe management of time-sensitive chemicals present.

Peroxide Forming Chemicals

Of the time-sensitive chemical situations most commonly encountered, peroxide forming chemicals seem to attract the most attention as can be shown by the number of published incidents (5-8). As the following incidents illustrate, there are some common misconceptions that can create a particularly hazardous situation if peroxide forming, time-sensitive chemicals are improperly managed.

An incident occurred involving an “empty” ether can found in a laboratory trashcan (9). A common misconception is that old, “empty” ether cans do not present a hazard. A technician collected the empty ether can in a pail with other items and transported it to a chemical fume hood in the hazardous waste storage facility. The following week a specialized chemical management team arrived to stabilize containers of time-sensitive chemicals. The technician remotely accessed the empty, metal can and introduced a dilute ferrous salt solution. As soon as the liquid entered the metal can, there was an explosion, and the metal can disappeared into many small pieces. A large fireball was observed exiting the top, front of the chemical fume hood. The cause of the incident was believed to be the reaction of peroxide crystals in the “empty” ether can with the mild reducing agent that was added.

Another common situation involved the proper disposal of older “Squibb” cans of ethyl ether. A previously opened, old “Squibb” can of anesthesia grade ethyl ether that contained

approximately 4% ethyl alcohol as an inhibitor was being stabilized (9). Because the inhibitor was thought to be present, this container of ether was not viewed as particularly hazardous. After remotely accessing the small metal can, an aliquot was withdrawn for application to a peroxide test strip. Since the liquid level was low, the can was tilted and a pipette extended into the liquid. After applying the liquid to the test strip, color developed representing a concentration of approximately 50-ppm peroxides. As the can was up righted, there was an immediate explosion resulting in a fireball that filled the fume hood. Cause of the incident was believed to be the formation of peroxide crystals in the top portion of the can. The slight handling of the metal can during the testing was enough mechanical shock to produce the explosion.

A nice shiny, metal can of ether is rarely viewed as potentially dangerous. Two nice, shiny cans of ether that had been continually used for four months, and subsequently stored for eighteen months, were to be tested for peroxides (10). The containers were observed to be one third full and tests indicated the liquid contained over 100 ppm peroxides. After chemically reducing all measurable peroxides using a ferrous salt solution, each can was inverted to wet all inside metal surfaces. Each solution was retested, and again found to have greater than 100 ppm peroxides. It was thought that the inverting of each can caused the dissolution of peroxide crystals located in the upper inside surfaces of the can. This incident illustrates how the outward appearance (e.g. a new, shiny looking metal can) does not necessarily indicate a safe situation.

Another frequently encountered misconception is that refrigeration will stabilize the time-sensitive chemicals. A specialized chemical management team was sent to remediate numerous containers of peroxide forming chemicals stored in a walk-in refrigerator (9).

Because of unusual safety considerations, it was decided that the stabilization work take place outside a door at the end of the rather long hallway. One at a time, each of two, old rusty cans of ethyl ether were put into separate pails containing vermiculite for cushioning and hand carried down the hallway toward the exit door. About fifteen paces down the hallway, one of the cans exploded. The cause of this incident was believed to be the formation of solid peroxide crystals in the metal can of ether. It was thought that the change in temperature provided enough physical stress on the solid peroxide crystal structures to initiate the explosion. The effectiveness of the inhibitor during refrigeration of a peroxide former will be discussed in a subsequent article.

It is commonly thought that measuring peroxide concentrations in solution using dip strips or other methods is accurate when this may not necessarily be the case. While stabilizing a container of sec-butyl alcohol over 20 years old, the initial peroxide test showed 30 ppm. (11). To chemically reduce the peroxides, a dilute ferrous salt solution was added, and the alcohol retested. After the addition of the reduction agent, the test strip indicated a peroxide concentration much greater than 100 ppm. The chemical seemed to be producing peroxides. Testing of other, old, short-chained alcohols in the 3 to 8 carbon range produced similar results (12). It was thought that this was due to the formation of polyperoxides which the test strips could not measure.

The polyperoxides may represent additional hazards when present in different solvents such as tetrahydrofuran (THF). For example, a glass container of THF approximately 14 years old was remotely accessed for stabilization (13). A thermocouple device was attached to the side of the container. The peroxide concentration was measured at 10 ppm and this low concentration of peroxides did not seem to present any safety concern. No

temperature change was observed during the neutralization of the peroxides using a dilute ferrous salt solution. A hydroquinone/ethanol solution was prepared and added to the container to inhibit the further formation of peroxides. Almost immediately the solution temperature rapidly increased. The THF container was placed in a previously prepared ice bath and the thermocouple relocated to the top of the bottle. The temperature at the top of the container increased to 136 deg. F, and remained there for at least twenty minutes. There was a serious risk of fire and explosion had the ice bath not been available. Similar behavior was observed in other efforts to stabilize THF (13).

Materials That Generate Additional Hazards Over Time

Chloroform should be treated as a time-sensitive chemical especially if it is not stabilized or is stabilized with amylene. In 1998, four students at the University of California, Los Angeles, were mildly poisoned by phosgene after using chloroform that had been stored at room temperature for three years in a brown glass bottle (14). Analysis of the container showed phosgene concentrations of 11,000 ppm in the liquid, and 15,000 ppm in the vapor space above it.

Generation of Time-Sensitive Metal Fulminates

A commonly used characterization test for aldehydes requires Tollen's reagent which is a solution containing silver nitrate, dilute sodium hydroxide, and ammonium hydroxide. Tollen's reagent solution, if stored for too long, can become unstable and explosive. An explosion occurred as a student put a pipette into a storage bottle of Tollen's reagent that was not freshly prepared (15). Several students were hospitalized with eye injuries as a result of the explosion that sprayed the students with glass and the caustic Tollen's reagent. A contributing factor in this instance was that an excess amount of Tollen's

reagent was prepared and stored for future use in this and subsequent experiments.

Heavy Metal Acetylides Formation

A commonly made error is to store chemicals in containers that are incompatible for long term storage. Figure (1) shows calcium carbide stored in a glass container with a bulging metal lid (16). The screw on lid present on this container was manufactured from metal with a high brass content. Upon prolonged storage, the calcium carbide reacted with moisture in the air to produce acetylene gas. The acetylene gas reacted with copper and other heavy metals present in the high brass content lid. The product of this reaction was heavy metal acetylides which were now located in the threads of the cap. Heavy metal acetylides of this type are extremely unstable and are prone to explosion. Simply the act of twisting the lid or bumping the container could provide enough energy to initiate an explosion.



Figure 1- Calcium Carbide Stored In a Glass Container With a High Brass Content Metal Lid. Note the Bulging Lid Indicating Acetylene Gas Inside The Container.

Time-Sensitive Issues and Gas Cylinders.

Another example of a chemical that is incompatible with its container over prolonged storage is anhydrous hydrogen fluoride (AHF). Anhydrous hydrogen fluoride is a colorless, corrosive and toxic liquid normally packaged in mild steel cylinders under its own vapor pressure of 2.1 kPa (0.3 psig.) at 20 °C. AHF over time will react with the mild steel of the cylinder to produce hydrogen which is a nonliquefiable gas. The build up of hydrogen gas will cause the pressure inside the cylinder to increase. Numerous incidents have been reported of sudden failure of AHF gas cylinders due to over pressurization (17). This usually occurs with AHF that has been in storage over a long period of time, typically for 15-25 years. If this over pressurization occurs in a cylinder with a pressure relief device, then the pressure relief device will actuate and allow the contents of the cylinder to be released. If no pressure relief device is present, such as on lecture bottles, then the over pressurization can result in the catastrophic failure of the cylinder (Figure 2). One lecture bottle of AHF stored for 14 years developed an estimated pressure of 2,400 psig. that was in excess of the nominal 1800 psig. cylinder pressure rating. A similar situation was recently reported in which anhydrous hydrogen bromide (AHBR) was stored for long periods of time in lecture bottle cylinders (18). Some of these lecture bottles of AHBR were found with pressures that, again, exceeded the 1800 psig. pressure rating of the cylinder. No instances could be found involving anhydrous hydrogen chloride cylinder over pressurizations.



Figure 2 – Anhydrous Hydrous Fluoride Cylinder, Before and After Catastrophic Failure. Note How The Failure Has Resulted in Fragmentation of The Cylinder.

A unique problem observed to occur with older gas cylinders containing corrosive gases involves valve degradation or the safety relief device. Many of these cylinders have been found with inoperable valves that will not release gas when the valve wheel is turned to open the valve. Another hazard is that attempts to open the valve can result in the entire valve stem being ejected from the valve body (19). Prolonged storage of corrosive gases in gas cylinders can corrode pressure relief devices causing them to fail. Failure of the pressure relief device or ejection of the valve stem (Figure 3) will allow the entire contents of the gas cylinder to be released. Cylinders containing corrosive gases should be very carefully managed.



Figure 3 – Valve Degradation With Anhydrous Hydrogen Bromide. The hole on the left has corroded over time. An original valve is on the right.

Conclusion

Several issues have been described in this paper. First, time-sensitive chemicals continue to be stored for so long that additional hazards are created that can put workers at increased risk. Second, workers many times do not realize that these materials have additional risks present which makes them even more dangerous. Third, the chemistry and management of time-sensitive chemicals is not well understood. Lastly, it appears that, when a time-sensitive chemical is stored too long and discovered, workers are unsure of how to safely mitigate or dispose of them. What is needed is a better understanding of the chemistry of time-sensitive chemicals, proper management techniques to control them, and appropriate procedures and properly trained personnel to mitigate aged time-sensitive chemicals when they are discovered. These topics will be discussed in subsequent papers.

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