Peroxide-Forming Chemicals

4 Ways to stop explosions, injuries, and added expenses:

1) Track shelf life
   A) label when tested and when to retest
   B) date when received
2) Handle with proper personal protective equipment
   A) gloves
   B) googles/safety glasses
   C) flame-resistant lab coat
   D) training
   E) Ask [the Dept. of Chemistry and Dept. of Environmental Health & Safety] for help
3) Store properly
   A) flammable storage cabinet if applicable
   B) avoid
      i) heat (keep in a cool place)
      ii) impact
      iii) friction
      iv) light (keep in a dark place)
4) Buy the right amount
   A) based on what will be used
   B) reduce the disposal of any un-used material (Dubiel).

The Department of Chemistry wants you to learn from our experiences.

Amides, Dioxane, Ethers, secondary alcohols, and Tetrahydrofuran (as well as other cyclic ethers) must be checked for peroxides. The University of Pittsburgh Department of Environmental Health and Safety (EH&S) recommends that all peroxide-forming chemicals should be tested every six months for peroxide content, and any chemicals that test positive should either be purified before use to remove the peroxide or discarded as chemical waste and replaced with fresh material. (http://www.ehs.pitt.edu/assets/docs/peroxide-forming.pdf). Ken Migliorese, a previous staff member, emailed the Department of Chemistry to remind us of the importance of doing peroxide testing on a

regular basis. The need to test for peroxides was made clear to us by a series of unfortunate explosions which occurred in the undergraduate organic teaching labs in 2008. We had multiple defective layers of protection that caused failures of safety measures and three catastrophic errors (Reason). The errors, or incidents, were three separate explosions that occurred in three separate laboratories on three separate days. Different bottles of the same reagent were used in each of these instances. The explosions occurred during a simple distillation to identify an unknown pure liquid by boiling point determination. Before the labs were run, instructors were cautioned not to let their students distill out all of the flask's content.

On Monday, January 28, 2008, while disassembling a distillation apparatus, there was an explosion. This first explosion was not reported until the Wednesday afternoon instructor meeting.

In the evening on Tuesday, January 29, 2008, a student distilled their unknown reagent to dryness. Instead of letting the system cool, the set-up was touched and exploded upon slight jarring. The student was cut on three different places of her forehead. The student was escorted to the emergency room by the University of Pittsburgh Police Department (the Pitt Police). Her cuts were checked for glass, and she did not need stitches. The instructor cut his finger while cleaning up the debris, afterward he had his hearing medically evaluated, and it was fine. The Tuesday explosion was reported the next morning. There was a meeting for the organic instructors that afternoon.

On Wednesday, January 30, 2008, after the instructors were directly told about the dangers of distilling to dryness, another explosion occurred. This time the distillation flask was reported not to be dry. The student noticed a white vapor moving above the liquid. While talking to the instructor and touching the condenser, an explosion occurred within seconds. The instructor suffered a minor cut on her lower lip while the student got several cuts on her face and glass stuck between her teeth. She also complained of pain and temporary loss of hearing in one ear. The instructor called the Pitt Police, who were not available for another 45 minutes. The instructor drove the student to the emergency room. One piece of glass embedded in the student's face was removed, her neck was x-rayed to look for more glass.

When the student returned to class the next week, she said she was absolutely fine (Migliorese). The third explosion was reported, and the unknowns were removed from the teaching labs and held for testing by the Department of Chemistry.

2-Propanol, "Unknown B", was the common reagent in all three explosions. The safety document available at the time (a Material Safety Data Sheet for 2-Propanol) clearly warned about the potential of organic peroxide formation and the possibility of explosions if the organic peroxide containing residue is heated or shocked (Migliorese). A Material Safety Data Sheet (an MSDS) is the predecessor of our current Safety Data Sheets (SDS). Samples of the 2-Propanol were checked by the mass spectrometer and several high molecular weight components were identified (mass/e^- 200-300). 2-Propanol unknowns were tested for organic peroxides with Potassium iodide, Water, and Starch solution. The bottles were found to contain significant quantities of organic peroxides using a published University of Washington EH&S method (EH&S Guidelines for Peroxide Forming Chemicals). The Washington EH&S method is similar to a Sigma-Aldrich Potassium Iodide Indicator method (Solvents Peroxide Forming Solvents).

In an effort to stop this type of problem from happening again, we made several changes at multiple levels. The first failure occurred on the level of chemical storage. The "unknown" was stored in a clear glass bottle which once contained a concentrated acid. At the start of each semester, new material was continually added to the old reagents to fill up the containers. Today we buy new amber glass safety coated bottles and replace the containers after 2 years of use. Amber glass may help keep out UV light and stop catalysis of organic peroxide formation.

The second layer of protection failed when we did not review the MSDS. The explosion happened with three samples of "Unknown B" that only contained 2-Propanol. The MSDS at the time said NOT to distill the 2-Propanol because of the potential to concentrate any peroxides formed (Fisher Scientific). 2-Propanol, a secondary alcohol, had formed into some potentially explosive organic peroxides. Today we do not use 2-Propanol as a boiling point unknown.

We only heard about the first explosion after another explosion had happened – a third failed layer of protection. Today we have a policy to report incidents within 24 hours, along with a form to hand into the undergraduate stockroom about lab issues including, but not limited to, leaks or problems with certified chemical fume hoods. That way we can know about any issues that need to be corrected.

The fourth level of failure was with quality control. We never tested the boiling point unknowns for peroxide content. Today we test the unknowns we distill for organic peroxide content, plus any other material that is or contains 2-Propanol, Amides, Ethers, etc. When testing, the test strip is dipped into a sample of the anhydrous flammable solvent and then Distilled Water is added to the strip. The peroxide test strip turned black when "Unknown B" was tested. That type of strip is ten times less sensitive the strips we now use. The test strips contain Starch and Potassium iodide, and when mixed with Water the analyte can turn the strip any degree of blue. Turning the test strip black meant there was a significant amount of peroxides in the 2-Propanol, that were beyond the scale of the test strip.

Butylated hydroxytoluene (BHT) stabilized Diethyl ether passes the ACS certified reagent standards when below 1 ppm of organic peroxides. Today we test for organic peroxides every 6 months, and we dispose of any material above or equal to 3 ppm. This would be a light sky blue color on a test strip.

http://www.nexternal.com/gallade/images/Env_test_quant.jpg

Today we have a positive hand-off measure. The bottles are tagged and the labels contain the test date, quantity of measurable organic peroxides, analyst's initials, and a re-test date.

Lack of proper equipment was the fifth factor contributing to the accidents. The students should not distill to dryness, but the last item disassembled from the distillation apparatus would be the round

bottom boiling flask from inside the, still warm, heating mantle. The distillation process in the teaching labs has since changed. We now have lab jacks, that way the heating mantle can be dropped down and pulled away from the flask when the heat is turned off.

It is well known that the presence of unintended peroxides can modify the course and outcome of many chemical reactions. Since the Department of Chemistry instituted this testing program in 2008, we have had no reported accidents involving peroxide-contaminated chemicals (Migliorese).

Upon reviewing current SDS, there are surprising inconsistencies in the Storage and the Stability and Reactivity sections of SDS's for 2-Propanol. SDS's from Fisher, Flinn Scientific, and Sigma-Aldrich were reviewed. A Thermo Fisher Scientific SDS does not seem to indicate the potential for organic peroxides to form. The Sigma-Aldrich SDS clearly notes the potential for organic peroxides to form. Plus, the Flinn Scientific SDS says "Shelf life: Fair. Organic peroxides may develop if exposed to light and air, which can result in explosions, especially when distilled. Avoid prolonged storage," under the Stability and Reactivity section ("Isopropyl Alcohol."). **The Department of Chemistry recommends using the SDS from the vendor or manufacturer that your material comes from.**

Please contact the Department of Chemistry and/or EH&S (412-624-9505) if you have further questions. To help with this testing EMD Millipore Sigma sells Catalog number 1100110002 Peroxide Test Method: colorimetric test strips 0.5 – 2 – 5 – 10 – 25 mg/L H_2O_2 in packs of 25 each. Other scientific suppliers sell similar test strips.

External Resources:

Peroxide Forming Chemicals Video on You(Tube) Published on Aug 20, 2014 by Triumvirate Environmental -- https://youtu.be/s8iB1zbg7Cc

Peroxide Formers Best Practices Online
By Ted Dubiel
http://www.triumvirate.com/blog/4-ways-you-could-be-mismanaging-your-peroxide-formers

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