TerranearPMC Safety Share

Week of May 16, 2016– Peroxides

Peroxides: These are chemical compounds that contain an oxygen–oxygen single bond or the double oxygen anion, $O2^{-2}$. One of the first synthetic peroxides, barium peroxide, was synthesized by Alexander von Humboldt in 1799 as a by-product of his attempts to decompose air. Nineteen years later, Louis Jacques Thénard recognized that this compound could be used for the preparation of a previously unknown compound, which he described as *oxidized water:* now known as hydrogen peroxide.

Many of us are familiar with hydrogen peroxide, as it is used for simple first aid when cleaning cuts. While hydrogen peroxide is considered a hazardous material due to its capability to cause severe burning of the eyes, skin and upper respiratory tract, the type we have in our medicine cabinets is generally a 3% solution (the remainder being water).

Because of its corrosiveness, peroxides have a bleaching effect on organic substances and therefore, are added to some detergents and hair colorants. Other large-scale applications include medicine and chemistry, where peroxides are used in various synthesis reactions or occur as intermediate products. With an annual production of over 2 million tons, hydrogen peroxide is the most economically noteworthy peroxide.

The most apparent concern of organic peroxides is their instability. As such, they can accidentally initiate explosive polymerization in materials with unsaturated chemical bonds. Most notably, *triacetone triperoxide* (TATP) and *hexamethylene triperoxide diamine* **(**HMTD) are highly susceptible to accidental detonation by shock, friction, and sparks. TATP is sometimes referred to as the "Mother of Satan" among certain clandestine militant groups.

And while peroxides are a manufactured commodity, TATP as well as other peroxides can accidentally form as a by-product in many commonly used reactions. These reactions have been known to occur during the synthesis of 3,4-Methylenedioxymethamphetamine or (MDMA), more commonly known as ecstasy or “E,” and the industrial production of phenol. This can occur through the accidental mixing of ketone solvents (most commonly, acetone) with waste materials containing hydrogen peroxide or other oxidizers and leaving the mixture standing for several hours. In addition, many liquid ethers in the presence of air, light and metals (which act as catalysts) slowly, over a period of months, form highly unstable ether peroxides such as diethyl ether peroxide. Therefore, ethers are often stored above potassium hydroxide, which not only destroys peroxides but also acts as a powerful desiccant (hygroscopic substance that induces or sustains a state of dryness).

Because peroxides are also strong oxidizers, they easily react with skin, cotton and wood pulp. For safety reasons, peroxide compounds are stored in a cool, opaque container, as heating and illumination accelerate their chemical reactions. Small amounts of peroxides, which emerge from storage or reaction vessels are neutralized using reducing agents such as iron (ferrous) sulfate. The safety measures in industrial plants that produce large amounts of peroxides require that equipment is located within reinforced concrete structures with foil windows, which would relieve pressure and not shatter in case of explosion. In addition, the products are bottled in small containers and are moved to a cold place promptly after the synthesis. The containers are made of non-reactive materials such as stainless steel, as well as some aluminum alloys or dark glass.

Obviously, peroxides need to be handled with extreme care. This means proper storage, handling as well as disposal.

The first step to properly protect ourselves and coworkers is to ensure these materials are properly stored. For instance, organic peroxides should always be stored in the containers that the chemical supplier recommends. Normally, these are the same containers in which the material was shipped. Repackaging can be very dangerous, especially when using contaminated or incompatible containers.

Containers need to be protected from impact or other physical damage, when storing, transferring or using them. **Never use combustible pallets, such as wood, for storing organic peroxide containers.**

Some liquid organic peroxides, such as methyl ethyl ketone peroxide, gradually decompose resulting in off-gassing. These peroxides should always be shipped in containers with specially vented caps. These caps relieve the normal buildup of gas pressure that could shatter an unvented container. Therefore it is important that these vent caps are checked regularly to ensure that they are working properly. Also, vented containers need to be maintained (stored) in an upright position and should NEVER have another container (box, bottle, etc.) stacked on top of it (as this could interfere with the caps' venting ability).

In general, organic peroxides should be stored:

- In well ventilated areas.
- Out of direct sunlight and away from steam pipes, boilers or other heat sources.
- At temperature as recommended by manufacturer/supplier. Always keep the storage area within the recommended temperature range.
- Supplied with adequate firefighting equipment, including sprinklers.
- Supplied with suitable spill clean-up equipment and materials.
- Free of ignition sources such as open flames, hot surfaces, burning tobacco and spark-producing tools and devices.
- Accessible at all times.
- Labelled with suitable warning signs.

Because peroxides are corrosive, appropriate (impervious) gloves should always be worn. This includes proper outer clothing (coveralls or aprons) and goggles or a full face shield. Because of their ability to splash, regular safety glasses (even with side shields) are generally not appropriate for handling peroxides. The specific material for gloves and coveralls needs to be prescribed by a S&H professional as peroxides are a complex group where not every type of glove (i.e nitrile, neoprene, etc) would be appropriate.

If the occupational exposure limits for airborne/inhalation exposures, such as OSHA PELs and ACGIH TLVs, are assessed to be approached or exceeded, and engineering controls are not feasible, respiratory protection needs to be considered. Once again, it is important that a S&H professional assess the specific scenario where peroxides may be encountered so that the most appropriate respiratory protection can be selected. It is typical to use a self-contained breathing apparatus with a full face-piece operated in the pressure demand (or other positive pressure mode) or a supplied air respirator. Many times, a typical air purifying respirator would not ensure workers are properly protected.

Organic peroxides are generally regulated as hazardous waste. Containers and other materials that are contaminated with organic peroxides must also be treated as hazardous waste and handled in a safe manner due to their unusual stability issues. DOT classification has established its own hazard category for organic peroxides: 5.2: Therefore, when disposing of (organic) peroxides, it is important to contact your Waste Management specialist to ensure the specific disposal requirements and procedures are met.

He that is taught only by himself has a fool for a master - Ben Jonson