Picric Acid – Hazards and Safe Usage

Picric acid (2,4,6-trinitrophenol, [$(NO_2)_3C_6H_2OH$]) is widely used in metallography labs for the common steel etchants known as picral, a 4% solution in ethanol, Vilella's reagent, 1 g picric acid and 5 mL HCl and 100 mL ethanol, and alkaline sodium picrate (2 g picric acid, 20 g NaOH, 100 mL water) for coloring M_3C and M_6C carbides, as well as several other formulations. Picric acid was formulated by Peter Woulfe, a British chemist, in 1771, although Glauber is claimed to have written about it in 1742. The name comes from the Greek word *pikros* which means bitter, as picric acid has a bitter taste (it is toxic). Initially it was used to dye fabrics yellow. In the early 20^{th} century, workers producing picric acid were sometimes called canaries, because their skin also became stained yellow.

The explosive nature of picric acid was discovered in 1885 in England which led to the 1888 development of an explosive called Lyddite, named after the location of the studies, Lydd, England. Another source states that the explosive nature of picric acid was first known in 1830, and it was proved to detonate in 1873. In 1894, Russian scientists manufactured artillery shells using picric acid salts and picric acid-based explosives were used in WWI. Anhydrous picric acid is related to TNT, a much more potent explosive. When concentrated, it will attack metals producing shock-sensitive salts that are explosive. This was discovered in 1916 at a French ammunition factory when a fire caused molten picric acid to wet a concrete floor, forming calcium picrate which detonated killing 170 people.

Fortunately, there have been no documented cases of explosions from picric acid in laboratories, according to Phifer [1]. If it is wet with water, it is not an explosive hazard and any attempt to blow it up by a bomb squad will only result in picric acid being spread all over the immediate area. The concern has always been in finding an old bottle that has dried up producing dehydrated picric acid, and if it has a metal cap, rather than a plastic cap. In such a case, shock-sensitive metallic picrates may have formed at the cap-bottle interface. The solution is to have a robot pick it up and re-hydrate the picric acid after opening the bottle under water. If the cap is plastic, and the acid has dried out, friction from opening the cap could cause detonation. The solution here is to place the bottle in a large bucket or tank of water and allow water to dissolve any dried picric acid on the cap threads. Leave the bottle in the water for a few days until some water can be seen inside the bottle. Then, while under water, open the lid and re-hydrate the picric acid.

Obviously, the wise lab manager checks the picric acid bottle periodically (which can vary with lab usage of picric in etchants) to make sure that the picric acid remains wet. Today, bottles are sold with at least 30% water content. A good practice is to keep a log of when the bottle has been checked and when water is added. Also, use only plastic or glass spatulas to remove picric from the bottle and add it to the etchant. Do not use metal spatulas and clean the cap and threads on the bottle and on the cap with a wet paper towel. If you have copper piping, do not dispose of picric acid by pouring it down the drain as explosive metallic salts could form.

Virtually all chemicals and solvents used in the laboratory are dangerous; hence we must develop good safe laboratory practices and teach our employees what to do to avoid problems. Personally, I have never heard of a problem in a metallography/materialography laboratory from picric acid – but, I know

of four accidents from nital (2-3% nitric acid in ethanol; one accident used isopropyl alcohol instead), which people consider to be very safe to use. Every dangerous chemical or solvent cannot be outlawed for use, or we will not be able to work. Even water can be considered as being dangerous, because every year many people drown, but we would never consider outlawing water. The solution is to establish a good laboratory safety program and train employees and develop safe working habits. Vander Voort [2-4] has summarized lab safety aspects as a sequel to the superb treatise by Anderson [5]. ASTM E 2014 lists a number of books on laboratory safety and is a good source of information on metallography lab safety.

1. R. Phifer, "Picric Acid: When is Panic Justified?," **Speaking of Safety**, Vol. 9, No. 2, 2000, pp. 1-3.
2. G.F. Vander Voort, **Metallography: Principles and Practice**, McGraw-Hill Book Co., NY, 1984; ASM International, Materials Park, OH, 1999, pp. 148-159.
3. R.C. Nester and G.F. Vander Voort, "Safety in the Metallographic Laboratory," ASTM **Standardization News**, Vol. 20, May 1992, pp. 34-39.
4. G.F. Vander Voort, "Laboratory Safety in Metallography," **Metallography and Microstructures**, Vol. 9, ASM Handbook series, ASM International, Materials Park, Ohio, 2004, pp. 1081-1089.
5. R.L. Anderson, "Safety in the Metallographic Laboratory," Westinghouse Res. Lab. Sci. Paper No. 65-1P30-METLL-P2, March 20, 1965.
6. ASTM E 2014-99 (2005), Standard Guide on Metallographic Laboratory Safety.