

Quenching Reactive Substances

Virginia Tech Chemistry Department

SECOND DRAFT of October 27, 2006 for Safety Committee review. These guidelines have not yet been approved as departmental policy.

1. **Purpose.** These guidelines are intended to assist laboratory personnel in quenching reactive substances safely so that they may be transferred to ordinary Hazardous Waste containers. Workers should not hesitate to ask for guidance from the Safety Committee before quenching an unfamiliar substance.

2. **Definitions.** In this context, a *Reactive Substance* is any compound or mixture that would react vigorously if added to a Haz-Waste container, potentially resulting in an unsafe release of either heat or gas. Hazardous Waste containers may contain water, dilute acids and bases, and various organic compounds. The term “quenching” means to convert the substance to one that is much less reactive.

3. **Reactive Substances** may include electropositive metals and alloys, organometallic compounds, hydrides, acid chlorides and anhydrides, peroxides, and carbonates.

4. **Highly Reactive Hydrides and Metals**, such as sodium hydride, potassium hydride, lithium aluminum hydride, sodium metal, potassium metal, or sodium-potassium alloy will release hydrogen rapidly when quenched. The substance should be covered with (or slurried in) a hydrocarbon solvent like toluene, preferably under a strong nitrogen or argon counterstream. The quench is done first with isopropanol or ethanol, then cautiously with water. Finally dilute sulfuric or hydrochloric acid is added until a neutral or slightly acidic pH is achieved. In all cases, when quenching a hydride or active metal, *the volume of hydrogen gas to be vented should be estimated* by recalling that 1 mole of gas occupies 22.4 L at standard temperature and pressure. Quenching rates should be chosen to allow enough time for gases and heat to be released in a controlled way.

5. **Distillation Pots.** When quenching distillation pots, one must exercise extreme care to ensure that lumps or domains of the reactive substance are not protected or isolated from the quenching agent by other residues such as benzophenone. Such mixtures must be fully quenched and pH-neutralized before transfer to waste containers.

6. **Less reactive hydrides and metals** such as lithium metal, calcium hydride, lithium hydride, or sodium borohydride can be quenched directly with water in a manner analogous to their more reactive counterparts (Item No. 2). Lithium can react directly with nitrogen gas – use argon. Zinc, magnesium, and aluminum can attain high “surface reactivity” during reactions (such as Grignard reactions or dissolving metal reductions). The surface “hot spots” can be quenched by treating the solid metal with water. The solid can then be transferred to a waste container, preferably one that does not also contain combustible items like paper or organic residues.

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7. **Acid Chlorides and Anhydrides** such as phosphorus pentoxide, thionyl chloride, boron trichloride, or trifluoroacetic anhydride should be quenched cautiously with water under a nitrogen or argon counterstream. Adequate ventilation must be ensured to carry off HCl, HBr, and other acidic fumes that may result. After the reactive material is quenched, the solution should be neutralized with sodium hydroxide, potassium hydroxide, or sodium bicarbonate before transfer to a waste container. If sodium bicarbonate is used, it must be back-neutralized with sulfuric or hydrochloric acid before the mixture may be added to a waste container (see “Carbonates” below).

8. **Organometallic Reagents** in sealed “Sure-Seal” bottles can be individually manifested and removed by the Hazardous Waste crew without further treatment. Bottles containing large amounts of leftover reagent, large amounts of residue, or highly pyrophoric materials such as trimethylaluminum, triethylaluminum, *tert*-butyllithium, or diethylzinc should be picked up by the Hazardous Waste crew for proper disposal. Other old bottles containing small amounts of residues from butyllithium, methyllithium, Grignard reagents, or alkylaluminum halides can be quenched as follows. The “Sure Seal” bottle cap is removed, and a 12-inch piece of 8-mm glass tubing connected to a nitrogen line with a moderate flow of nitrogen is quickly inserted into the bottle to create a counterstream. Some toluene is added to rinse down the sides of the bottle and to provide a thermal reservoir. Then, acetone is cautiously added to quench the reactive substance. Then water is added, and finally the mixture is acidified to a neutral pH before transfer to a waste container.

9. **Inorganic Carbonates** may be neutralized in aqueous solution using hydrochloric or sulfuric acid until no more carbon dioxide is evolved.

10. **Hydrogen Peroxide.** **[THIS PART MAY VIOLATE STATE DEQ REGULATIONS AND HAS NOT PASSED UNIVERSITY HEALTH AND SAFETY APPROVAL]** H₂O₂ is perhaps most commonly used in combination with sulfuric acid to form a highly aggressive cleaning agent known as “Piranha Solution.” (Typically, a fritted-glass funnel is charged with a few milliliters of 30% hydrogen peroxide solution, and then an equal volume of concentrated sulfuric acid will be added. Never add the peroxide solution to the acid!) Under no circumstances should peroxides be added to ordinary Hazardous Waste containers. Combinations of peroxides and organics can form treacherous, touch-sensitive explosive mixtures. We recommend that *small amounts* of “Piranha Solution” should be diluted by addition to 100 volumes of water, and that the dilute mixture should be disposed in the sink with plenty of additional water.

Labs that make frequent use of Piranha should consider an alternative product known as “NoChromix” (www.godax.com). NoChromix is a inorganic peroxygen formulation that is mixed with concentrated sulfuric acid to form a cleaning solution. After making up the solution it must be stored in a vented bottle to prevent a build-up of pressure. The mixture can be used to clean a variety of glassware including fritted filters and NMR tubes.