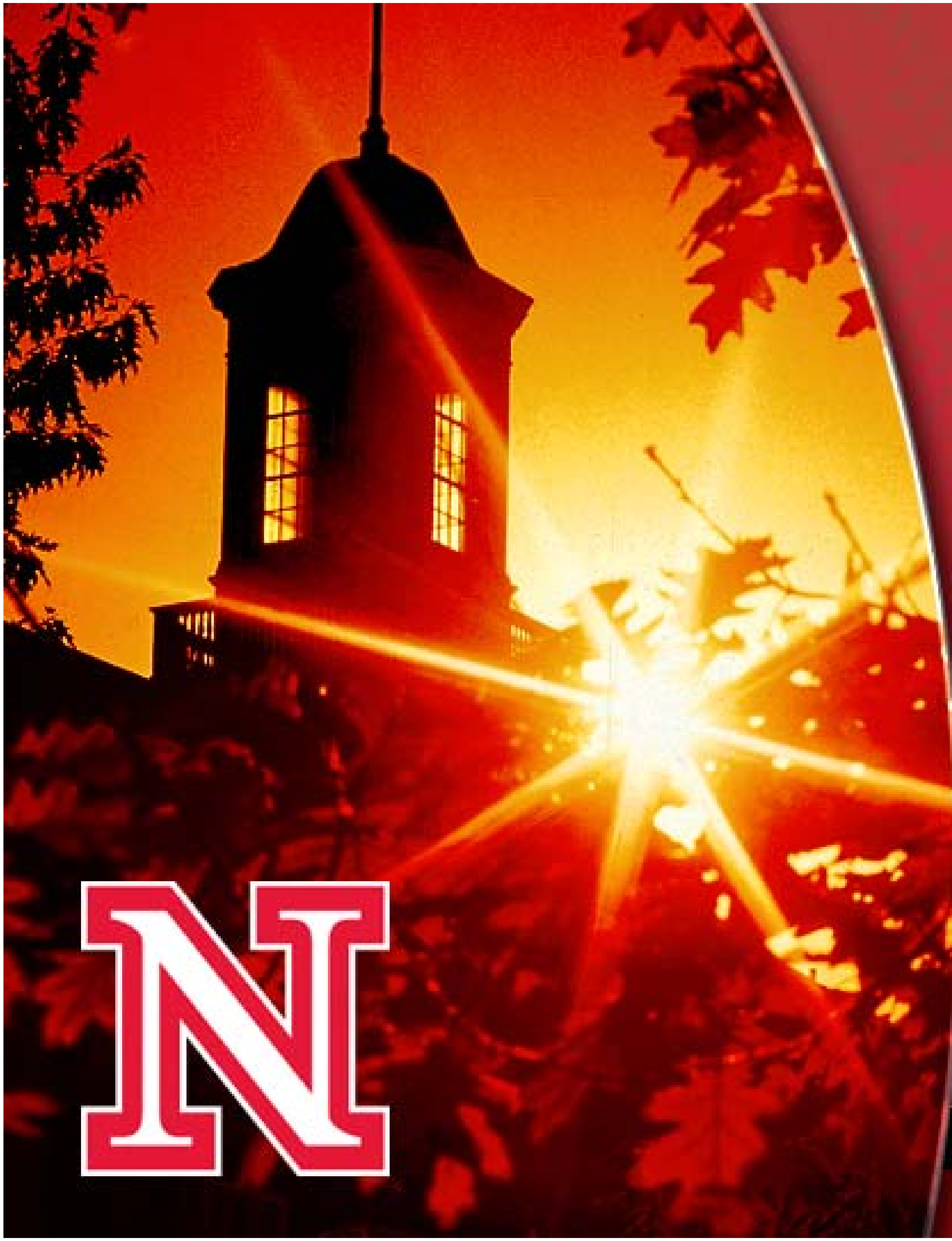

Unstable, Reactive & Energetic Chemicals

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Background

- **Unstable, reactive and energetic compounds use at colleges and universities has come under scrutiny**
  - **US Chemical Safety and Hazard Investigation Board (CSB)**
  - **Occupational Health and Safety Administration (OSHA)**
- **Why?**
  - **Recent accidents**

Texas Tech, January 20, 2010

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- Graduate student was synthesizing a known energetic chemical (a nickel hydrazine perchlorate derivative)
- Had no formal training with the material/hazards
- Exceeded limits allowed to synthesize (limit 100 mg; made 10 gm)
- No PPE (not even safety glasses)
- Was 'gently' grinding in a mortal and pestle
- Lost three fingers and permanently damaged one eye
- UNMC 1993 similar incident but with a triperoxide. Graduate student lost one finger and damaged two others.

University of California Los Angeles, December 29, 2009

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- Graduate student was drawing pentane containing tert-butyl lithium into a syringe
- Had no proper training
- Syringe came apart in her hands
- Suffered third degree burns to 43% of her body
- Died 18 days later
- Was not wearing any PPE
- Clothing she was wearing was synthetic and flammable
- Initially ran away from a safety shower before running to it
- The UCLA Regents and graduate student's professor are currently facing criminal charges

Other Incidents

- January 2012 – sodium azide explosion; graduate student hospitalized with serious burns to hands, body, and face
  - Similar incident Oct 2011 (from attempting to scrape 4g of NaN3 out of a vial)
- May 2011 – HCl and TiCl4 explosion (water was involved), graduate student hospitalized with severe cut to arm and acid in eyes
- 2010-2011 – Several cases of students hospitalized following explosions of demonstrations involving heating of nitrates with sugars or glycerin

- What about UNL?

September 1990, Hamilton Hall

- Graduate student attempting to recycle tetrahydrofuran:
  - Unclear if any stabilizer remained in solvent.
  - Distilled under air (favoring peroxide formation)
  - No reducing agent employed to destroy peroxides.
- Resulting explosion sent shards of flask through hood sash, severely lacerating student.
- The explosion shattered additional bottles of used THF (16L) stored adjacent to apparatus. The resulting explosion and fire destroyed the hood completely and badly damaged the lab.
- Water damage from a broken pipe reached the basement

Hazard Assessments are Needed

- Also called a 'Job Safety Assessment' (JSA)
- Consists of:
  - Identifying hazards
  - Identifying receptors
    - What is at risk (equipment, people, etc.)
  - Evaluating risks
    - Includes the likelihood of something going wrong and
    - The magnitude of the consequences
  - Actions to eliminate hazards and minimize risk

Identify Hazards – MSDS Part 1

- Material Safety Data Sheet (MSDS)
  - One of the most important sources for information
  - Read even for chemicals you are going to synthesize on your own (if available)
  - Read one from the product manufacturer
    - Not all MSDSs are created equal
  - Read others:
    - Fisher Scientific
    - Sigma-Aldrich
    - Avantor (previously JT Baker/Mallinckrodt)
- My experience is that many fail to read and fully understand the MSDS

Identify Hazards – MSDS Part 2

- Understand the warnings, examples:
  - **Spontaneously combustible** means the material can begin to burn without an obvious external ignition source
  - **Pyrophoric** means the material can ignite spontaneously in air
  - **Air reactive** might mean the product is pyrophoric…or it might just mean it degrades when exposed to air
  - Other important warnings:
    - Shock sensitive, peroxide-former, water reactive, unstable, uninhibited, monomer, explosive, violent

Identify Hazards – MSDS Part 3

- Read the section on incompatibilities
  - Does the work expose the chemical to anything listed?
  - As a chemist, incompatibilities might be just what you are looking for
- Read the MSDS critically (example; sodium azide):
  - The Department of Transportation (DOT) classifies it as a poison
  - The National Fire Protection Agency (NFPA) classifies it as an extreme health hazard but just a moderate reactivity (explosive) hazard
  - The MSDS indicates it can explode when heated, create shock sensitive compounds, or evolve toxic gases worries me more

Identify Hazards - Beyond MSDS

- Read the label on the container
  - The language should agree with the MSDS
  - If anything is different, find out why
  - I have seen container labels describe greater hazards than what was found on an MSDS
- Read other literature
  - Manufacturer product use
  - Research papers and protocols
    - Very important for chemicals not commercially available (likely no MSDS available)
    - Same concepts as for MSDSs apply
  - Standard operating procedures

Specific Chemicals/Classes

- Azides
- Picrates
- Nitro compounds
- Peroxide-formers
- Metal hydrides
- Low-molecular weight alkynes
- Reactive organo-metallics
- Organic peroxides
- Others?

Azides

- Sodium azide is the most common
  - Water soluble
  - Most common use is as an anti-microbial
  - Also used to inflate vehicle air-bags
  - Can explode if heated
  - Spontaneously forms insoluble shock sensitive compounds when exposed to some metals/salts and metal surfaces (generally avoid any metals; any metals salts other than salts of alkalai metals)
    - Copper drain pipes have been as source of explosions

Picrates

- Most common are picric acid and picrylsulfonic acid
  - Both are tri-nitrophenol based compounds
  - Most commonly used as biological stains
  - Relatively water soluble
  - When dry can detonate if initiated
  - Spontaneously form insoluble shock sensitive compounds when exposed to metals/salts and metal surfaces
  - Friction with dried chemical in container lids is reportedly a source of detonations. Do not attempt to open old or "discovered" bottles of picric acid.

Perchloric Acid/Perchlorates

- Perchloric acid was once widely used for digestion of biological samples. But:
  - Spontaneously ignites or explodes in presence of oxidizable organics.
  - Vapors create shock-sensitive perchlorates in exhaust ventilation.
- Alkali metal perchlorates relatively safe. However, avoid any exposure to heavier metals or their salts (Ag, Pb, etc.) as these perchlorates are extremely shock-sensitive. (Note: mercuric perchlorate sometimes still used as a reagent.)

Nitro Compounds

- Related to picric acid and picrylsulfonic acid
- The ratio of molecule size to number of nitro group substitutions is the concern
  - Nitrotoluene is not much of a problem
  - Trinitrotoluene (TNT) is
  - Nitrocellulose is poly-nitrated
    - Common into the 1950s for making movie film, photographic negatives, and wood sealers
    - Is it the degree of nitration that separates flammable solids from explosives?
- Stability varies; some (nitrocellulose) can become unstable over time

Peroxide-Formers

- Consist of some ethers and aldehydes, p-dioxane, THF, some alkenes and amides, and styrene among others
- Over time can develop -O-O- bonds which are unstable
  - Risk of peroxide formation is chemical and use specific
- Some products are 'inhibited' (i.e. contain a chemical to scavenge oxygen)
  - Inhibitors are eventually used up
  - Distilling solvents also leaves the inhibitor behind as a still bottom
- Beware the 'light' container that should have had more within it

Metal Hydrides

- Examples include sodium hydride and lithium aluminum hydride
- Used as reducing agents in organic chemistry
- Will spontaneously ignite on exposure to the air
- Will react violently with water
- Are usually dispersed in mineral oil

Low Molecular Weight Alkynes

- Ethyne (acetylene) is the most common
- Used in organic chemistry synthesis reactions
- Some polymerize spontaneously
- Most are very reactive
- Acetylene must be dissolved in acetone for safe use and can be only moderately compressed

Reactive Organo-Metallics

- N-butyl lithium is one of the most common
- Can be used as a ‘superbase’ in organic synthesis reactions
- Most are dissolved in an organic (flammable) solvent
- Are water reactive
- Moisture in the air can result in reactions that lead to fires

Organic Peroxides

- Are characterized by an -O-O- bond
- Benzoyl peroxide and methyl ethyl ketone peroxide are examples
- Sometimes used to initiate polymerization reactions
- Combine an oxidizing functional group with oxidizable organics
- Some are shock and/or temperature-sensitive
  - SADT (self accelerating decomposition temperature)
    - Some are below room temperature
- Others ignite easily and burn intensely

Hazard Assessment Recap

- Identify hazards –
  - DONE
- Identify receptors
  - What is at risk (equipment, people, etc.)
- Evaluate risks
  - Includes the likelihood of something going wrong and
  - The magnitude of the consequences
- Actions to eliminate hazards and minimize risk

Identify Receptors

- This one is simple
- The receptor is you and/or your coworkers

Evaluate Risks

- If used improperly, the risk of something going wrong is high
- The potential magnitude of the consequences are very high
  - Amputations
  - Shrapnel injuries
  - Thermal and/or chemical burns
  - Significant exposure to toxic chemicals
  - Death

Hazard Elimination

- Are less dangerous alternatives available?
  - For sodium azide there is an alternate anti-microbial from Kathon® Preservatives
- For other products used in a research setting, options might be limited
- Now what?

Minimize Risk

- Read, understand, and follow MSDSs and other safety information
- Understand procedures used to transfer or otherwise handle chemicals. These should be:
  - Written
  - Reviewed by the Principle Investigator & lab workers
  - Kept readily accessible for easy reference
- Where possible, practice transfers and other chemical manipulations using safe substitutes or do ‘dry runs’
- Have other, more experienced researchers ‘critique’ your transfers and other manipulations

Minimize Risk

- Do not vary from established protocols and research work unless approved by professors/supervisors
- Reaction scale – many are lethal at a mole scale but not at a millimole scale
- Wear appropriate PPE
  - Lab coats; flame retardant ones are available
  - Safety glasses/goggles
  - Face shield
- Closed toe shoes
- Long pants
- Avoid synthetics; even those that don't burn are likely to melt onto your body; wear cotton or wool instead

Minimize Risk

- Use fume hoods and other shielding equipment as much as possible
  - Place horizontal hood sashes in front
  - Keep vertical hood sashes down
  - Use a portable transparent shield
- Properly secure all apparatus
  - This includes product containers where appropriate
- Minimize other chemicals in the hood
  - If something goes wrong; there is less chemical available to react
- Do multiple things right

Closing Thoughts

- Read the articles in the links provided for the UCLA prosecution and UNMC case
- In the UNMC case especially, note how the court evaluated the responsibilities of both the graduate student and professor
  - This will likely be the standard to which all parties will be held in the event of an incident
- See also the ACS Task Force draft report 'Creating Safety Cultures in Academic Institutions'

EHS SOPs

- **JOB SAFETY ASSESSMENTS**
  - http://ehs.unl.edu/sop/s-JSA.pdf
- **USE AND STORAGE OF PEROXIDE-FORMING CHEMICALS**
  - http://ehs.unl.edu/sop/s-peroxides.pdf
- **PYROPHORIC CHEMICALS**
  - http://ehs.unl.edu/sop/s-pyrophoric_chemicals.pdf

Other Information Sources

- Aldrich Technical Bulletin AL-134 Handling Air Sensitive Reagents
- Aldrich Technical Bulletin AL-164 Handling Pyrophoric Reagents
- EHS Colloquium on Pyrophorics
  - http://ehs.unl.edu/training/Colloquium/

Questions/Comments?