Energetic Materials Research Safety

Safety Documents

Explosive Chemicals Research Laboratory should minimally have the following in place:

- A Chemical Hygiene Plan
- An Explosive Safety Plan
- Laboratory Facility Requirements
- PPE Plan

Chemical Hygiene Plan

- Guidelines to handle, label and store hazardous laboratory chemicals based on characteristics
- Identify and understand the chemical and physical hazards (SDS; literature).
- Safety protocols to reduce exposure, injury from violent reactions.
- Required Personnel Protective Equipment
- Location and use of emergency equipment
- Emergency procedures: fire and chemical spill, explosion
- Consistent appropriate labeling
- Safely dispose of chemical waste (environmental as well as compatibility)

Chemical Hygiene Plan alone is not Enough

- Strict explosives and personnel limits
- Approved and signed Standard Operating Procedures (SOPs) for all explosives operations
- Training Program for explosives laboratory personnel
- Peer Review System for use of new energetic materials and explosives processes and operations
- Energetic materials facilities explosives safety requirements

Past Incidents

- 1998 NSWC IHDIV.(Naval Surface Warfare Center (IHDIV, NSWC)). Powder ignition by ESD. No injuries, some equipment damage. Root cause: SOP and facility needed update for controlling ESD.
- 2009 NSWC IHDIV. Spontaneous Ignition of Nanoaluminum perfluorotetradeconoic acid. Severe burns. Root cause: operator deviated from approved Lab Review Form.
- 2010 TTU. Nickel hydrazine perchlorate synthesis. Explosion with critical injury: student lost three fingers, his hands and face were burned, and one of his eyes was injured after the chemical he was working with detonated.

Findings of CSB Investigation of Texas Tech

- The physical hazards inherent in the research were not effectively assessed, planned for, or mitigated
- The university lacked safety management accountability and oversight
- Strict explosives limits never followed
- Previous incidents with preventative lessons were not documented, tracked, and formally communicated
- The funding agency, with a control over the research did not prescribe any safety provisions
- OSHA standards and guidelines have been developed to promote hazard evaluation methodologies in an industrial setting, similar resources that address the unique cultural and dynamic nature of an academic laboratory setting have not been generated
- OSHA standard was not created to address physical hazards of chemicals, but rather health hazards

DOT Explosive Class

- **Division 1.1** – mass explosion hazard,
- **Division 1.2** – projection hazard but not a mass explosion hazard.
- **Division 1.3** – fire hazard and either a minor blast hazard or minor projection hazard or both, but not a mass explosion hazard
- **Division 1.4** – minor explosion hazard. The explosive effects are largely confined to the package and no projection
- **Division 1.5** – Very insensitive explosives that have a mass explosion hazard but are so insensitive that there is little probability of initiation or of transition
- **Division 1.6** – Extremely insensitive articles that do not have a mass explosive hazard and that contain only extremely insensitive detonating substances

Examples of Energetic Materials

- **Primary explosives:** can be initiated by dropping, impacting, friction or electrostatic discharge. E.g.. Mercury fulminate, lead azide, lead styphnate
- **Secondary explosives:** sensitive to heat, shock, impact, friction, ESD. Examples of military high explosives: TNT, RDX, HMX, C4,
- **Propellants**: nitrocellulose (single base), nitrocellulose and nitroglycerine (double base), nitrocellulose/nitroglycerine/nitroguanidine (triple base), ammonium perchlorate/aluminum/binder (composite)

Maximum Allowable Limit: Material/Personnel

- Restrict the number of personnel and amount of energetic material to the lowest possible minimum at all times
- Dedicated laboratory with posted explosive limits.
- Never store excess material: minimum required for the operation present in the laboratory at the time of the operation.
- Two man rule: never work alone.

Training

- Mandatory training for everyone working directly or coming in contact with energetic material
- Established training programs for certification
- Documentation of the training
- Must be qualified to understand the SOP
- Update training and reinforce good habits with refreshers

SOP: components

- All operations shall be performed in accordance with written and signed Standard Operating Procedures.
  - materials
  - laboratory equipment
  - experimental procedures
  - detailed hazard analysis
  - safety requirements and risk mitigation
  - signature page signed by managers and certified operators

SOP contd.

- Written Standard Operating Procedures for the general operation and energetic materials handling requirements

– site diagram, explosives and personnel limits, – hazardous chemicals used, – safety and process equipment, – documentation requirements, – PPE, housekeeping, use of fume hoods

- Signed and approved by responsible departmental parties and Office of Environmental Health and Safety
- Signed by Process Supervisor and Workers
- Signatures along with validation statement to have read and understand the SOP.

Laboratory Documentation

- Documentation required before conducting the explosive operation, – Laboratory Notebook, – Lab Review Form, – Process Review Form, –SDS on file
- Detailed procedure in written detail, – Reactions, – Chemicals reagents required, – Step-by-step procedure, – Special equipment required
- Signed by responsible manager or designee
- Copy on file in department office and at work site

Peer Review system

- Peer review ensures that safety concerns of new materials, processes, equipment, and operations are addressed by more than one competent professional.
- Process Review Committee
- Operations Safety Committee

Laboratory Facilities

- Designated laboratory for explosives operations with posted explosives and personnel limits
- Locked when unattended. Controlled access when operations are in place
- ‘Red/Green’ placard at the door to indicate ‘explosives present’ or ‘no explosives present.’

Storage and Handling

- Laboratory energetic materials storage: – store behind shielding, – explosive proof refrigerator, – limited amounts; do not store excess, – store in Velostat bags or containers; never glass with screw top caps.
- Laboratory energetic materials handling: – conductive mats, conductive bench top or grounded steel tops, – use wooden in place of metal spatulas, – paper filters; never sintered glass filters, – teflon sleeves on rotovap
- do not grind with mortar and pestle; grind with ball-mill or other approved remote procedure.

Storage and Operations

- Storage of Explosive Hazardous Waste (EHW).: – Store EHW behind a shield, – Limit storage of EHW to no more than one week, – Avoid overnight storage of EHW
- Shielding Requirements
- Determine appropriate grounding policy and explosion proofing for unique electronic equipment.

ESD Hazards

- To avoid accumulation of static charge on sensitive materials follow the below guidelines:
  - Ensure all electrical equipment is grounded.
  - Do not wear nylon or other synthetic fabrics that possess the tendency to build up static charges.
  - Keep concentrations of solvents and dusts in the air as low as possible.
  - Store extremely static sensitive materials only in grounded containers
  - Perform work with static sensitive materials on conductive surfaces.
  - Keep the humidity in the atmosphere to the appropriate level for the material being handled (40-60 percent humidity).

Safety Precautions

- **Safety Precautions**: Necessary precautions must be taken when present or working
  - Observe personnel and explosive safety limits
  - Note of chemicals, explosives, propellants, oxidizers used or present in the laboratory.
  - Reminder that energetic materials can be activated in four ways: friction, electrostatic discharge, impact, and heat.
  - Requires appropriate protective safety clothing and equipment
  - Observers and visitors refrain from handling materials when they are not certified on an SOP

Safety Precautions Contd.

- **Safety Precautions**: Necessary precautions must be taken when present or working in the laboratory:
  - Identify hearing protection, gloves, and respirator for specific operations as necessary
  - When working with exposed, solid ESD sensitive or uncharacterized energetic materials wear conductive-sole shoes, or leg stats and stand on a conductive mat.
  - Identify exits and muster points in case of an emergency
  - Identify location of cleanup equipment in case of a spill

Safety precautions

- Separate the experimental setup with proper shielding and an additional safety screen in the fume hood.
- Cover the glassware with adhesive films to reduce the fragmentation in case of explosions,
- In addition to lab coat, gloves, safety glasses wear a face protection shield, ear protection, a leather jacket with arm protection.
- For hand protection use leather gloves (welding type), ideally in combination with steel interwoven Kevlar® gloves
- Start the first experiments on a small scale of only a few mg and increase the scale gradually
- Keep solid material wet or soaked with solvent as long as possible.
- Try to obtain solid products of small particle sizes. Smaller particles/crystals are less sensitive to mechanical stress. Recrystallization experiments should thus be cooled down very quickly under stirring.
- Do not use metal, use spatulas made of wood or Teflon®.
- Keep sufficient distance between the material and your body. Do not touch the potential explosive material directly and use gripping devices to maneuvre the container that encloses the compound.
- Wear ESD protective clothing and antistatic shoes. The laboratory floor should be ESD conductive

Compliance and Enforcements

- Regular group inspections conducted by responsible parties to identify deficiencies and record findings (Inspection Team):
  - Supervisor, Team Leader, Worker
  - OEHS representative
- Corrective action plans are submitted within a given time frame to address findings.
- Enforcement may be needed to correct negligence (loss of certification).

Explosive hazardous waste

- The following become explosive-hazardous waste when discarded. The EPA waste code is D003.
  - Energetic materials (i.e., propellant, explosives, initiators)
  - Rags and solvents contaminated with energetic materials
  - Do not store explosive contaminated liquids in screw cap containers
  - Explosive solid waste stored in conductive Velostat bags

Successful ESD Program

- Establishing an ESD task force to outline the requirements of the program, implement the program, review progress against milestones, and follow up to ensure the program is continuously improved and upgraded.
- Conducting a facility evaluation to help identify the sources of ESD and establish static control measures.
- Setting up an audit program.
- Selecting ESD protective materials and equipment.
- Establishing a training and ESD awareness program.

ESD Control Practices

- Grounding
- Wearing foot straps and testing them before entering the protected area
- Conductive flooring
- ESD Policy
- Mobile carts have conductive wheels and drag chains
- Conductive chairs
- Unneeded items are not brought in to the ESD protected area. Everyone who enters the area must abide by the rules for the protection to be effective.
- **DO NOT** enter these areas without proper understanding of the ESD control procedures implemented in the area.

ESD Controls

- Conductive flooring
- Dissipative work surfaces
- Personal grounding
- Grounded work benches
- Conductive carts with drag chains
- Conductive chairs

Warning Signs

To control and eliminate the effects of ESD:

- Remove unneeded static objects from your workstation - keep objects you need a safe distance away from sensitive components and assemblies.
- Use a topical antistat, if possible, to eliminate static build up on objects that are necessary to do your job.
- Minimize movement and friction.
- Protect sensitive parts from the charges around them - Use ESD protective packaging.
- Place components and assemblies only on a dissipative mat or dissipative work surface.
- All personnel, surfaces and equipment must be grounded to drain off any charges that are created.
- Keep work surfaces clean and free of dirt build-up.

Controlling ESD

- Before you enter an ESD protected area you must put on special footwear. This protective footwear helps prevent static as you walk. Ground straps allow the user to stay at or near ground potential.
- you must test the foot wear before you begin work. Foot wear must be tested twice per day. At the test station lift one foot and touch the tester. Don't wear shoe grounders without resistors around an exposed electrical hazard. Don't wear shoe grounders at all around hazards that are over 250 volts.

ESD Control Programs

- The best prevention program is a combined effort aimed at the prevention and the controlled elimination of static charges, through the practice of proper behavior/procedures, workstation design and layout, environmental controls, tooling and component handling.

Clothing Requirements

- Non-static generating clothing shall be worn in ESD-protected areas or static dissipative smocks shall be worn as an outer garment. Finger cots and gloves, when worn in an ESD-protected area, shall be made of static dissipate, lint-free, particle-free materials

Humidification

- The relative humidity shall be monitored and maintained in ESD-protected work areas at 30% to 70%. At levels below 30%, additional precautions shall be employed (e.g. air ionizers, humidifiers, etc.).

Identification Markings

- ESDS items, equipment and assemblies shall be identified so as to warn personnel before any ESD damaging procedure can be performed.

Personnel grounding System

- Personnel grounding devices (such as wrist straps) shall be supplied to all personnel working with or handling ESD items to prevent the accumulation of dangerous electrostatic charge levels.

Prohibited Materials

- The area shall maintained in a clean and orderly condition. Smoking, eating and drinking in ESD-protected areas shall not be permitted. Unapproved tools, static generating materials, and/or materials unessential to the fabrication area are also prohibited at the workstation.

Workstation Grounding

- All work surfaces/workstations in an ESD-protected area shall be static dissipative and electrically connected to the common point ground system.

Workstation Identification

- The ESD-protected area shall be clearly identified by prominently placed signs and marking systems (barrier tape, partition, rope guard, etc.). Access to such areas shall be limited to trained and equipped personnel.

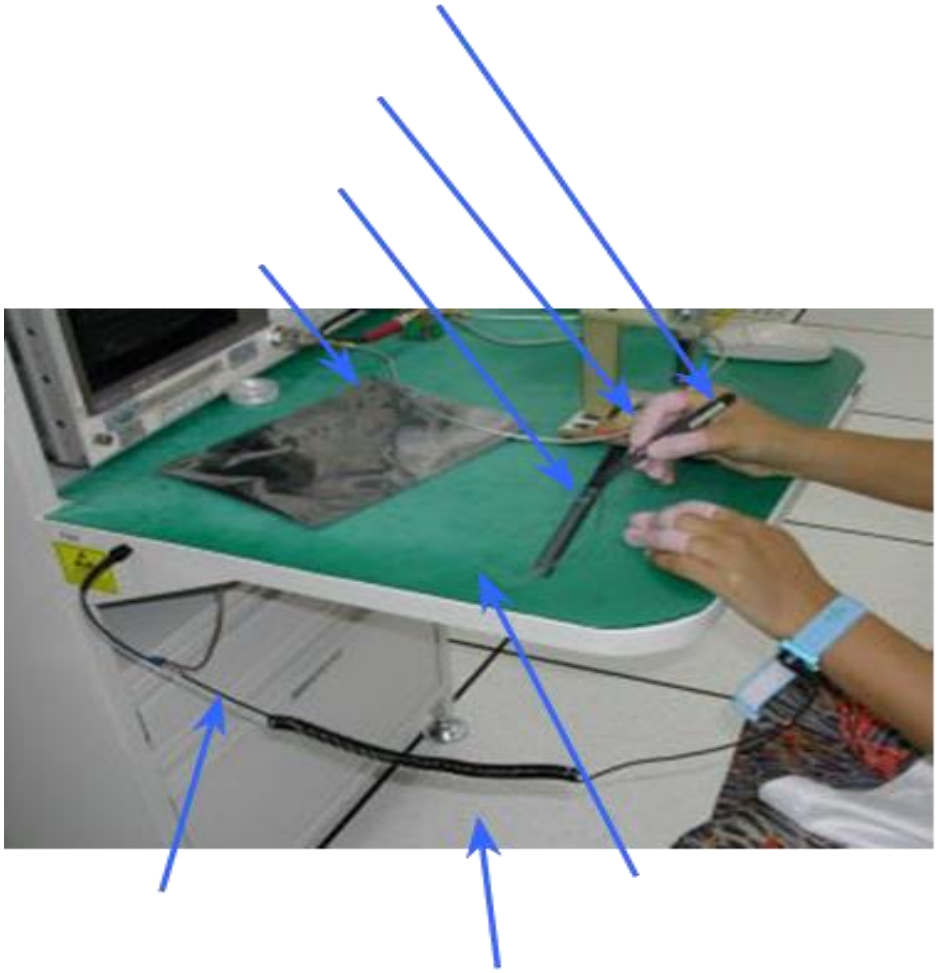
Sources of ESD

Work surfaces	Waxed, painted or plastic surfaces.
Floors	Waxed, common vinyl tiles, sealed concrete
Clothes	Common smocks, non-conductive shoes, synthetic materials (e.g. nylon)
Chairs	Vinyl, fiber-glass, finished wood
Packaging	Common plastic bags, foam, trays, tote boxes
Assembly area	Spray cleaners, heat guns, blowers, plastic tools (e.g. solder suckers, brushes), cathode ray tubes.

What are typical examples of static charge inducing situations?

Means of static generation	RH 10-20%	RH 65-90%
	RH-Relative humidity	
Walking across a carpet	35,000 V	1,500 V
Walking on a vinyl tile floor	12,000 V	250 V
Vinyl envelopes for work instructions	7,000 V	600 V
Worker at bench	6,000 V	100 V

An example of a static-safe work bench



Testing Requirements

Test	Item	Test Parameters	Verification Intervals			
			Daily	Weekly	Quarterly	Yearly
1	Work surface	$\geq 1 \times 10^6$ ohms and $< 1 \times 10^9$ ohms			X	
2	Protective Floor Resistance	$< 1 \times 10^9$ ohms. After cleaning the floor shall be checked and the data recorded.			X	
3	Protective floor grounding	$> 1 \times 10^5$ and $< 1 \times 10^9$ ohm from the floor surface to the equipment ground.			X	
4	Wrist strap	1×10^6 ohms ± 20% or user defined value	X			
5	Foot wear grounding	$< 35 \times 10^6$ ohms	X			

Summary

- Explosives chemical research requires additional safety standards beyond a Chemical Hygiene Plan.
- Additional safety precautions are needed for handling, storing, and disposing Class 1 explosive materials.
- Set number of personnel and amount of energetic material to the lowest possible minimum—minimize exposure in the designated laboratory.
- Designated laboratory for explosives operations with posted explosives and personnel limits