Chemical

SAFETY AND SECURITY TRAINING

Chemical Safety and Security Officer Training

Irbid, Jordan

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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company,
for the United States Department of Energy's National Nuclear Security Administration
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Sandia National Laboratories

Chemical Management

Best Practices

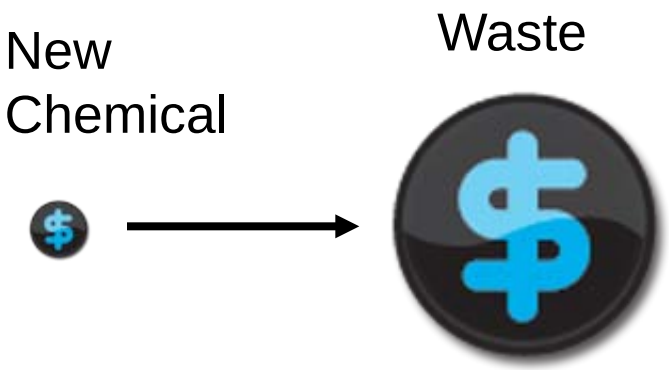
Cradle - to - grave care of chemicals

Receipt → **Storage** →

Use → **Disposal**

Chemical Management is a Best Practice for Safety *and* Security

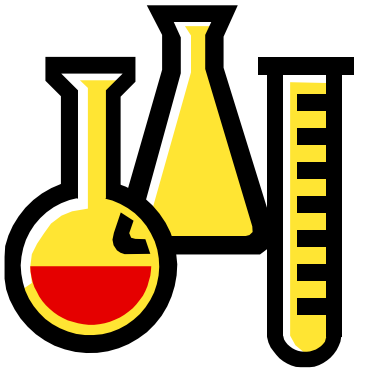
- **Reduces hazardous waste**
- **Reduces cost**
  - **New purchases**
  - **Waste disposal**
  - **More efficient**
- **Improves security**
  - **Insider threat**
  - **Outsider threat**
- **Facilitates environmental compliance**
- **Improves quality of research**
- **Improves quality of lab instruction**



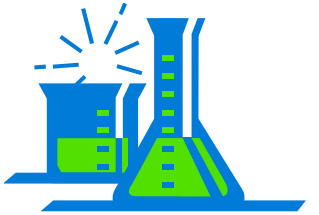
Proper chemical management program has several essential elements

Chemical Management Elements

- Source reduction
- Procedure for chemical ordering and disposal
- Inventory and tracking
- Storage in stockrooms
- Access control
- Recycling of chemicals, containers and packages



Plan experiments in advance!



What chemicals are needed?

How much is needed?

How will the chemicals be handled?

What are the reaction products?

How will the chemical be stored?

How will disposal take place?

Inventory management

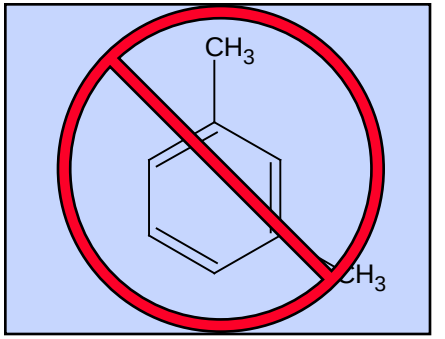
Less is Better !

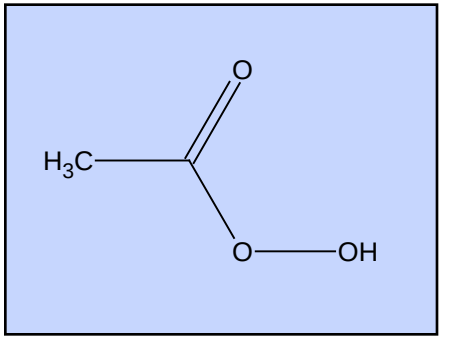
- Order only what you need
- Reduce size of experiment
- It costs less to store
- It costs less to dispose

"Less is Better: Guide to minimizing waste in laboratories", Task Force on Laboratory Environment, Health and Safety, American Chemical Society, 2002. http://membership.acs.org/C/CCS/pub_9.htm

Substitute reagents to reduce waste

- Citrus based solvents for xylene in histology lab
- Peracetic acid for formaldehyde for cleaning kidney dialysis machines
- Non mercury thermometers
- Enzyme and peroxide based cleaners for chromerge (NoChromix)
- When purchasing automated equipment think of chemical waste





Best practice - ordering and stocking chemicals

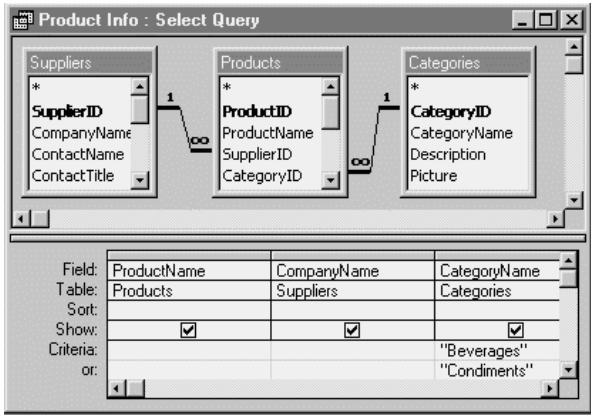
- See if your institution already has it (surplus)
- Order minimum needed (large quantities are not a bargain)
- Check on special storage (refrigeration, dry box…)
- Mark the receipt /open date (unstable chemical)
- Can it eventually be disposed of (rad waste, mixed waste)

Ordering chemicals- chemical inventory

- **Database or Spreadsheets are tools to track the chemical inventory**
  - **Barcoding can be used**
  - **Chemicals can be found easily**
  - **Chemical ages can be tracked**
  - **Chemical standards maintain traceability**
  - **Disposal can be documented**
- **Physical reconciliation**
  - **Assures accuracy of database**
  - **Provides visual inspection of chemical condition**

Inventory and tracking

Database or spreadsheet designs

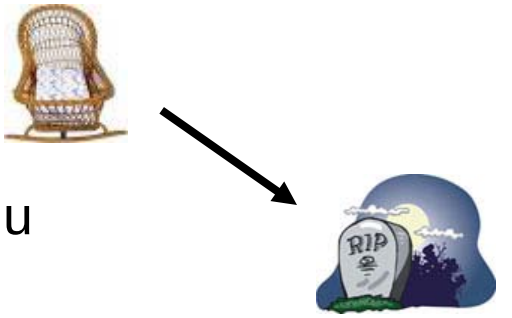


Home made – Access or Excel programs

Freeware – Based on Access or Excel

Commercial – Chemicals and MSDS included

Database helps safely track and report chemical storage and use



Searches and Reports:

- Find an (M)SDS
- Chemical Inventory Search Menu
- Chemical Regulatory Reports Search Menu
- Find Chemical Storage Locations

Transfers, Removal, Verification and Inventory Entry:

- Transfer or Remove a Bar-coded Chemical from the Inventory
- Verify Chemical Inventory Menu
- Add Chemical Inventory
- Chemical Exchange Menu

Procedures, Forms and Links:

- See Inventory procedures, forms and other documents
- See Other Chemical Related Links

Inventory queries

Chemical or tradename search

CAS number search

Ingredient search

Location/organization search

Location owner search

Requester search

Barcode search

Query result for toluene – barcode, location, department, quantity and order date

BARCODE	LOCATION	DEPT	QUANTITY	UNIT	Purchase Date
AQ00600682	NM/518/1111	1725	1	L	10/24/2006
AQ00602185	NM/518/1123	1111	100	mL	11/20/2006
AQ00582298	NM/518/1302	1131	1	L	8/8/2006
AQ00602186	NM/518/1302	1131	100	mL	11/20/2006
AQ00602187	NM/518/1302	1131	100	mL	11/20/2006
AQ00582307	NM/518/1302	1131	4	L	8/8/2006

(M)SDS and Certificates of Analysis may also be included

Chemicals likely to be useful in other labs

ACIDS

Acetic acid (glacial)
Hydrochloric acid
Sulfuric acid

SOLVENTS

Dichloromethane (methylene chloride), Acetone Chloroform, Ethyl acetate, Glycerol, Hexanes Isopropyl alcohol, Methanol, Petroleum ether Toluene, Xylenes

OXIDIZERS

Bromine, Potassium chlorate, Potassium dichromate, Silver nitrate

POISONS

Indicators, Iodine (solid or solution) Metals (powders, dust, shot)
Sodium, calcium, silver, and potassium salts

Excess chemicals are made available to others and can be searched

CHEMICAL NAME	MSDS	QTY	STATE	PURCHASE DATE	OPEN?
DEVCON 5 MINUTE EPOXY KIT	NL203800	2.5 OZ	Liquid	07/25/2001	Not Open
5 MINUTE EPOXY KIT	NL203800	2.5 OZ	Liquid	08/06/2003	Not Open
TOLUENE	OHS23590	500.0 ML	Liquid	03/25/1999	Not Open
TOLUENE	OHS23590	500.0 ML	Liquid	03/25/1999	Not Open

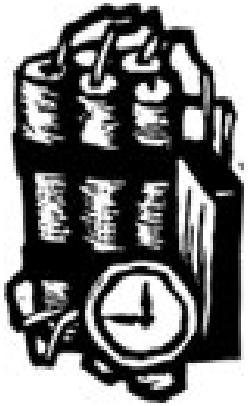
Inventory management

Less is Better !

It's Safer!

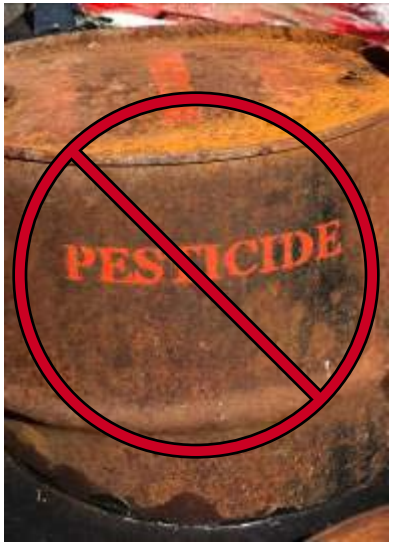
It may be cheaper to order diethyl ether in large containers

But, if it's opened for a long time—peroxides can form!



Inventory management – chemical aging

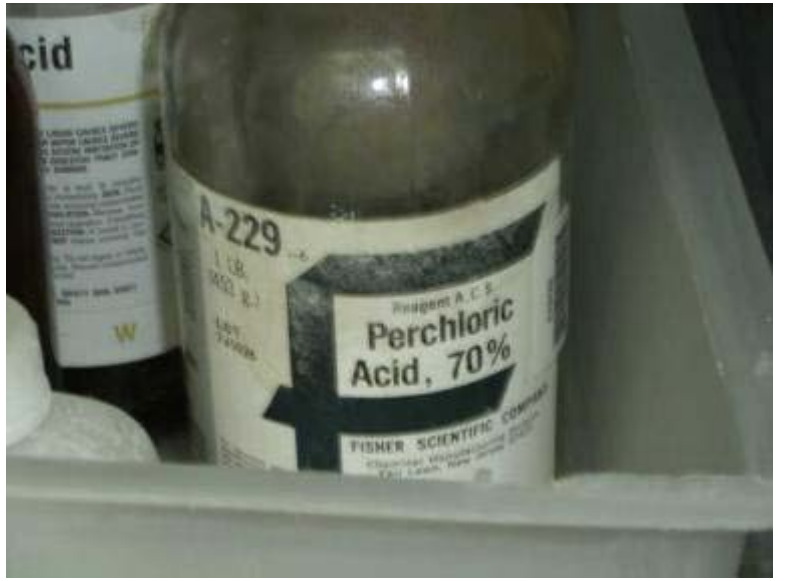
- How old are your chemicals?
- Some chemicals degrade over time
  - rotate stock
  - label & date
- Chemical assays have expiration dates



Explosives and Reactives

Examples:

- Peroxide-forming - ethers
- Perchlorate-forming – perchloric acid
- Water/moisture sensitive – Na, K, Li, LAlH, flammable metals



Control measures:

- Inventory control
- SOPs, inspections

Inventory management

-R-O-O-R-

Peroxide Forming Chemicals

Even with inhibitors they can become dangerous over time

- **discard or test if unsure**
- **label & date**

when received,
when opened, and
provide expiration date

Peroxide test kits and strips should be available

Peroxide forming chemicals

- Peroxide formation is caused by an autoxidation reaction.
- The reaction is initiated by light, heat, introduction of a contaminant or the loss of an inhibitor (BHT).
- Inhibitors slow, but do not stop peroxide formation.
- Most organic peroxide crystals are sensitive to heat, shock, or friction.
- It is important not to let peroxide forming chemicals evaporate to dryness or accumulate under screw caps.

-R-O-O-R-

Peroxide forming chemicals

Peroxides can explode when exposed to thermal or mechanical shock

Examples: ethers, dioxane, tetrahydrofuran

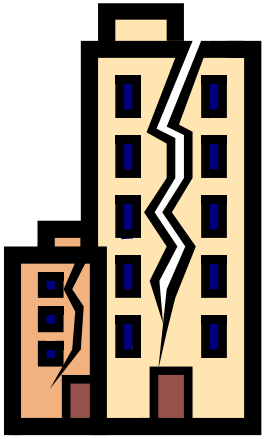
References:

There are excellent websites on peroxide forming chemicals and their hazards, use, storage, and disposal. For example, see:

http://www.med.cornell.edu/ehs/updates/peroxide_formers.htm

Chemical storage

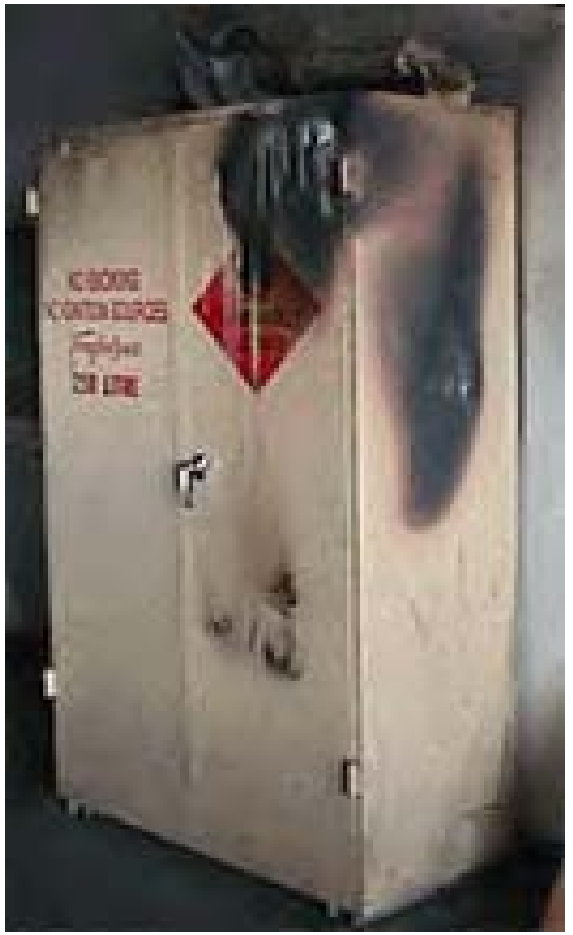
- Protect chemicals during normal operations
- Protect chemicals during unexpected events
  - Floods
  - Tidal waves
  - Earthquakes
  - Typhoons
  - Hurricanes



Chemical storage: Basic concepts

- Separate incompatible chemicals
- Separate flammables/explosives from ignition sources
- Use flammable storage cabinets for large quantities of flammable solvents
- Separate alkali metals from water
- Separate acids and bases

Use flammables storage cabinets



Chemical storage: Basic concepts

- **Store nitric acid separately**
- **Store large containers on bottom shelves**
- **Lock up drugs, chemical surety agents, highly toxic chemicals**
- **Do not store food in refrigerators with chemicals**

Compressed Gas Cylinders

- Uses
- Types
- Hazards
- Control Measures
  - Inventory control
  - Procurement authorization
  - Training
  - Inspection

Chemical storage: Gas cylinders

- Secure (chain/clamp) and separate gas cylinders
- Screw down cylinder caps
- Store in well-ventilated area
- Separate & label empty cylinders
- Store empty cylinders separately
- Separate flammable from reactive/oxidizing gases

Improper gas cylinder storage

Damage from Gas-cylinder fire

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An Accident Waiting to Happen

CSB video: Compressed gas fire

Chemical storage: Good practices

- Limit access
  - Label “Authorized Personnel Only”
  - Lock area/room/cabinets when not in use
- Be sure area is cool and well ventilated
- Secure storage shelves to wall or floor
- Shelves should have a ¾” front lip
  - In earthquake territory, have a rod several inches above shelf

Chemical storage: Bad practices

- **Do Not Store Chemicals**
  - on top of cabinets
  - on floor
  - in hoods
  - with food or drinks
  - in refrigerators used for food
  - where there are wide variations in temperature, humidity or sunlight

Chemical storage: Containers

- Don’t use chemical containers for food
- Don’t use food containers for chemicals
- Be sure all containers are properly closed
- Wipe-off outside of container before returning to storage area
- Transport/carry all containers safely
  - Preferably use outer protective container

Improper chemical storage

Never use hallways for storage

Safety Hazard!!

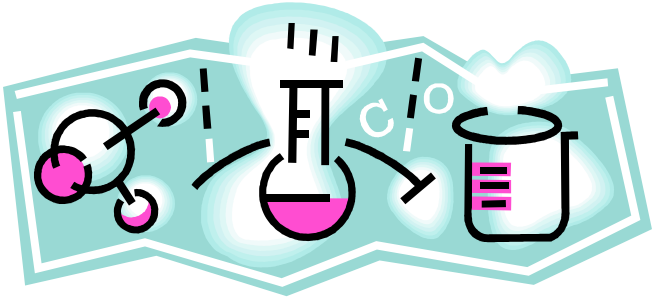
Blocks exit path in emergencies!!!

Chemical storage: Good practices

- **Separate incompatible chemicals**
  - **Organize chemicals by compatible groups**
  - **Alphabetize chemicals only within compatible groups**

Suggested shelf storage groups: Organics

- Acids, anhydrides
- Alcohols, amides, amines
- Aldehydes, esters, hydrocarbons
- Ethers, ketones, halogenated hydrocarbons
- Epoxies, isocyanates
- Azides, peroxides
- Nitriles, sulfides, sulfoxides
- Cresols, phenols



From: "School Chemistry Laboratory Safety Guide," US NIOSH Publication 2007-107

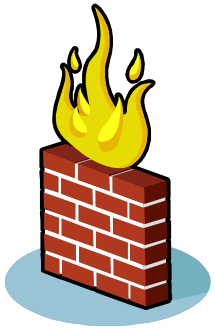
Suggested shelf storage groups: Inorganics

- Metals, hydrides
- Halides, halogens, phosphates, sulfates, sulfides
- Amides, azides, nitrates, nitrites
- Carbonates, hydroxides, oxides, silicates
- Chlorates, chlorites, perchlorates, peroxides
- Arsenates, cyanides, cyanates
- Borates, chromates, manganates
- Acids
- Arsenics, phosphorus, sulfur

From: "School Chemistry Laboratory Safety Guide," US NIOSH Publication 2007-107

Best practice: access control

- Proper training of chemical handling personnel



- Only trained and approved personnel
  - have access to stock room and keys
  - administrative privileges to inventory and database

- Locked doors and cabinets for controlled substances
  - Radioactive materials
  - Drugs and consumable alcohol
  - Explosives (special handling facility)
  - Dual use chemicals
  - Hazardous waste - high toxicity chemicals

References

"Less is Better," American Chemical Society, Washington DC, 2003, available online: http://membership.acs.org/c/ccs/publications.htm

"School Chemistry Laboratory Safety Guide," US NIOSH Publication 2007-107, Cincinnati, OH, 2006, available on-line: http://www.cpsc.gov/CPSCPUB/PUBS/NIOSH2007107.pdf

"Prudent Practices in the Laboratory: Handling and Disposal of Chemicals," National Academy Press, 1995, available online: http://www.nap.edu/catalog.php?record_id=4911

Break

Other Hazards in a Chemical Laboratory

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Physical Hazards

Conditions, besides chemical, biological or radiological conditions or circumstances, that can cause injury, illness and death:

- Fire / Asbestos
- Centrifuges
- Cryogenics
- Ergonomic
- Office
- Physical stress/strain
- Construction
- Noise
- Heat/cold
- Sunlight
- Non-ionizing radiation
- Mechanical
- Electrical
- Housekeeping
- Spills/trips

Asbestos-Containing Materials

- Gloves
- Lab hoods
- Lab benches

Johns-Manville
TRANSITE® PI
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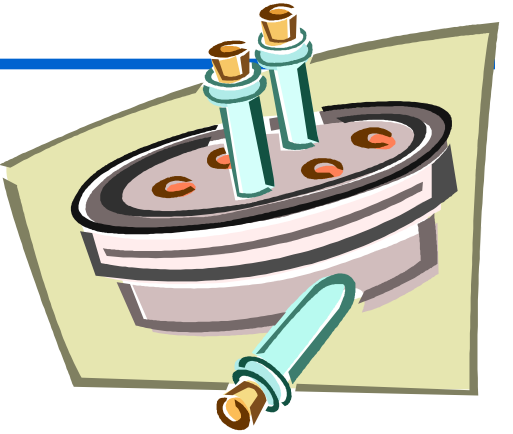
Centrifuge Equipment

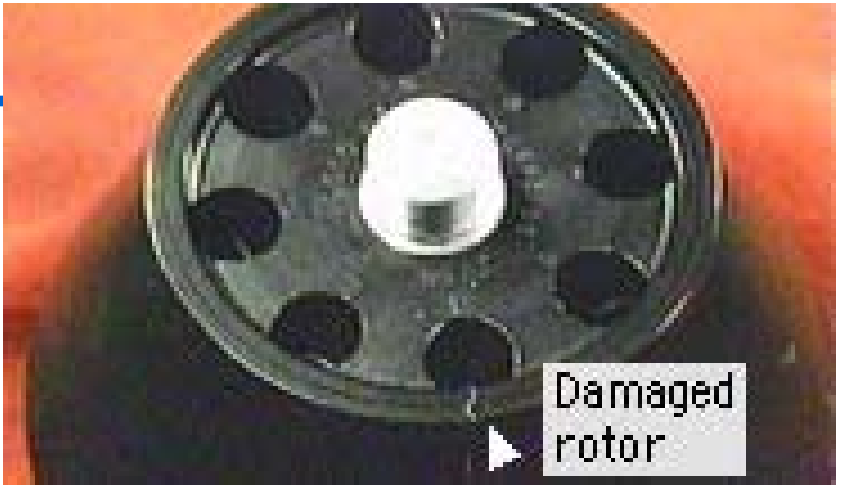


- Uses
- Hazards
- Control of hazards
  - Only authorized users can use equipment
  - Users must be trained
  - Assign responsibility to lab tech
  - Include in periodic lab inspections

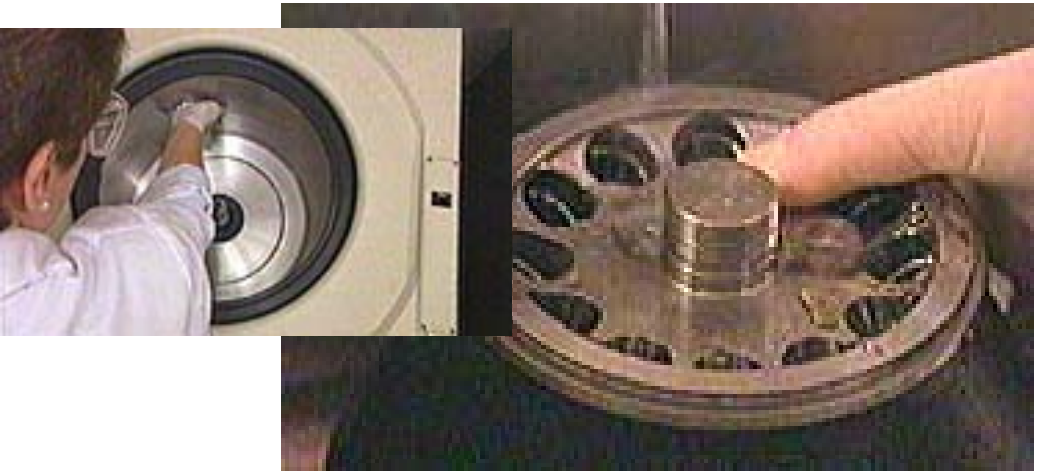
- Rotor
- Drive Shaft
- Motor
- Cabinet provides varying degrees of protection

Centrifuge Safety

Don’t overload …

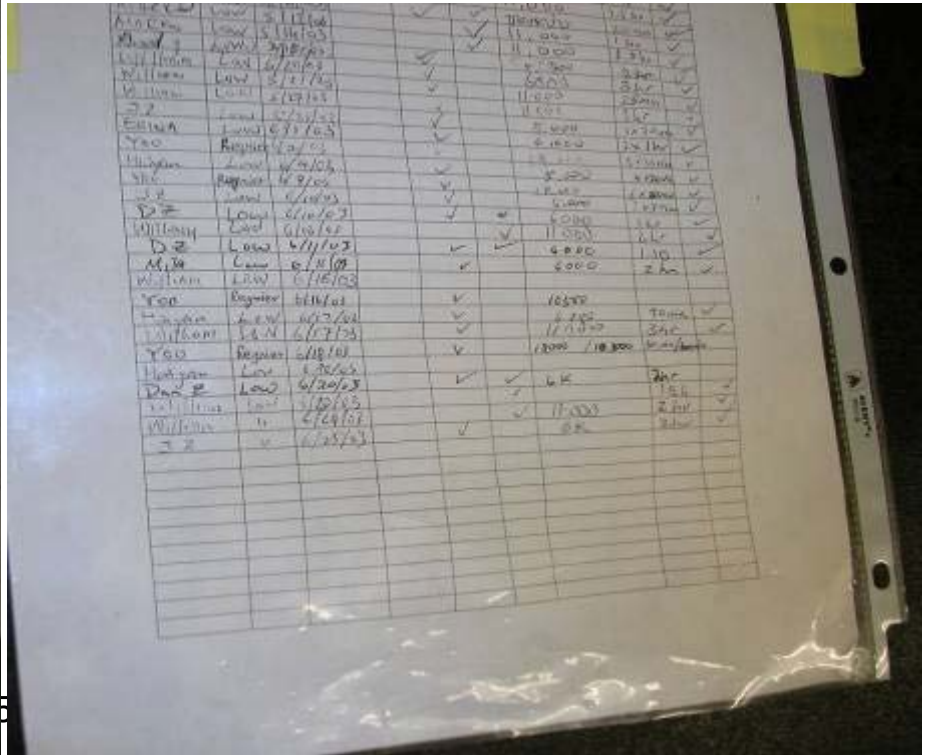


Check rotor for cracks



Keep rotor and centrifuge clean …

Set it up right…



Chemical storage: Cryogenics

- Store cryogenics separately from other chemicals
- Store cryogenics (liquid nitrogen) & dry ice in well ventilated areas
- Use proper PPE (including eye protection) when handling & moving cryogenics
- Do not use cryogenics in closed areas

Cryogens

- What are they?
- Uses
- Hazards
- Control
  - training
  - inspection

CY04

Cyrogen Storage

Exploding liquid nitrogen cylinder ruins lab.

Dry Ice

- What is dry ice?
- Uses
- Hazards
- Control measures

Housekeeping

Sm Eu
Er Tm
ISO 9002 CERT

Do <u>not</u> use hoods for storage!

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Don’t block hood air flow.

Place large equipment in a hood on 5 cm blocks to allow air flow around and under equipment.

Safety shields can block airflow and reduce hood effectiveness.

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Don’t block hallways and exits!

Access to emergency equipment is <u>essential</u>.

Always check that equipment is not blocked.

Food is never allowed in laboratories.

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What’s Wrong With This Picture?

Open-toed shoes are not allowed in laboratories.

Employees are not allowed to wear gloves, lab coats or other PPE outside the lab.

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Working Alone/Unattended Operations

- **Working Alone**
  - ***Avoid!***
  - **Murphy's Law will get you!**
    (Anything that can go wrong, will go wrong!)
  - **Use the "Buddy System"**
- **Unattended Operations/Reactions**
  - **Caution! Prime sources of fires, spills and explosions**
  - **Check periodically!**
  - **Fail-safe provisions**
  - **Leave the lights on to indicate the presence of an unattended activity**
  - *Post appropriate signs and emergency phone #'s*
  - **Notify those potentially impacted by malfunction**

Electrical Hazards

- **Can be a significant problem**
  - **Frayed cords, no UL-listing, overloaded circuits**
  - **Static electricity**

- **Hazards**
  - **Fires, electrical shock, power outages**

- **Control**
  - **Inspect, act immediately, education**

Check to see that all outlets are grounded and that the polarity is correct.

Storage should be at least 1 m from electrical panels, mechanical rooms, air ducts, heaters, light fixtures.

Don’t store combustibles in mechanical rooms or electrical closets.

In emergencies it may be necessary to access these panels quickly.

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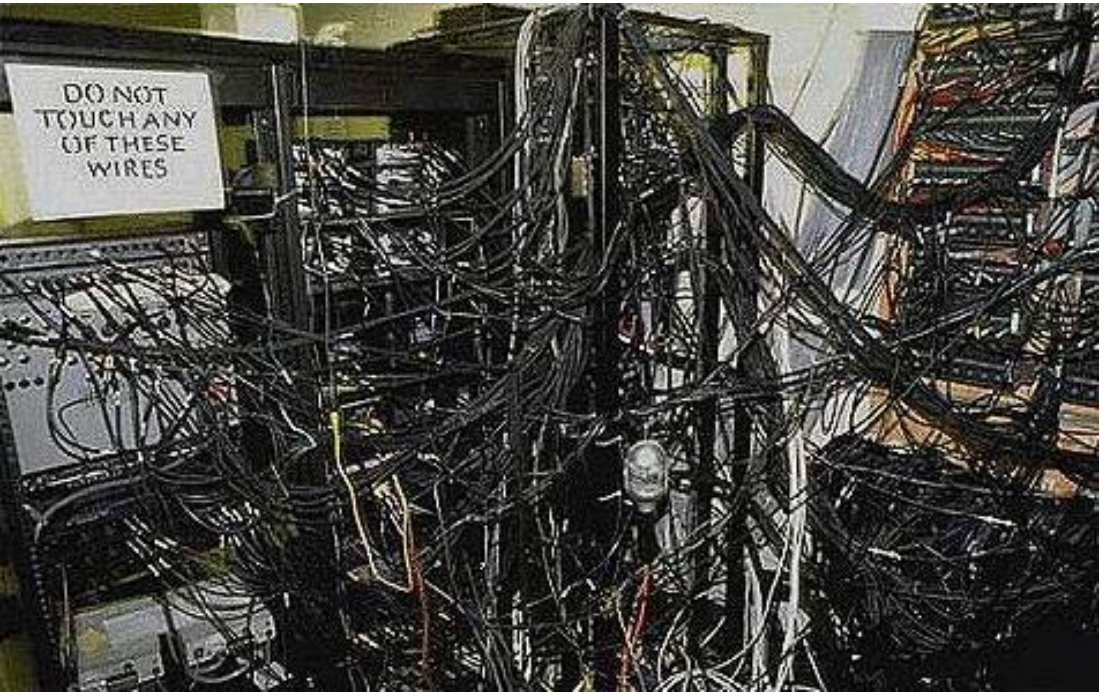
Multi-outlet strips must be approved and <u>not</u> used for high-amp equipment.

(e.g., ovens, refrigerators)

Don’t Do This…



Heating Mantles

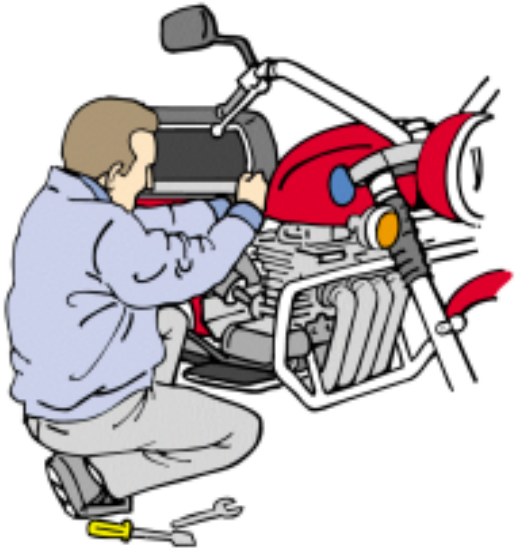
- **Uses**
- **Hazards**
- **Unshielded rheostats**
- **Control measures**

Ergonomics

- **Types of hazards**

- **Why be concerned with Ergonomics?**

Awkward Posture

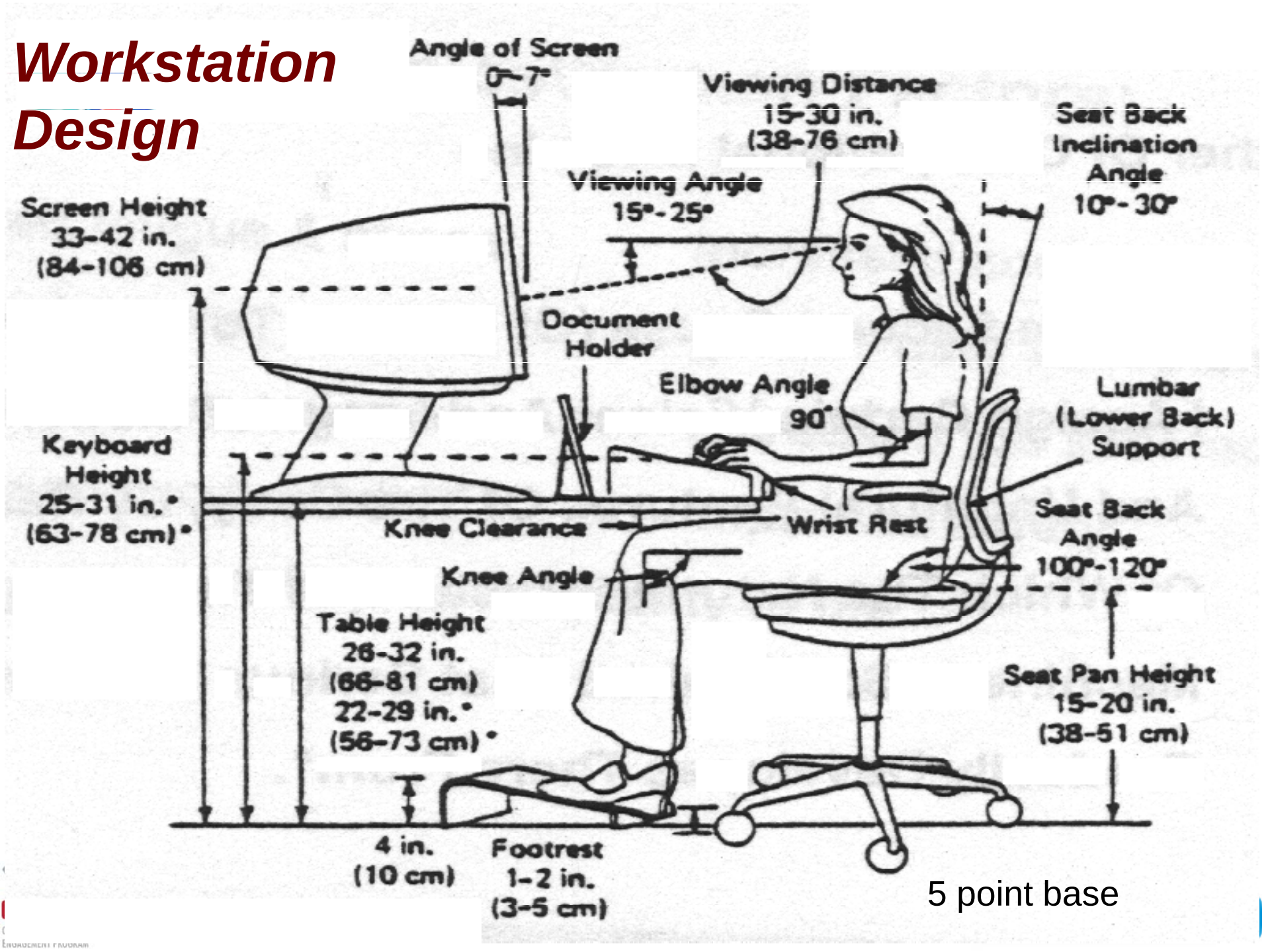


Too low

Too far away

Too high

Workstation Design



5 point base

Workstation Design Rules

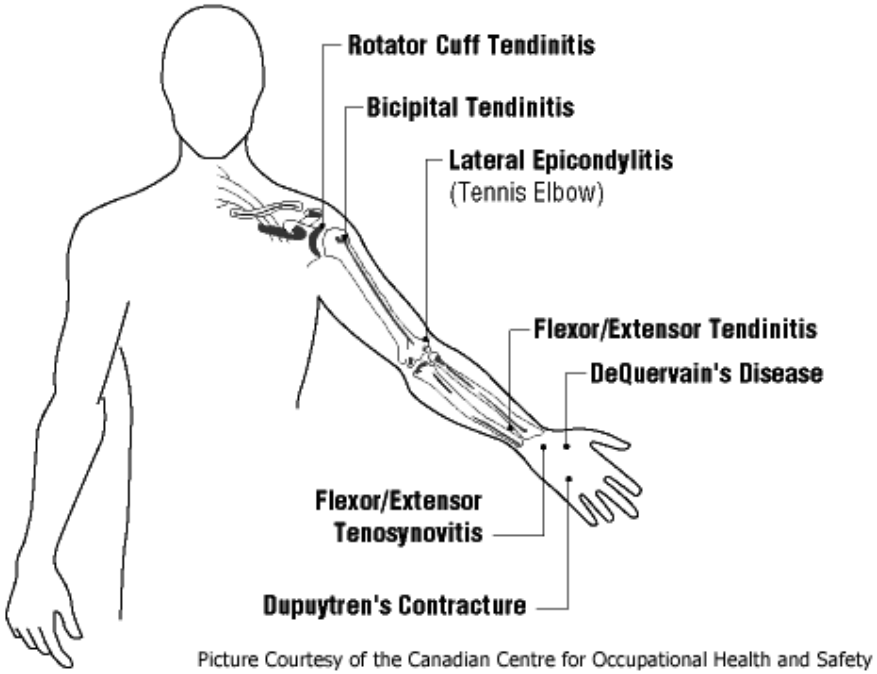
- Chairs: 5 cm and 110 degree rule
  - Adequate lumbar support
- Neutral wrist position
- Elbow 90 degree at “keyboard home row”
- Screen below eye level
  - Copy at same height
- Illumination: prevention of glare
- Breaks: rest eyes and body

Repetitive Motion Disorders

About 15 to 20% of workers in jobs requiring highly repetitive motion of shoulders, arms, wrists or hands develop repetitive motion disorders.

Disorder	Affected Site
Carpal Tunnel Syndrome	Wrist
Tendonitis	Elbow, wrist, hand
Tenosynovitis	Elbow, wrist, hand
Epicondylitis	Tennis elbow
Reynaud's phenomenon	"White finger"
Ulnar neuropathy	Fingers

Examples:



Picture Courtesy of the Canadian Centre for Occupational Health and Safety

- ***DeQuervain's Syndrome:*** Tenosynovitis affecting the tendons on the side of the wrist and the base of the thumb
- ***Flexor/Extensor Tendinitis:*** Tendinitis affecting the tendons in the wrist
- ***Stenosing Tenosynovitis (Trigger Finger):*** Tenosynovitis affecting the tendons in a finger or thumb
- ***Bicipital Tendinitis:*** Tendinitis affecting the biceps tendon
- ***Rotator Cuff Tendinitis:*** Tendinitis affecting the tendons in the shoulder
- ***Lateral Epicondylitis (Tennis Elbow):*** Tendinitis affecting the tendons on the outer side of the elbow
- ***Medial Epicondylitis (Golfer's Elbow):*** Tendinitis affecting the tendons on the inside of the elbow

Ergonomics

BLONDIE
WHAT COULD BE CAUSING MY LOWER BACK PAIN, DOCTOR?
I'M NOT SURE
DO YOU WORK IN A BENT-OVER POSITION?
NO, I SIT STRAIGHT UP AND I HAVE A GOOD BACK SUPPORT
HMMM... WELL, WE'LL FIGURE IT OUT IN TIME
DID THEY FIND OUT WHY YOUR BACK HURTS?
NOT YET

Freezers

- Ultra low temperatures
  - -20°C, -80°C
  - Upright vs. walk-in
- Emergency power
- Labels

- Precautions
  - *No dry ice in freezers!*
  - Improper storage
- PPE

Glassware Handling

- **Potential Hazards**
  - **Ergonomics**
  - **High temperature**
  - **Broken glassware**
  - **Improper use**
- **Control**
  - **Inspection**
  - **Training**

Beware of contaminated Glassware, especially if broken!

Autoclave Explosion

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High Pressure Reactions

- **Experiments carried out at pressures above 1 atmosphere (~1bar, 760 Torr, ~100,000 Pa).**
  - **Use of supercritical fluids (CO_2)**

- **Hazards**
  - **Explosions, equipment failure**

- **Control Measures**
  - **SOPs, training, engineering controls, inspection**

BÜCHI 461 Water Bath
14 7:59

Vacuum Work

- **Uses**
  - Aspiration
- **Hazards**
  - Injury due to glass breakage
  - Toxicity of chemical contained in vacuum
  - Fire following flask breakage
  - Contaminated pump oil
- **Control Measures**
  - SOPs, inspection, education

Mechanical hazards like open drive belts with pinch points must have shields and guards.

Oil pumps need drip pans to contain oil.

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Noise

- Elevated noise levels can be a problem.
- Potential Hazards
  - Example: bone-cutting saws, mechanical water aspirators.
- Control Measures
  - Inspections, PPE, warning labels, training.

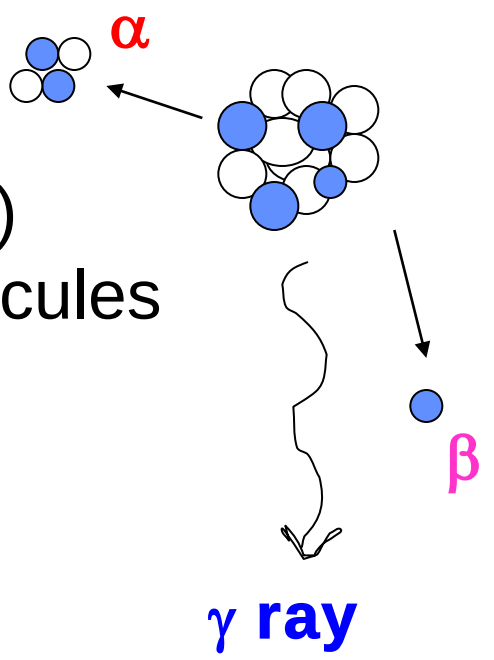
Magnetic Fields

- **Uses – NMR, MRI**
- **Hazards**
  - **Magnetic field**
  - **High voltage**
  - **Cryogenic liquids**
    - e.g., nitrogen, helium
  - **Other hazardous materials in lab**
- **Control Measures**
  - **Control access to area**
  - **Training**
  - **Warning signs**

Hazardous Area

Ionizing vs. Non-ionizing Radiation

- **IONIZING RADIATION**
  - Particulate or electromagnetic
  - Charged (α, β) or uncharged (γ, X, n)
  - Causes **ionization** of atoms or molecules



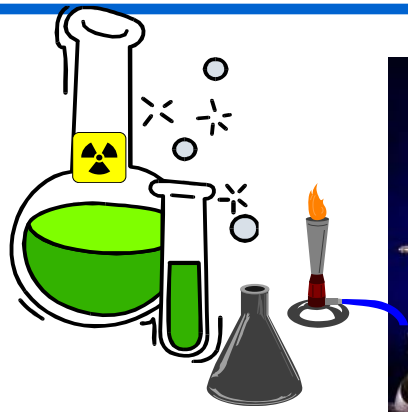
- **NON-IONIZING RADIATION**
  - Electromagnetic (UV, IR, MW, RF)
  - Can not ionize atoms or molecules

Common Uses of Ionizing Radiation

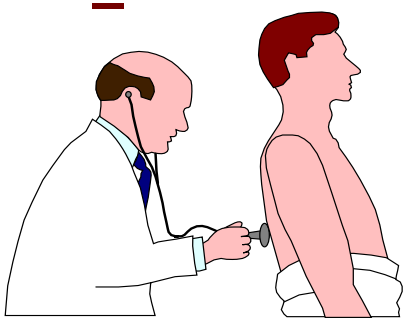
Research & Development

$^{14}_{6}C$ $^{35}_{16}S$ $^{3}_{1}H$

$^{125}_{53}I$ $^{32}_{15}P$



Medical



X-Rays

Tim Boyle / Getty Images file

Electron Microscopes

- Types
  - SEM, TEM
- Hazards
  - X-rays
- Control of hazard
  - Periodic maintenance
  - Conduct radiation survey
  - Include in personnel radiation safety program

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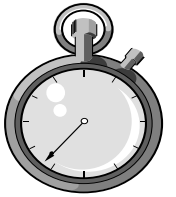
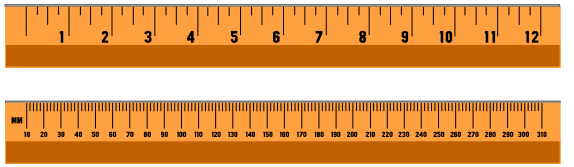
Chemical
SAFETY AND SECURITY TRAINING

Protect yourself by:

- **TIME** – Limit time near source

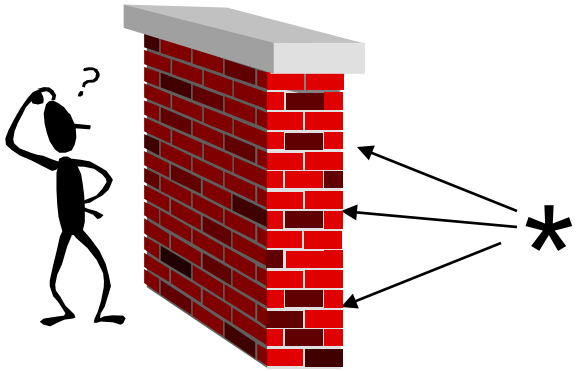


- **DISTANCE** – Stay away

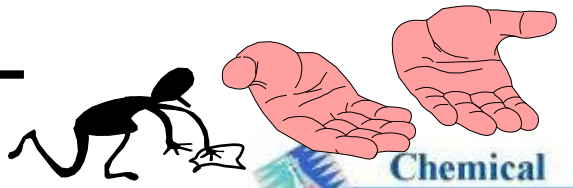


$$I_2 = I_1\left(\frac{d_1}{d_2}\right)^2$$

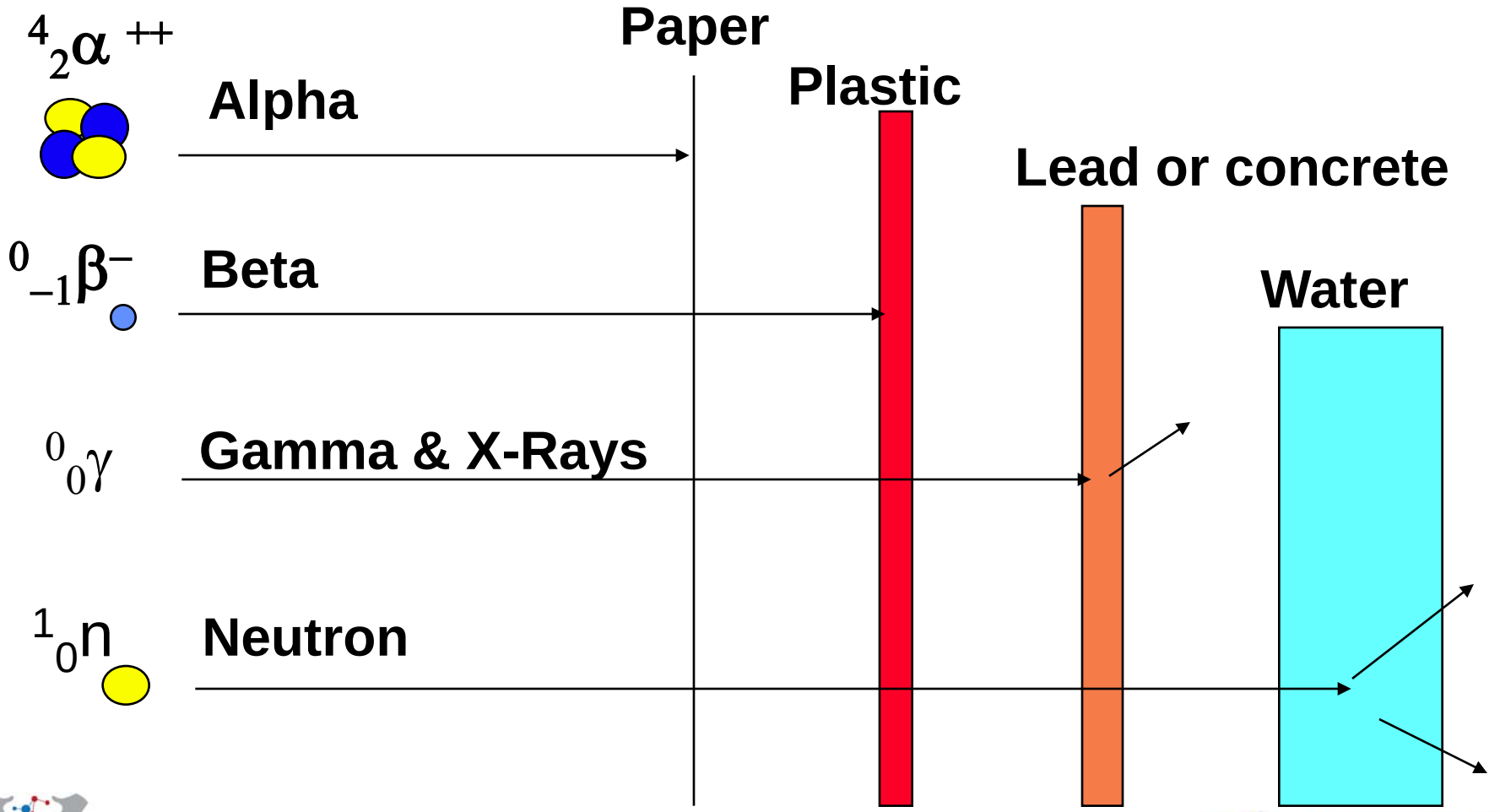
- **SHIELDING** – Absorb energy



- **CONTAMINATION CONTROL**



Shielding Materials



Non-Ionizing Radiation

- UV, Visible, IR, Lasers
- Hazards
  - Skin erythema
  - Eye injuries
- Control Measures
  - Training, PPE, warning signs and labels, interlocks

Radio-frequency & Microwaves

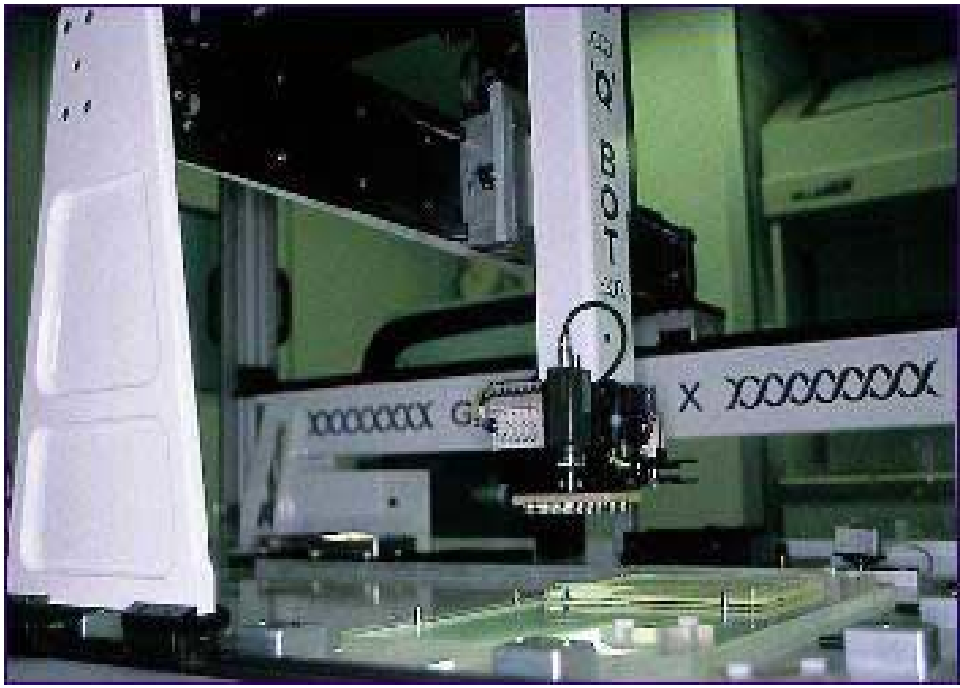
- Uses
  - RF ovens and furnaces
- Hazards
  - Cataracts, sterility
  - Arcing – use of metal in microwave
  - Superheating of liquids
  - Explosion of capped vials
- Control Measures
  - SOPs, education, inspection

Robotics

- **Free-moving parts**
  - **“Struck by” injuries**
- **Noise**
- **Lasers**

Robotics

Aerosol Generation



Robotics

Sharps, Needles, Blades

Hazards

- Needlesticks
- Cuts
- Contamination

Sharps, Needles, Blades

- **Control Measures**
  - SOPs
  - Training
  - Modify work practices
  - Engineering Controls

Slips, Trips, Falls

- Most common injuries
- Causes
  - Chemical spills and leaks
  - Improper work practices
- Control Measures
  - SOPs, proper equipment, effective communication, engineering controls

Control of Hazards

- **Think!**
- **Develop SOPs, safety manual, policies**
  - **reviewed and approved by management**
- **Research protocol review**
- **Install engineering controls**
- **Provide PPE**
- **Provide training**
- **Conduct inspections, routine & unannounced with lab supervisor**
- **Document and *follow-up***
- **Take action**

Any Questions?

Lunch

Fire Protection and Prevention in Chemical Laboratories

Fires

- **Preventable**
- **Caused by unsafe practices**
  - **Electrical safety violations**
  - **Uncontrolled use of flammable and combustible materials**
- **Control**
  - **Inspect, inspect, inspect**

Educate, educate, educate!

Home Fires

1 million fires and 8,000 deaths annually in the US

Leading causes:

- **Cigarettes**
- **Heating/cooling equipment**
- **Electrical**
- **Matches, lighters, candles**

Industrial Fires

- **Fifth leading cause of accidental death**
  - Vehicles, falls, poison, drowning, fire
- **Most dangerous industries from fire hazard:**
  - Mines
  - Grain elevators and mills
  - Refineries
  - Chemical plants
- **Leading causes:**
  - Electrical
  - Smoking
  - Friction
  - Overheating
  - Hot surfaces

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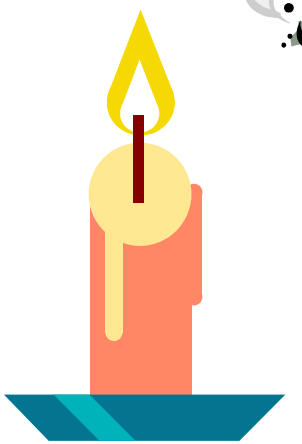
Fire Causes in the US

Factory Mutual

25,000 fires/over 10 yrs:

- **Electrical 23%**
- **Smoking 18%**
- **Friction 10%**
- **Abnormal process temp. 8%**
- **Hot Surfaces 7%**
- **Improper open flames 7%**
- **Arson 3%**



Key Elements of Fire Safety

Get occupants out

Minimize property loss and interruption

Fire Containment/Suppression

Common Myths

- **Fire will light the way out**
  - Smoke cloud & soot
- **Plenty of time to escape**
  - 1 min from small to inescapable fire
- **People are killed by the flames**
  - #1 killer in fires is CO, not flames
- **Wait to be rescued**
  - No! Act to save self
  - Ladders can reach to about 6th floor
- **Can not prepare for a fire**
  - Preparation can save your life

It’s the Smoke…

Facial Burns

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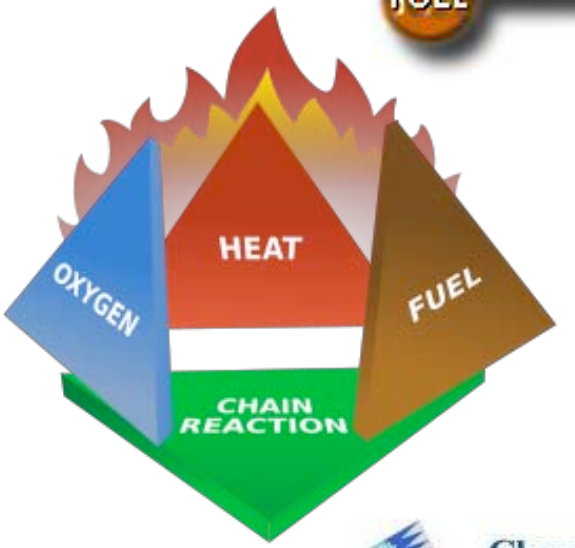
Fire

- A fire must have four things to ignite and maintain combustion:
  - Fuel
  - Heat
  - Oxygen
  - Chain reaction



Flash Point

- **Flash point:**
  - The minimum temperature at which a liquid gives off enough vapor to form an ignitable mixture.
  - In general, the lower the flash point, the greater the hazard.
- **Flammable liquids:**
  - have flash points below 38ºC
  - are more dangerous than combustible liquids
  - may be ignited at room temperature
- **Combustible liquids:**
  - have flash points at or above 38ºC
  - Can pose serious fire and/or explosion hazards when heated

Flammability/Explosive Limits

Above UFL/UEL, mixture is **too rich to burn**

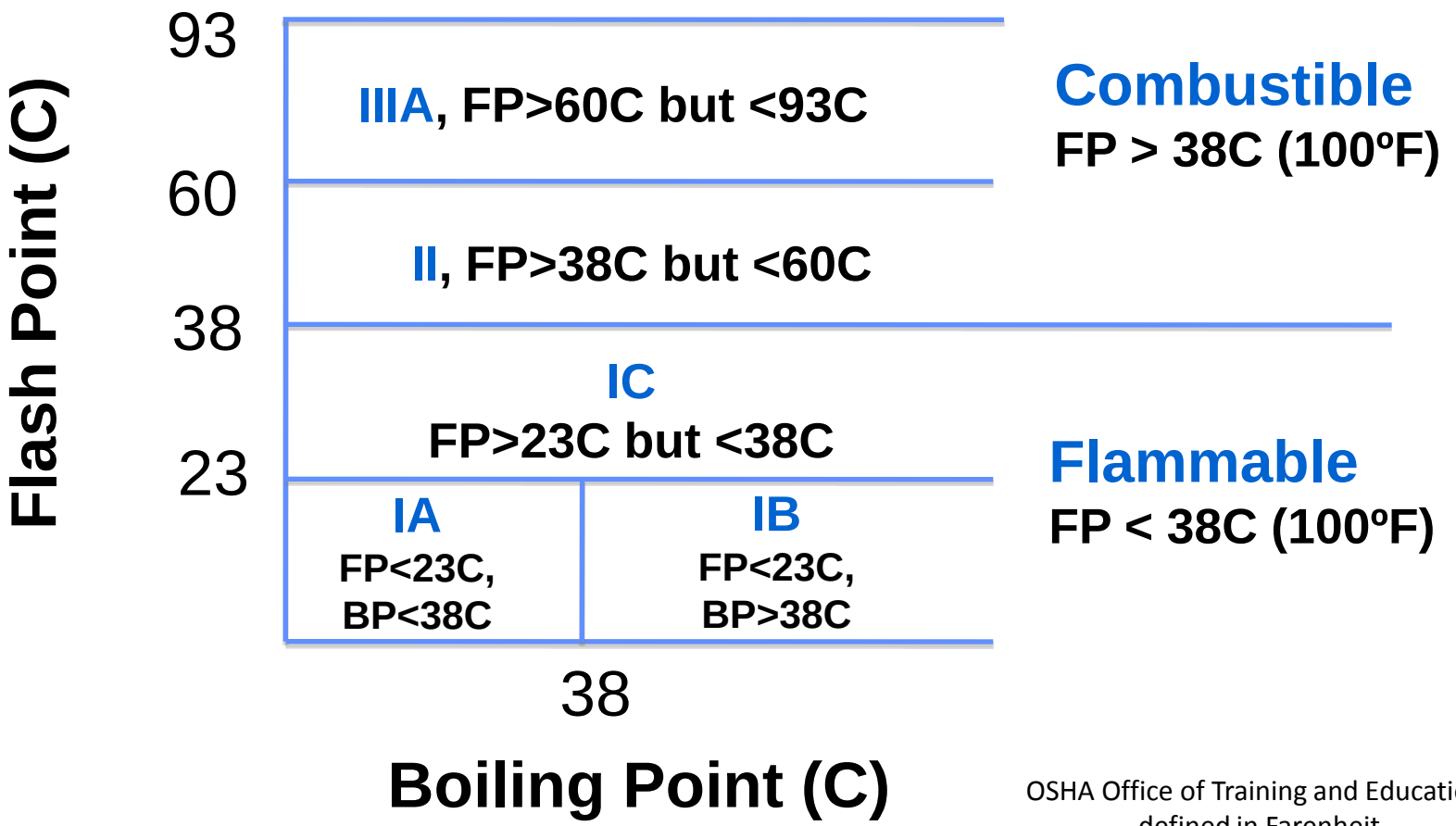
Upper Flammability/Explosive Limit (**UFL/UEL**)

Flammability/Explosive Range

Lower Flammability/ Explosive Limit (**LFL/LEL**)

Below LFL/LEL, mixture is **too lean to burn**

Classes of Flammable and Combustible Liquids



OSHA Office of Training and Education, defined in Farenheit

Classes of Some Flammable Liquids

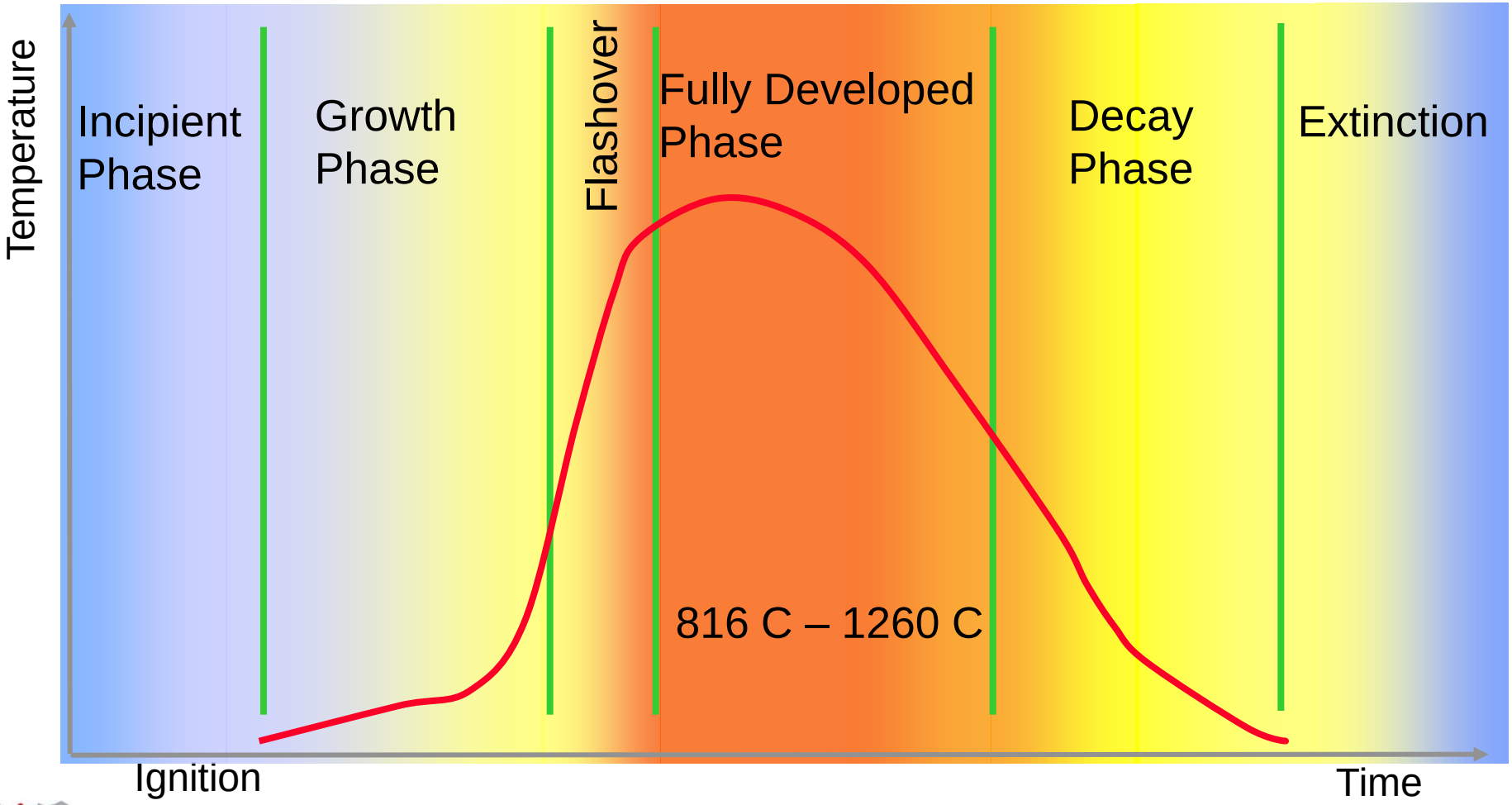
	Common Name	Flash Point (C)
CLASS IA	Ethyl Ether	- 45
CLASS IB	Gasoline	- 43
	Methyl Ethyl Ketone	- 6
	Toluene	4
CLASS IC	Xylene	27 - 46
	Turpentine	35

Fire Safety Program Components

A good plan for safe use of flammable and combustible liquids contains at least these components:

- **Control of ignition sources**
- **Proper storage**
- **Fire control**
- **Safe handling**

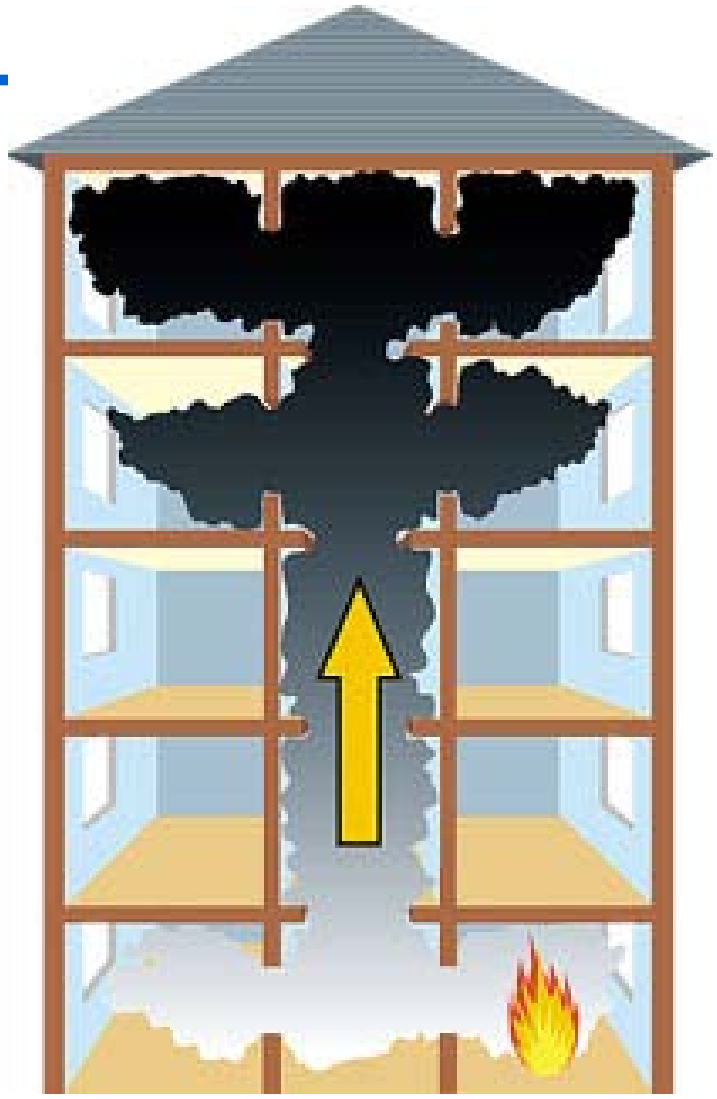
Fire Behavior



Fire Behavior

- Hot expanding gases move vertically
  - Tightness of construction
  - External winds
  - Internal/external temperature
  - Vertical openings
    - Stairways
    - Elevator shafts
    - Ventilation shafts

Stack Effect



Vapor Volume

Volume of gas formed when a liquid substance evaporates

Computed from specific gravity and vapor density

$$\text{Vapor Volume } (m^3/\text{liter}) = \frac{0.829\ (\text{SpG})}{\text{Vapor density}}$$

Example: What is the vapor volume of a liter of acetone?
[SpG = 0.9, relative to water; Vapor density = 2, relative to air]

$$\text{Vapor Volume } (m^3/l) = \frac{0.829\ (0.9)}{2} = 0.373\ m^3/L$$

Vapor Volume

What is the probability of forming a combustible mixture if a 4 liter container of acetone is used in a room 3 x 4 x 2.5 m?

[LEL = 2.5%; assume incomplete mixing factor 5]

Volume of the space = 30 m^3

Vapor volume = 0.373 m^3/L

Vapor volume necessary to form a Combustible mixture:

$$30\ m^3 \times 0.025 = 0.75\ m^3$$

$$\frac{0.75\ m^3}{0.373\ m^3/\ L} = 2.01\ L$$

Applying the mixing factor of 5:

2.01 L / 5 = 0.40 L

[About = 1 coffee mug]

Since it doesn't take much more than "1 coffee mug" of acetone to form a combustible mixture, the probability appears to be high!

Housekeeping…

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Flammable Liquid Containers

Tool Cleaning (Acetone)

Fire Hazards

- **Sources of fuel**
  - Flammable liquids
  - Flammable gases
  - Wood, paper, cardboard
  - Oil soaked rags

Train employees to notice & report fire hazards

Periodic inspections

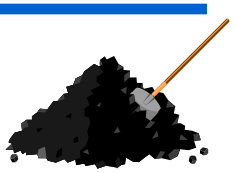
Drills

- **Sources of heat (ignition)**
  - Electrical circuits:
    - Shorts, sparks
    - Arcs (switches)
    - Heat build-up
  - Hot surfaces
  - Space heaters
  - Hotplates, coffee pots, coffee makers
  - Welding
  - Smoking
  - Open flames
  - Static electricity

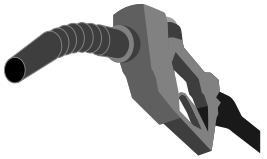
Classification of Fires

With recommended extinguisher distances

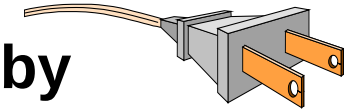
- **A** Ordinary combustibles – cloth, paper, wood, coal — ~23 m



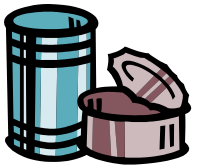
- **B** Flammable/combustible liquids, gases, greases and oils - gasoline, diesel fuel — ~15 m



- **C** Energized Electrical equipment cables, motors — nearby



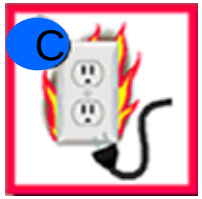
- **D** Combustible metals - sodium, magnesium, titanium — ~23 m

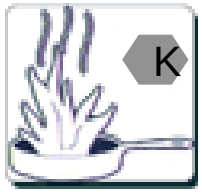


- **K** Restaurant grease fires associated with cooking — nearby

Classification of Fires

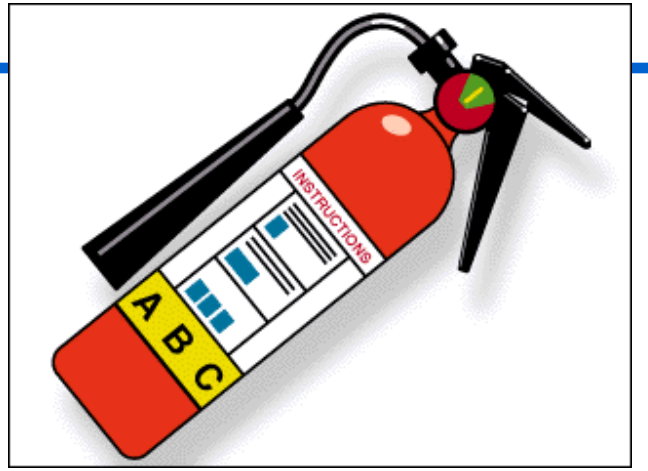
- **A** Extinguish by cooling or smothering.
  (water)
- **B** Extinguish by inhibiting release of combustible vapors or interfering with the chemical reaction-release of OH radicals.
  (CO_2 or dry powder: monoammonium phosphate)
- **C** Extinguishing agent must ***not*** be conductive.
  (CO_2 or dry powder)
- **D** Extinguishing agents must absorb heat and not react with the metal.
  (special dry powder, sand)
- **K** (Special liquid chemicals)





Fire Extinguishers

Dry Chemical



CO_2

Water

Placed within ~15-25 m

Annual & Monthly inspections

Large Fire Extinguisher

Fire Extinguishers

Fire Alarm Systems

- **Will it be recognized and followed?**
  - Audible, visual, public address systems…
- **What about deaf or blind employees?**
  - Are there “dead spaces”…
- **System reliability**
  - System failure may not be obvious
  - Supervised systems (built-in monitoring)
  - Testing, maintenance and backup systems

Fire Detection & Alarms

- **Thermal**

- **Heat**
  - Fixed temp
  - Rate of rise
    - ~6 to 8 C/min (12 to 15ºF/min)

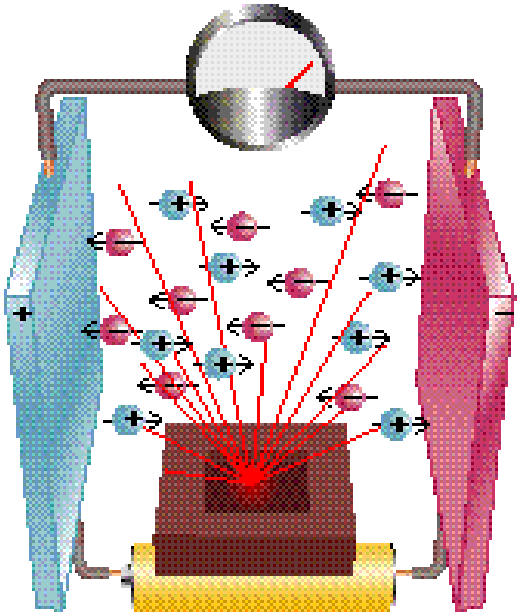
Issues:

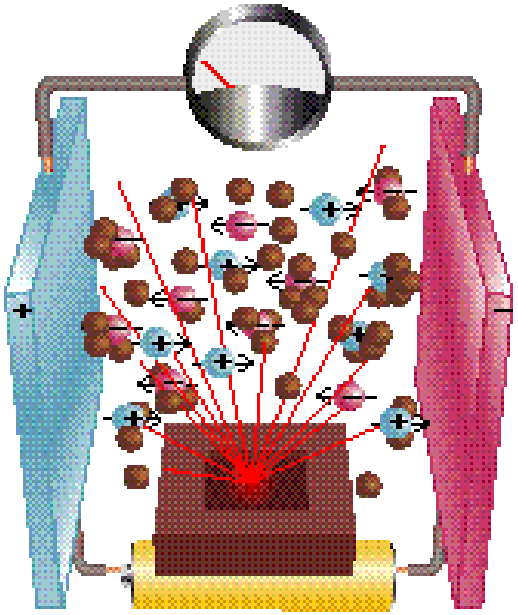
Testing

Dust, corrosion, hot processes, weather, mechanical damage

- **Smoke**
  - Photoelectric
    - IR from smoke
  - Ionization
    - Ionize smoke
- **Flame Detectors**
  - Flames – IR or UV
- **Gas Sensors**

Smoke Detectors





- Alpha particles from Americium-241 (red lines) ionize the air molecules (pink and blue spheres).
- The ions carry a small current between two electrodes.
- Smoke particles (brown spheres) attach to ions reducing current and initiate alarm.

False Alarms

False alarms may be triggered by construction dust created during renovations

Manual Pull Stations

- Manual Pull Stations are devices located on the wall (usually near an exit)
  - Sends a signal to the building's fire alarm system when activated
  - Places the building into alarm

People are reluctant to sound fire alarms!

Responding To A Fire

Employee Training

Few employees know how to *effectively* use extinguishers!

Need for training:

- Upon initial employment
- Annual refresher

Emergency Response (phone numbers)

Using a Fire Extinguisher

P Pull
A Aim
S Squeeze
S Sweep

Video Courtesy of Washington State Emergency Management Division, Public Education Program

Water

- **Water is highly effective on Class A fires, by cooling down the fire and surrounding atmosphere.**
- **Water is usually available.**
- **It can be used to cool down the firefighting team to prevent heat exposure.**

Disadvantages

- Water should NOT be used to control a B or C fire.
- Inadequate pressure or too high pressure can cause problems.
- The volume of water can be restricted by the length of water lines and hoses (frictional loss ~3500 Pa for every 3 meters of 4 cm diameter hose).
- The fire nozzle can clog due to non-filtered materials in the lines.
- Hydrogen can be produced if water is applied to very-hot fires.

Electrical Fires

- **Pull the plug out or switch off the power at the fuse box. This may stop the fire immediately.**
- **Smother the fire with a fire blanket, or use a dry powder.**
- **Never use water on it.**

WHAT TO DO IF SOMEONE CATCHES ON FIRE

If *you* should catch on fire:

STOP - where you are
DROP - to the floor
ROLL - around on the floor

This smothers the flames, possibly saving your life.

Remember STOP, DROP and ROLL

If a *co-worker* catches on fire:

Smother flames by grabbing a blanket or rug
Wrap them in it.
Could save them from serious burns or death.

WHEN NOT TO FIGHT A FIRE

Don’t fight a fire, when:

- It is bigger than a waste paper bin
- One extinguisher is not enough
- The fire is spreading beyond the spot where it started
- Smoke is affecting your breathing
- You can't fight the fire with your back to an escape exit
- The fire can block your only escape
- You don't have adequate fire-fighting equipment

DON'T FIGHT THE FIRE YOURSELF

CALL FOR HELP

Remember

When…

- **The extinguisher runs out of agent**
- **Your path of escape is threatened**
- **The extinguisher proves to be ineffective**
- **You are no longer be able to safely fight the fire**

…LEAVE THE AREA IMMEDIATELY!

Storage Guidelines

- All storage must be at least 1 m from electrical panels. In some emergency situations it will be necessary to access these panels quickly.

Improper Storage in front of Electrical Panel

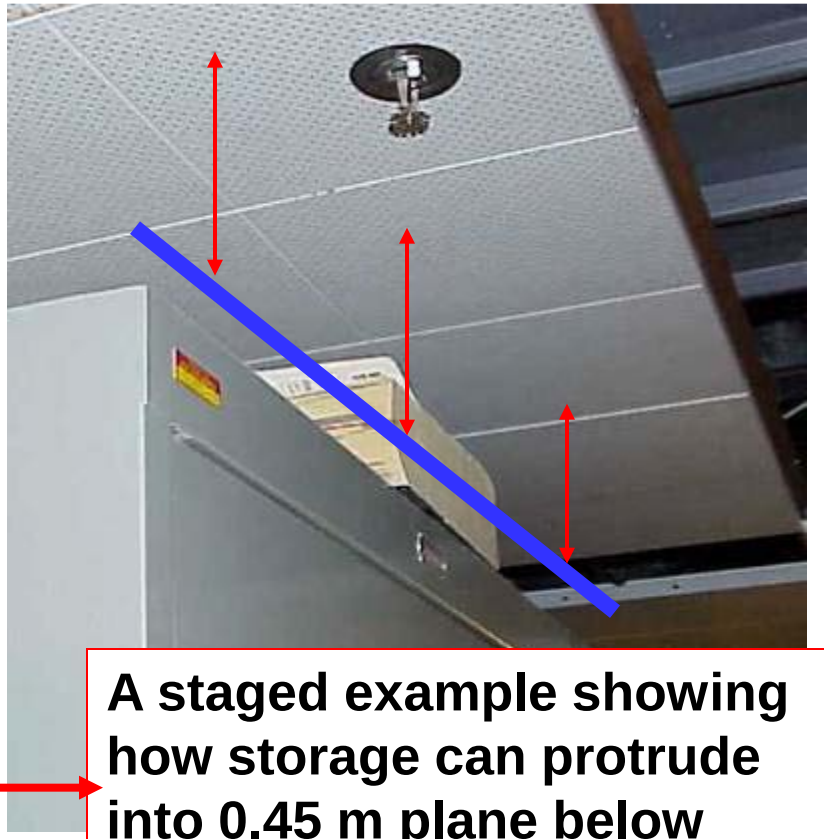
- Maintain at least 1 m clearance from heating surfaces, air ducts, heaters, and lighting fixtures.
- Storage of combustible materials in mechanical rooms is prohibited.

Improper Mechanical Room Storage

Storage Guidelines

- No storage is allowed in corridors and stairwells. A cluttered hallway could slow down emergency evacuation.

- Storage must not exceed a plane of 0.45 m below sprinkler heads or smoke detectors. Storage that breaks this plane may prevent sprinkler heads from fully covering room during a fire.



A staged example showing how storage can protrude into 0.45 m plane below sprinkler heads.

CHE
ENGAGEMENT PROGRAM

Myths about Sprinkler Systems

- **A sprinkler system will cause excessive water damage**
  - Sprinklers use a fraction of water compared with a fire hose.
  - Sprinklers release ~30 – 90 liters per minute compared to a fire hose at ~190 – 475 liters per minute.
  - Sprinklers operate very early in the fire development, and consequently require a smaller quantity of water.
- **When a fire occurs, every sprinkler head goes off**
  - Sprinkler heads are individually activated by fire.
  - > 50% of the fires are controlled by ≤ 4 sprinkler heads, and in many instances fires are controlled with one sprinkler.
- **The pipes burst due to freezing**
  - Sprinklers can be protected with various forms of frost protection, such as installing a dry system or providing heating elements to protect the sprinkler systems.

More Myths about Sprinkler Systems

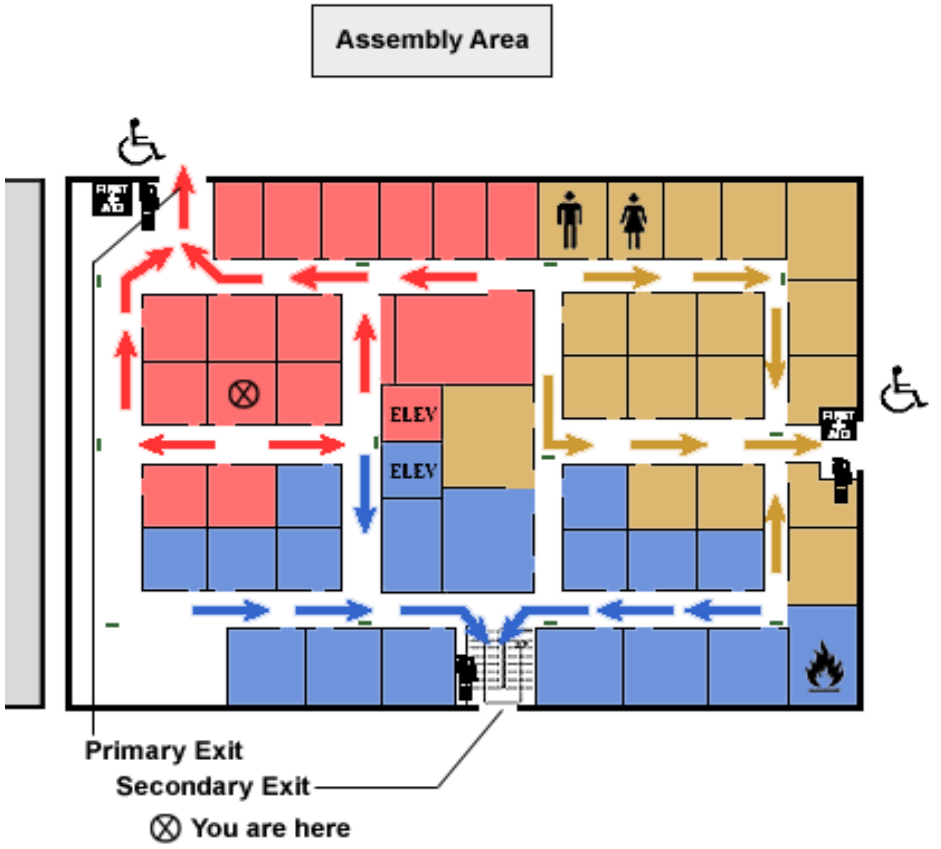
- **Sprinkler systems might accidentally go off**
  - Sprinklers are very reliable; the chances of going off without mechanical assistance are 1 in 16 million; Fork lift truck drivers soon learn to avoid them.
- **Smoke detectors provide enough protection**
  - Smoke detectors provide early warning and save lives, but do nothing to extinguish a fire or protect those physically unable to escape on their own.
  - Too often, battery operated smoke detectors fail to function because the batteries are dead or have been removed.
- **Sprinklers are designed to protect property, but are not effective for life safety**
  - Sprinklers can reduce property losses up to 85%.
  - Combining sprinklers and early warning systems can reduce overall injuries, loss of life and property damage by 50%.

Fire Safety Planning

- **Construction**
  - Building materials
  - Fire-resistive ratings (minutes to hours)
  - Interior finishes (3 classes: A, B, & C)
- **Containing the fire**
  - Stair enclosures and fire walls
  - Separate building units or zones (control spread)
  - Fire doors
  - Smoke, heat and noxious gases control
  - Exits
- **Egress**
  - Two ways out, exit to safe area

Egress – Exit Route

- Continuous and unobstructed path from any point within a workplace
- Consists of three parts:
  - Exit access
  - Exit
  - Exit discharge



Egress – Exit Route

- Exit routes must be permanent
  - Exits must be separated by fire-resistant materials
  - Openings into an exit must be protected by an approved self-closing fire door that ***remains closed or automatically closes in an emergency***
  - Unobstructed
- Well marked

Egress – Exit Route

- **Exit Doors:**
  - **Must *not* be Blocked or Locked**
  - **Can use a panic bar**
  - **Must be well marked**
  - ***Open in direction of travel***

Best Practices: Safety During a Fire…

- Stairs have a bar blocking the steps going down to indicate ground level fire egress
- Keep fire exits and stairwells free from any obstruction to allow for an easy exit during a fire emergency

Emergency Lighting

Proper storage of Flammables is an important part of Fire Safety

Limit quantities stored

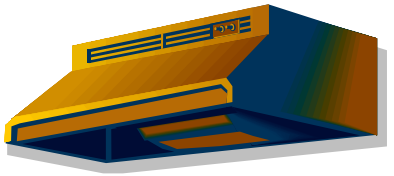
Safety cans

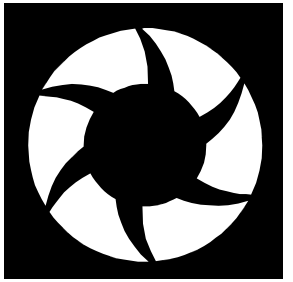
Secondary Containment

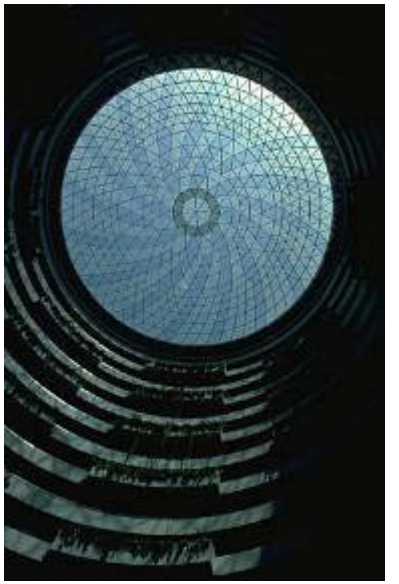
Flammable storage cabinets, rooms or buildings

Ventilation

Always provide adequate ventilation to reduce the potential for ignition of flammable vapors.







Storage Containers

- Oily Rags
- Drying process exothermic
- Container (reduces fire risk)
  - Limits oxygen.
  - Encourage air circulation to remove heat.
  - Limits access to ignition source.

Storage Containers

- **Containers should be tightly sealed when not in use.**
- **Approved safety cans are recommended for smaller quantities.**
  - The spring-loaded safety cap prevents spillage.
    - Prevents vapors from escaping
    - Acts as a pressure vent if engulfed in fire
    - Prevents explosions and rocketing of the can

Flame Arrester Screen

- **Prevents fire flashback into can contents.**
- **Double wire - mesh construction**
- **Large surface area provides rapid dissipation of heat from fire so that vapor temperature inside can remains below ignition point.**

Storage Areas

Flammables should be stored in an approved cabinet in a cool, well ventilated area to avoid pressure buildup and vaporization

Flammable Storage Cabinets

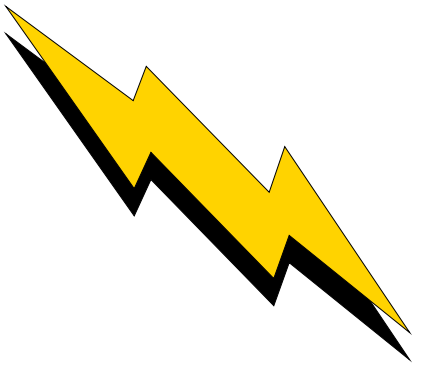
Storage Cabinets

- Not more than 225 L of Class I and/or Class II liquids, or not more than 450 L of Class III liquids permitted in a cabinet.
- Must be conspicuously labeled, **“Flammable - Keep Fire Away”**
- Doors on metal cabinets must have a three-point lock (top, side, and bottom), and the door sill must be raised at least 5 cm above the bottom of the cabinet.

Flammable Storage Cabinets

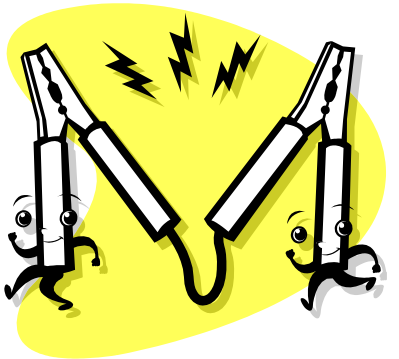
Static Electricity

- Generated when a fluid flows through a pipe or from an opening into a tank.
- Main hazards are fire and explosion from sparks containing enough energy to ignite flammable vapors.
- Bonding or grounding of flammable liquid containers is necessary to prevent static electricity from causing a spark.



Transfer Techniques

- **Static electricity** is generated by contact and separation of dissimilar materials**:**
  - Fluid flow through a pipe or into a tank
  - Agitation or mixing
  - Splash filling of containers



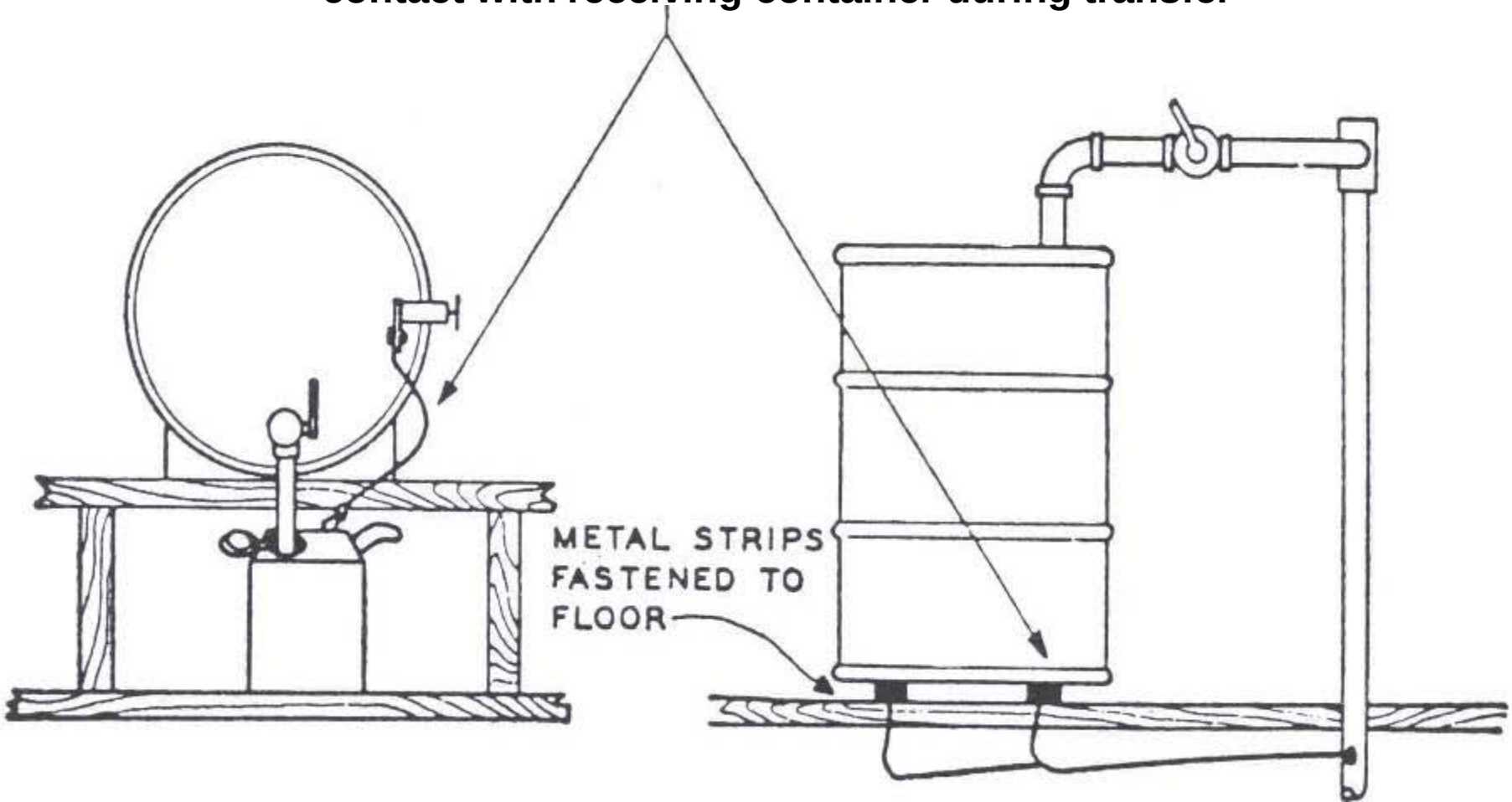
- **Bonding and grounding:**
  - **Bonding:** eliminate charge difference between objects
  - **Grounding:** eliminate charge difference between object and ground; drain charge

Transfer Techniques

- **Bond containers**
  - Each container is wired together
  - One container is connected to a good ground point to allow any charge to drain away safely
- **Limit use of plastic containers to small volumes (< 4L)**
  - No easy way to bond plastic containers

Control of Static

Bond wire necessary except where containers are inherently bonded together, or arrangement is such that fill stem is always in metallic contact with receiving container during transfer



Mart

Fire Prevention Inspections

- **Minimize size of fires**
  - Control storage of combustible and flammable materials
- **Reduce possibility of a fire**
  - Control ignition sources
- **Ensure fire protection equipment is operational**
  - Fire extinguishers not blocked
- **Ensure exits are maintained**
  - Don’t block egress pathways
  - Don’t prop open fire doors

Violations

Violations

6-Way Multi-plug

Multi-plug

Any Questions?

Break

Safe/Secure Transport of Chemicals

Transport References

UNECE, "Globally Harmonized System Of Classification and Labeling of Chemicals (GHS)," 1st edition, 2003, online,

http://www.unece.org/trans/danger/publi/ghs/ghs_rev00/00files_e.html

International Airlines Transportation Association, Dangerous Goods Regulations(DGR), 2008, not online,

http://www.iata.org/ps/publications/9065.htm

UN International Maritime Organization (IMO),

http://www.imo.org/

European Union (EU) Transport Activities

http://europa.eu/

US Department of Transportation (DOT)

http://www.dot.gov

International Shipping Fines

- For international shipments fines are severe
  - up $250,000 fine + 5 years prison in US
- Apply to scientists improperly transporting
  - samples
  - test material
  - specimens
- Dangerous Goods Regulations are set by:
  - IATA: International Air Transport Association

Modes of transport

- Air
- Ship
- Rail
- Road

- Vehicle (car/truck)
- Cart, Bicycle
- Hand carry

Transport Destinations

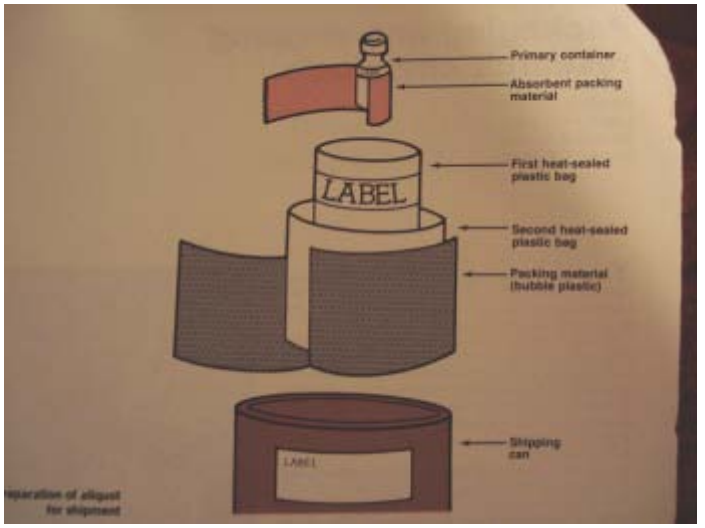
- International
- Domestic
  - Within the building
  - Within the organization
    - Same location, different building
    - Different location
  - Different City/Province/State/Island

Always expect the unexpected

CSP
CHEMICAL SECURITY
ENGAGEMENT PROGRAM
SAFETY AND SECURITY TRAINING

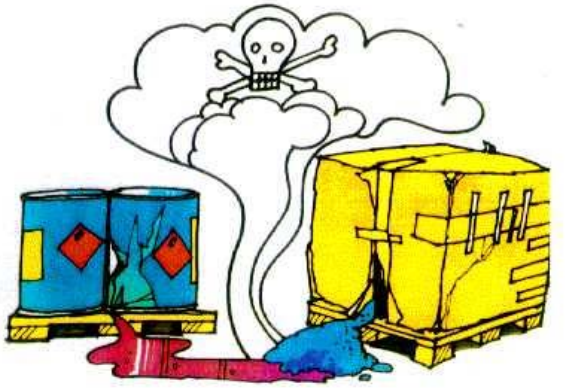
Universal Safety/Security Concept

Container within a Container



Take Precautions

- **Proper Packaging**
- **Spill and leakage protection**



Small spills from many cars daily: when counted together make...

What is a hazardous chemical shipment?

- Corrosives
- Dry ice
- Explosives
- Flammables
- Gases
- Flammable liquids
- Flammable solids
- Genetically modified organisms
- Infectious substances
- Magnetized material
- Oxidizing substances
- Radioactive substances
- Toxic substances
- Aerosols

Are there special shipping requirements?

What are the physical and chemical properties?

dry ice, refrigeration?

Are specific containers required?

size, strength, composition

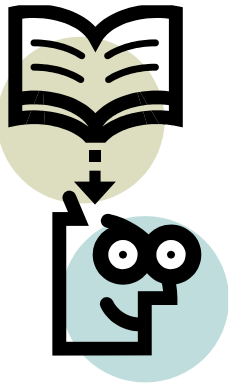
Specific transport concerns

- Quantities, exclusions, limitations

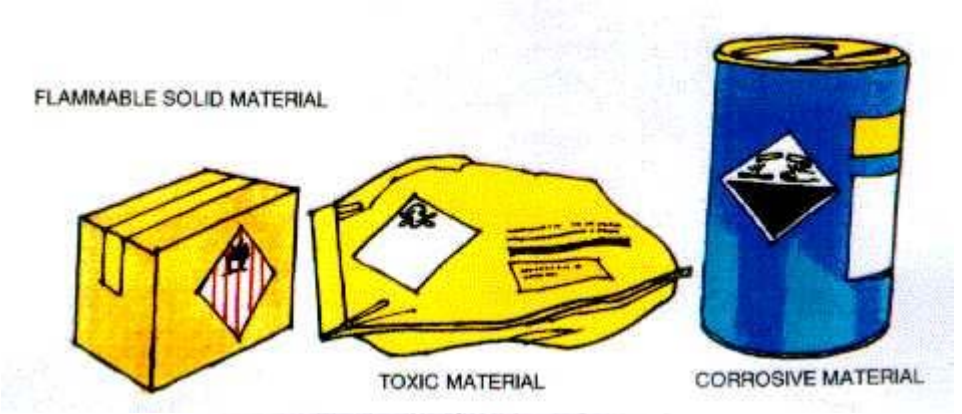
- Restricted routes:
  - tunnels
  - bridges
  - populated areas

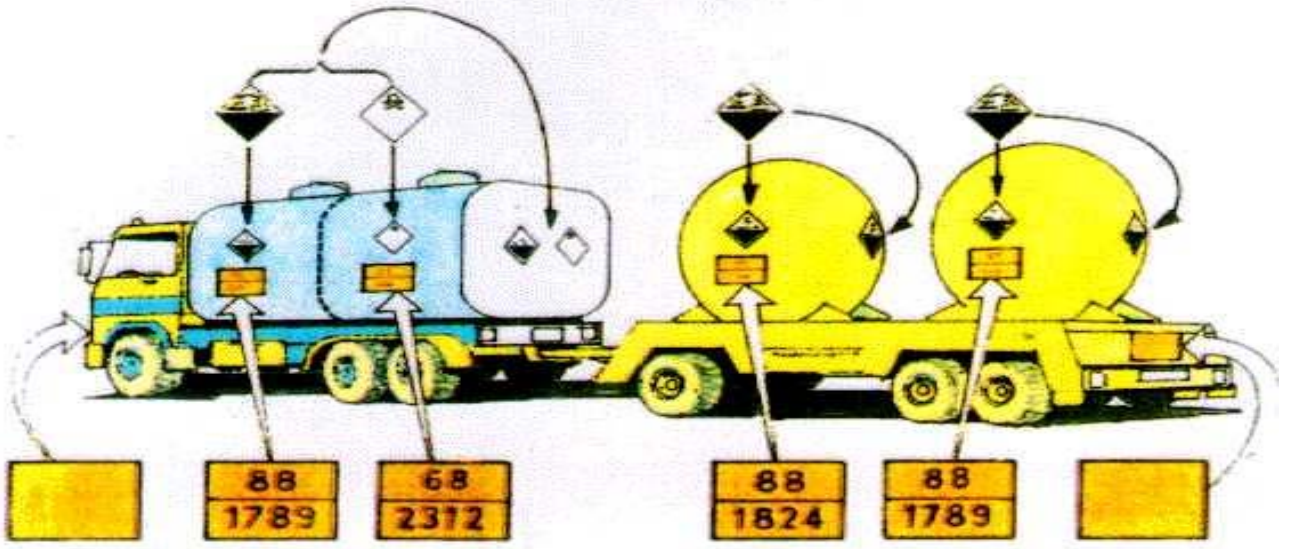
Sender/Shipper Should Know

- Who transports the material?
- How is it transported?
- How is it packaged?
- Are transporters knowledgeable and prepared?
- Is there safety documentation?
- When did it leave, arrival time?
- Did all material depart and arrive as scheduled?



Labels and Placards





Labels continued

properly and fully identify material

use proper, full chemical name
no abbreviations
ID codes, e.g., UN Numbers

specify
quantities, concentrations,
number of containers

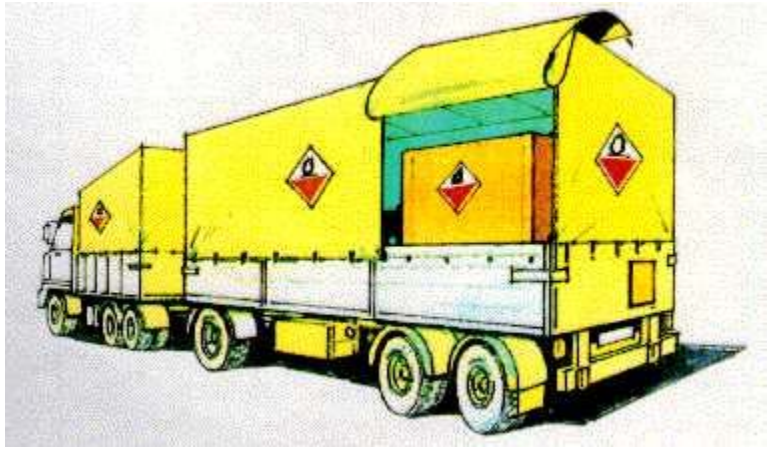
Labels continued

indicate specific hazard class
according to regulations

include
emergency information
contact names
24/7 phone numbers

language(s)
proper universal symbols

Placards



size
shape
location (4 sides)
securely fixed
permanent markings

Documentation

shipping order
bill of lading
manifest
full shipper, receiver addresses
packing & labeling certification
verification of receipt

Documentation continued

FLINN SCIENTIFIC INC.
"Your Safer Source for Science Supplies"
Material Safety Data Sheet (MSDS)

MSDS #: 5.00
Revision Date: September 24, 2002

Section 1 — Chemical Product and Company Identification

Acetic Acid; Glacial

Flinn Scientific, Inc. P.O. Box 219 Batavia, IL 60510 (800) 452-1261
CHEMTREC Emergency Phone Number: (800) 424-9300

Section 2 — Composition, Information on Ingredients

Acetic Acid; Glacial
Synonyms: vinegar acid, ethanoic acid
CAS#: 64-19-7

Section 3 — Hazards Identification

Clear colorless liquid, strong vinegar odor.
Corrosive, causes severe burns to eyes and skin. Moderately toxic by ingestion, inhalation and skin absorption. Fumes can be suffocating.
Class II Combustible Liquid.

FLINN AT-A-GLANCE
Health-2
Flammability-2
Reactivity-2
Exposure-3
Storage-3

0 is low hazard, 3 is high hazard

Section 4 — First Aid Measures

Call a physician, seek medical attention for further treatment, observation and support after first aid.
Inhalation: Remove to fresh air at once. If breathing has stopped give artificial respiration immediately.
Eye: Immediately flush with fresh water for 15 minutes.
External: Wash continuously with fresh water and mild liquid soap for 15 minutes.
Internal: Give 1 to 2 cups of water or milk, followed by a gastric antacid, such as milk of magnesia. Do not induce vomiting. Call a physician or poison control at once.

Section 5 — Fire Fighting Measures

Class II Combustible liquid. When heating to decomposition, emits irritating fumes.
Flash Point: 103 F (OC) Upper: 19.9% Lower: 4.0% Ait: 867 F
Fire Fighting Instructions: Use triclass, dry chemical fire extinguisher. Firefighters should wear PPE and SCBA with full facepiece operated in positive pressure mode.

NFPA CODE
H-3
F-2
R-0

Section 6 — Accidental Release Measures

Restrict unprotected personnel from area. Remove all ignition sources and ventilate area. Contain spill with sand and absorbent material, neutralize with sodium bicarbonate or calcium hydroxide and deposit in sealed bag or container. See Sections 8 and 13 for further information.

Section 7 — Handling and Storage

Flinn suggested chemical storage pattern: Organic #1. Store with acids, anhydrides and peracids. Store away from Nitric Acid. Store in a dedicated acid cabinet and away from any source of water; if an acid cabinet is not available, store in a Flinn Saf-Cube. Use and dispense in a hood.

Section 8 — Exposure Controls , Personal Protection

Avoid contact with eyes, skin and clothing. Wear chemical splash goggles, chemical-resistant gloves and chemical-resistant apron. Use ventilation to keep airborne concentrations below exposure limits. Always wear a NIOSH-approved respirator with proper cartridges or a positive pressure, air-supplied respirator when handling this material in emergency situations (spill or fire).
Exposure guidelines: TWA 10 ppm, STEL 15 ppm (OSHA, NIOSH)

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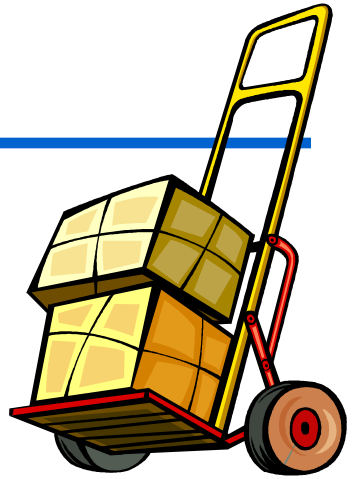
Safety Data Sheets

follow up documentation

require incident/accident reports

Handling



Where, how, who, packs shipment?

Special equipment needed to load & unload?

Where, how, who opens shipment?

Handling continued

Should package be opened in a hood?

Is material radioactive?

Is monitoring equipment needed?

Is special storage needed on receipt?

Who requires training?

- Managers
- Packers
- Handlers
- Loaders
- Drivers
- All shipping and receiving personnel
- Mailroom personnel

Emergency Preparation

- Transportation accidents/incidents:
  - Organization reports
  - Police reports
  - Emergency contacts
- Spill and leakage control:
  - prevention
  - minimization
  - spill clean up kits
  - PPE

Who is responsible of damages if a leaking drum spills dangerous material? You?

Emergency preparation continued

- Emergency contacts
  - Regulation requirements
    - local, national, international

- Public relations
  - Designate spokesperson beforehand
  - Be responsive to public concerns

Plan ahead

- **Have a plan**

- **Remember:**
  - **Anticipation**
  - **Recognition**
  - **Evaluation**
  - **Control**

Safety equipment should have a routine check.

Unsafe Transport of Gas Cylinders

Acknowledgement

International Labour Organization (ILO)

International Occupational Safety and Health Centre (CIS)

Programme on Safety and Health at Work and the Environment (SafeWork)

http://www.ilo.org/public/english/protection/safework/cis/index.htm

Any Questions?

REACH and the Global Harmonized System for the Labeling of Chemicals

CSP
CHEMICAL SECURITY ENGAGEMENT PROGRAM

Chemical
SAFETY AND SECURITY TRAINING

REACH

Registration, Evaluation, Authorisation of Chemicals

2007 EU regulation; replaces 40 existing acts to create a single system for all chemicals

- requires authorization to use, manufacture and import
- to track and manage chemical risks and provide safety information
- proposes to integrate REACH with GHS
- creates European Chemical Agency (ECHA, Helsinki, Finland

REACH

Life of the chemical from

Cradle-to-the-Grave

Manufacturing

Importing

Marketing

Use

Waste stream

CSP
CHEMICAL SECURITY ENGAGEMENT PROGRAM

Chemical
SAFETY AND SECURITY TRAINING

REACH

- Comprehensive legislation to ensure European authorities know and condone what chemicals are used as they enter the EU supply train
- Objective is to protect human health and the environment by recognizing and classifying hazardous chemicals so they are handled safely
- REACH & GHS are not equivalent or optional but separate legislation with parallel requirements

REACH

- The responsibility for proving whether a chemical is hazardous or non-hazardous is on the manufacturer and supplier not the government

- The responsibility also includes documentation, tests, classification, risk exposure, labeling, safety data sheets

- ECHA will store the information in the International Uniform Chemical information Database (IUCLID)

REACH

Four Steps

1. Registration
2. Evaluation
3. Authorization
4. Restriction

ECHA maintains database

REACH: Registration

Importers and manufacturers of substances in quantities over 1 ton/yr must register their substance with ECHA

- Registration began June 2007
  - **December 1, 2010**
    - **≥ 1000 tons per year**
      - **carcinogenic, mutagenic, or reproductive toxin ≥ 1 ton per year**
      - **substances classified as dangerous for aquatic environment ≥ 100 tons per year**
  - **June 1, 2013**
    - **manufactured or imported at 100-1000 tons per year**
  - **June 1, 2018**
    - **manufactured or imported at 1-100 tons per year**

REACH: Evaluation

Authorities will review registration and request further information or testing to determine the impact of the substance on human health and the environment

Decides next steps:

- **action for authorization**
- **align classification & label**
- **other action**

REACH: Authorization

Decisions on what substances require an authorization or restriction are carried out for substances that pose the most concern, such as carcinogens and mutagens

Three steps:

- SVHC (Substances of Very High Concern)
  - carcinogenic, mutagenic and reprotoxic substances, persistent, bio-accumulative and toxic
- Prioritize
- Authorization provided

REACH: Restriction

- **Limit uses**
  - **Where no viable alternative exists, a research and development plan to derive a suitable alternative is developed**

- **Ban substance**
  - **where there is an unacceptable risk to human health and the environment.**

REACH: Concern

A potential concern may be creating country specific safety data sheets and labels that are compatible with the GHS proposal

REACH: Resources

About REACH: http://guidance.echa.europa.eu/

http://ec.europa.eu/environment/chemicals/reach/reach_intro.htm

REACH Help:
http://echa.europa.eu/help_en.asp#helpdesks

About ECHA: http://ec.europa.eu/echa

Globally Harmonized System

for Classification and Labeling of Chemicals (GHS)

International UN standardization for classification, safety data sheet format, and labeling of chemicals using pictograms, signal words, and hazard warnings

US OSHA is reviewing GHS for adoption

GHS

- United Nations proposed system to internationally standardize chemical communication
- Countries will adopt on their own timeframe
- 2008 - UN goal for world-wide implementation

GHS Implementation

Intergovernmental Forum on Chemical Safety (IFCS) – adopted GHS implementation goal of 2008. The US participates and agreed to work toward this goal

Japan, Korea, New Zealand – various stages of adopting & implemented GHS

European Union – 2010 deadline for GHS substance classification

Canada – Assessing how to adopt and implement GHS

United States – Assessing impact of GHS, plans to adopt GHS by 2009. DOT expects to have changes in place by 2009

GHS Benefits

- Uniform Communication
- Better Safety
- Improved International Trade
- Lower cost

GHS Changes

MSDS now named: “SDS” (Safety Data Sheet)

Labels will be standardized with:

- **signal words**
- **hazard statements**
- **precautionary statements**
- **pictograms**
- **elimination of US, Canadian and EU labels**

GHS Labeling

Information required on a GHS label:

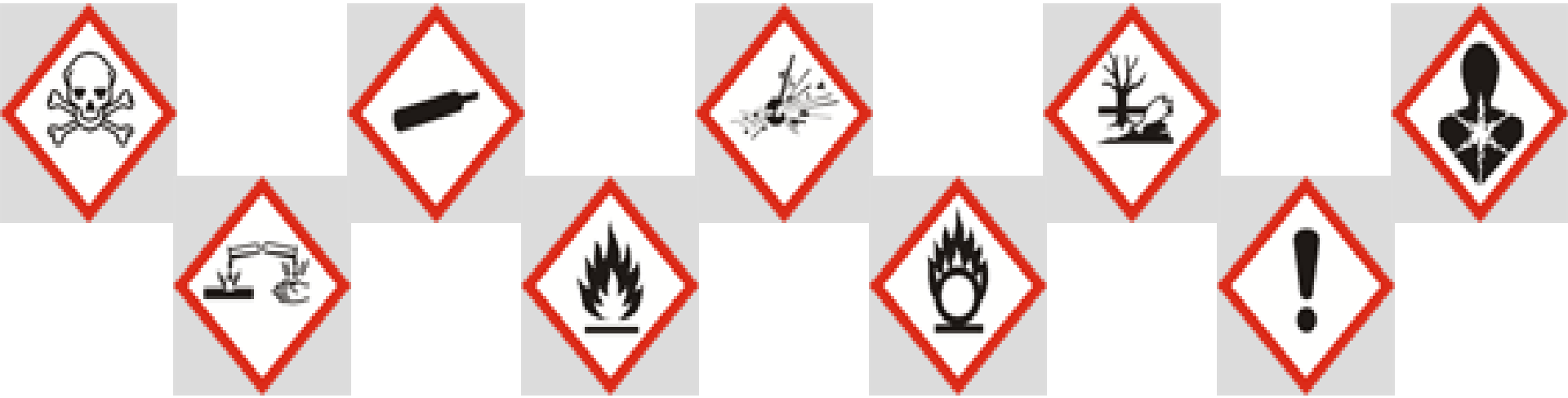
- **Pictograms**
- **Signal words**
- **Hazard statements**
- **Precautionary statements and pictograms**
- **Product identifier**
- **Supplier information**

Changes to (M)SDS

GHS name: Safety Data Sheet (SDS)

- **Format:**
  - **16 sections required in specified order (as per ANSI MSDS format in US Regulations presentation)**
- **Reclassification:**
  - **(MSDS) Health & Physical Hazards**
  - **(SDS) Environmental Hazards**
- **Building Block Approach**
  - **each country can select portions of GHS to adopt**
  - **Not every country will require all categories or all hazards**

Examples of GHS Pictograms



Differences between REACH and GHS

- REACH and GHS have different scopes but there are many links between the two regulations
- REACH aims to produces information on hazards, risks, and risk management
- GHS aims to harmonize classification and labeling of materials
- GHS is a UN recommendation which applies across countries, including the EU

Differences between REACH and GHS

- REACH intends to replace current EU classification criteria with GHS. REACH has provisions for safety data sheets based on GHS.
- GHS intends to apply classification and labeling beginning December 1, 2010, when the new GHS regulation will be available.
- Substances will be phased in the first 3.5 years. Mixtures will be given an additional 4.5 years for reclassification.

Globally Harmonized System

Resources

http://www.unece.org/trans/danger/publi/ghs/ghs_rev02/02files_e.html

http://www.unece.org/trans/danger/publi/ghs/presentation_e.html

http://www.osha.gov/dsg/hazcom/ghs.html