Chemical
SAFETY AND SECURITY TRAINING

Chemical Safety and Security Officer Training

Kuala Lumpur, Malaysia
December 2010

SAND No. 2010-7455 P
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
under contract DE-AC04-94AL85000.

Sandia National Laboratories

Lab Visit

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

Key Elements of Fire Safety

Get occupants out

Minimize property loss and interruption

Fire Containment/Suppression

Common Myths

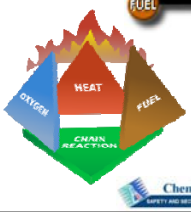
- **Fire will light the way out**
  - Smoke cloud & soot
- **Plenty of time to escape**
  - 1 min from small to inescapable fire
- **People are killed by the flames**
  - #1 killer in fires is CO, not flames
- **Wait to be rescued**
  - No! Act to save self
  - Ladders can reach to about 6th floor
-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

It's the Smoke…

Facial Burns

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

OSHA Office of Training and Education

Flammability/Explosive Limits

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

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

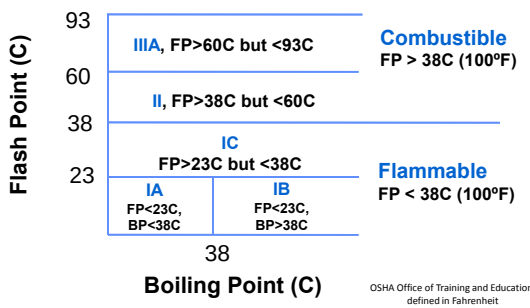
Flammability/Explosive Range

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

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

Defined in terms of the amount of fuel in air.

Classes of Flammable and Combustible Liquids



OSHA Office of Training and Education, defined in Fahrenheit

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

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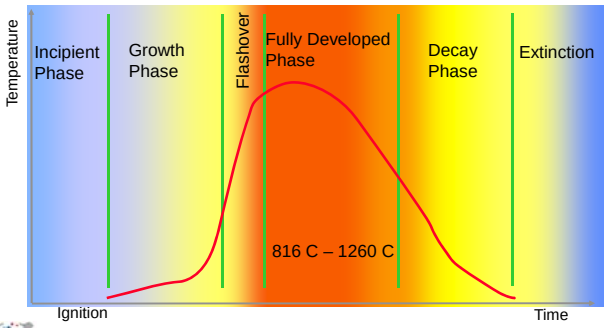
Fire Safety Program Components

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**

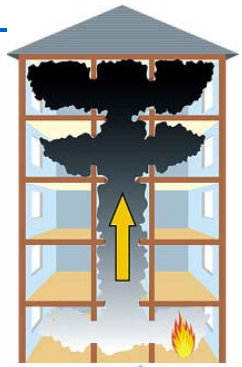
Fire Behavior



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

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

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…

Flammable Liquid Containers

Tool Cleaning (Acetone)

Fire Hazards

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

Train employees to notice & report fire hazards

Periodic inspections

Drills

Classification of Fires

With recommended extinguisher distances

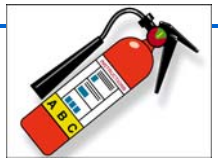
- **A** **Ordinary combustibles – cloth, paper, wood, coal** **~23 m**
- **B** **Flammable/combustible liquids, gases, greases and oils - gasoline, diesel fuel** **~15 m**
- **C** **Energized Electrical equipment cables, motors** **nearby**
- **D** **Combustible metals - sodium, magnesium, titanium** **~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



Water

Placed within ~15-25 m

Annual & Monthly inspections

CO_2

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)

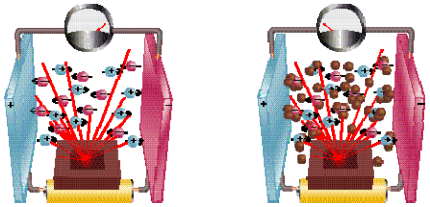
Issues:

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:
- Initial training
- 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:

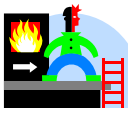
- It is bigger than a waste paper bin
- One extinguisher is not enough
- The fire is spreading beyond the spot where it started
- Smoke is affecting your breathing
- You can't fight the fire with your back to an escape exit
- The fire can block your only escape
- You don't have adequate fire-fighting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

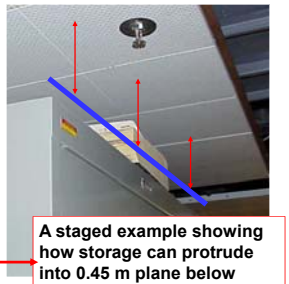
Improper Storage in front of Electrical Panel

- 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.

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 – 100 liters per minute compared to a fire hose at ~200 – 500 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

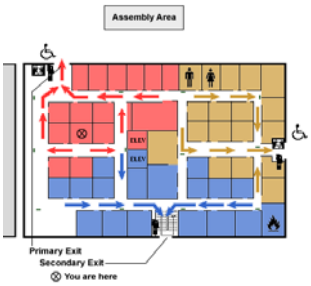
- **Sprinkler systems might accidentally go off**
  - Sprinklers are very reliable; the chances of going off without mechanical assistance are 1 in 16 million; Fork lift truck drivers soon learn to avoid them.
- **Smoke detectors provide enough protection**
  - Smoke detectors provide early warning and 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

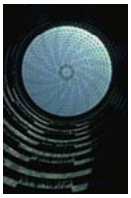
Safety cans

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

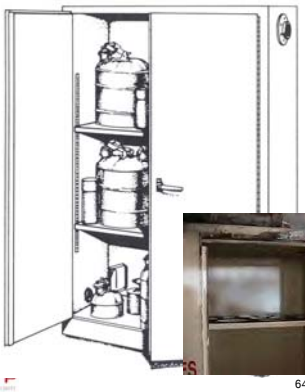
Flammable Storage Cabinets

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.

OSHA Office of Training and Education

Flammable Storage Cabinets



Static Electricity

- Some flammable liquids accumulate a static electric charge, which can release a spark that ignites the liquid
- 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

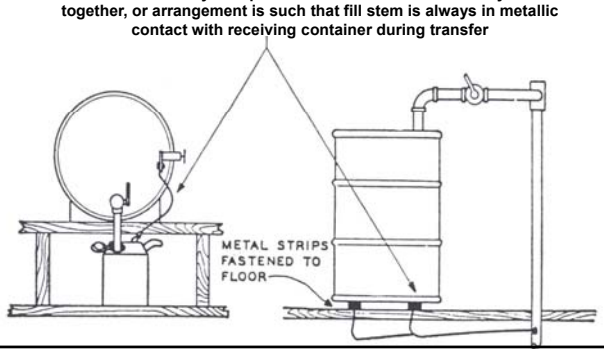
benzene toluene gasoline xylene

Transfer Techniques

- **Bond containers**
  - Containers are wired together before pouring
  - 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



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

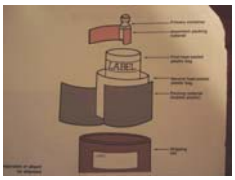
- Air
- Ship
- Rail
- Road

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

Always expect the unexpected

Universal Safety/Security Concept

Container within a Container



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 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

Documentation

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

Documentation continued

Safety Data Sheets

follow up documentation

require incident/accident reports

Handling

Where, how, who opens shipment?

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

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**

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

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

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 – OSHA proposed rulemaking at end of 2009. DOT has adopted some parts, still working on others.

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

Questions?
Open Discussion
Homework