Chemical Reactivity and Storage

Presented by QBE

Loss Control Services

QBE®

Objectives

- To understand basic terminology relating to chemical hazard classes and reactivity
- To be able to identify chemicals that pose a high potential risk for property loss or injury
- To be able to identify common incompatible chemicals that might be stored together

Pretest

What are the 4 principles for good chemical storage?

Match the following chemicals to the appropriate reactivity hazard:

___Peroxides	A- Air Sensitive
___Acrylic Resins	B- Spontaneous Peroxide Formation
___Metal Dusts	C- Strong Oxidizers
___Ethers	D- Polymerization Hazard
___Hydrogen	E- Reducer

Explain why intentional chemistry processes are a major concern from a potential loss standpoint.

List 10 things that should be reviewed when evaluating chemical storage areas.

Former Ammonium Nitrate Plant

Potential Losses Relating to Chemicals

- Property
  - Fire
  - Explosions
  - Environmental Release
- Workers Compensation
  - Respiratory Disease
  - Dermatitis
  - Chemical Burns
  - Physical Injuries
- General Liability

Use of Chemicals

Manufacturing Processes

- Chemical Product Manufacture
- Paint Manufacture
- Plating
- Metal Heat Treating
- Metal Cleaning
- Metal Degreasing
- Printing
- Plastics
- Concrete Additives
- Food Additives
- Adhesives
- Circuit Boards

Distributors

- Warehouses
- Stores

Ancillary Activities

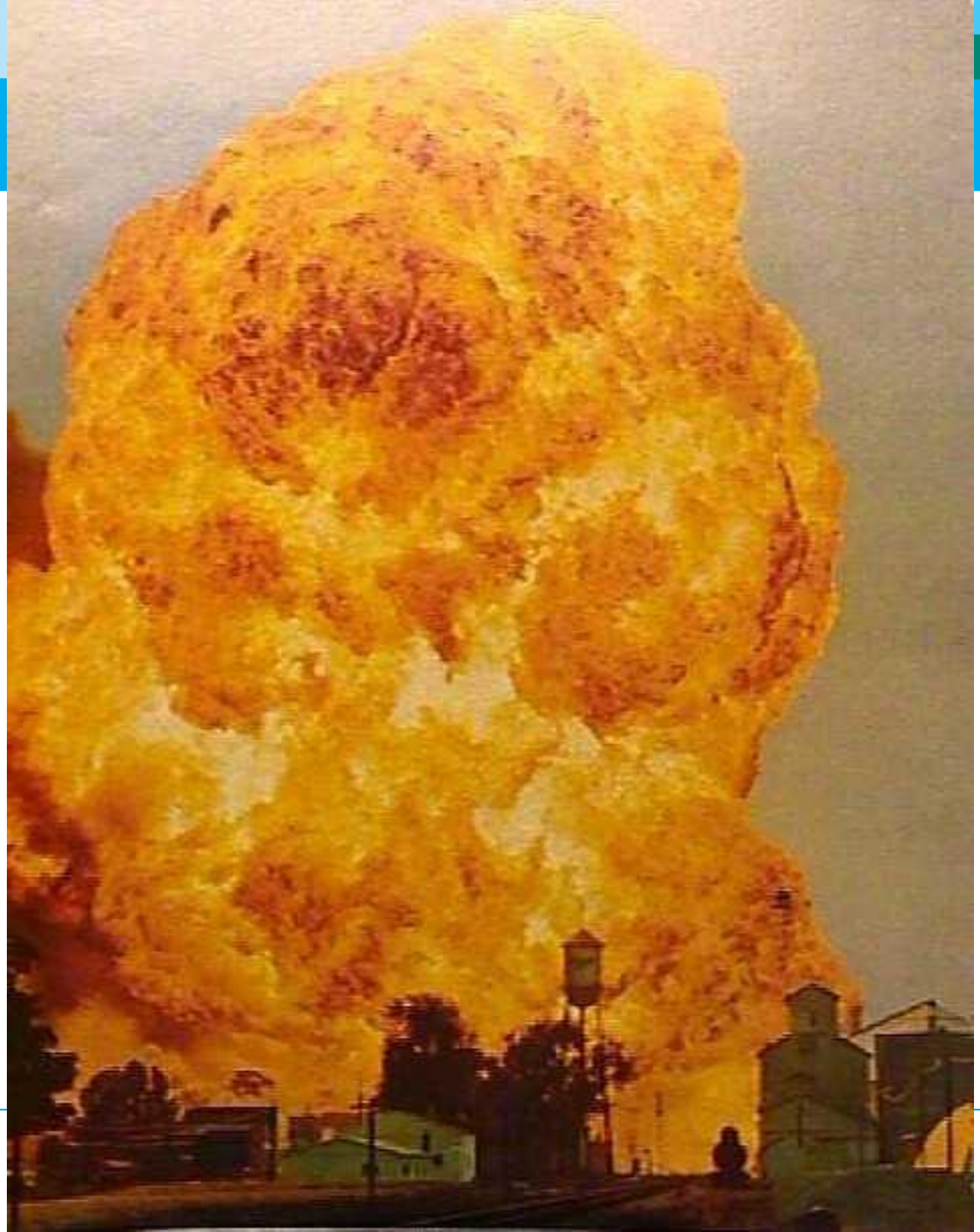
- Painting
- Waste Treatment
- Water Treatment
- Sanitation/Janitorial
- Laboratories
- Pest Control
- Swimming Pools
- Fertilizers
- Lawn/garden Chemicals
- Ammonia Refrigeration

Terminology

- Oxidizer
- Polymerization
- Reducer
- Pyrophoric
- Alkali
- Acid
- Explosives
- Reactive

Basic Chemistry

- Oxidizers want to gain electrons to be more stable
- Reducers want to lose electrons to be more stable
- The stronger the oxidizer, the more it wants to gain electrons
- The stronger the reducer, the more it wants to lose electrons



Strong Oxidizers

- Fluorine
- Chlorine
- Ozone
- Persulfates
- Peroxides
- Perchlorates
- Dichromates
- Chromates
- Permanganates
- Hypochlorites
- Nitrates
- Nitrites
- Liquid oxygen
- Chlorates

Reducers

- Finely divided metals
- Hydrazine
- Hydrides
- Hydrogen
- Aniline
- Sodium
- Lithium
- Potassium

Chemical State

- Solid
- Liquid
- Gas

Scale of Chemical Use

Scale of Chemical Use

Chemical Reaction Equipment

Scale of Chemical Use

Other Storage Issues

Other Safety Equipment

Flammables

- Not addressed in this presentation
- Store according to NFPA and QBE property guidelines

Water Reactive Chemicals

- Alkali metals (lithium, sodium, magnesium)
- Hydrides (diborane, sodium hydride)
- Peroxides (sodium peroxide)
- Carbides (calcium carbide)
- Oxides (sodium oxide)
- Phosphides (aluminum phosphide)
- Anhydrides (acetic anhydride)

Polymerizable Chemicals

- Chemical chain reaction of monomers to form polymers
- May self react
- May react vigorously with water
- May give off hazardous gases
- May cause high pressure in storage container
- Inhibitors are used to prevent reaction

Polymerizable Chemicals

- Acrylic acid
- Acrylonitrile
- Ethyl acrylate
- Methyl acrylate
- Methacrylic acid
- Vinyl acetate

Unstable/Shock Sensitive Chemicals

- Very unstable
- React vigorously
- Mechanical shock, elevated temperature or pressures can cause reaction

Unstable/Shock Sensitive Chemicals

- Ammonium perchlorate
- Azo, diazo or azide chemicals
- Fulminates
- Hydrogen peroxide
- Organic peroxides
- Nitro or nitroso compounds
- Picric acid
- Perchloric acid
- Triazines

Air-Sensitive Compounds

- Reactive with oxygen in air
- Usually pyrophoric
- Usually stored under inert gas or liquid

Air-Sensitive Compounds

- Metalic dusts (zinc, nickel, titanium)
- Alkali metals (potassium, sodium, magnesium)
- Hydrides (diborane, barium hydride)

Organic Peroxides

- Compounds having two oxygen atoms joined together (peroxy)
- Severe fire and explosion hazard
- Burn rapidly and intensely
- May be strong oxidizers
- Plastics and rubber industries
- Used as accelerators, activators, catalysts, curing agents, hardeners, initiators or promoters
- Solids liquids and pastes
- Can be formed spontaneously

Organic Peroxides

- Methyl ethyl ketone peroxide
- Benzol peroxide
- Hydrogen peroxide
- Peracetic acid
- There are many other peroxides

Spontaneous Peroxide Formation

- Some chemicals can form peroxides during storage
- Light and heat can cause peroxide formation
- Prolonged storage of susceptible chemicals

Spontaneous Peroxide Formation

- Ethers
- Tetrahydrofuran
- p-Dioxane
- 2-Propanol
- 2-Butanol
- Methyl isobutyl ketone
- Styrene
- Vinyl acetate

NFPA Standards

- NFPA 430- Code for Storage of Liquid and Solid Oxidizers
- NFPA 432- Code for Storage of Organic Peroxide Formulations
- NFPA 484- Code for Combustible Metals, Metal Powders and Metal Dusts
- NFPA 490- Code for Storage of Ammonium Nitrate
- NFPA 495- Explosive Materials Code

Swimming Pool Chemicals

- Strong oxidizers
- 3.8 million swimming pools in U.S.
- Kill bacteria, fungi, viruses by releasing chlorine

Swimming Pool Chemicals

Inorganic

- Calcium hypochlorite (Cal hypo)
- Lithium hypochlorite
- Sodium hypochlorite (bleach)
- Chlorine gas (large pools)

Organic

- Trichloroisocyanuric acid (Trichlor)
- Potassium dichloroisocyanurate (Dichlor)
- Sodium dichloroisocyanurate (Dichlor)
- Sodium dichloroisocyanurate dihydrate (Dichlor)
- Brominated Hydantoin

Swimming Pool Chemicals

Cal hypo + Chlorinated Isocyanurate + Water = Chlorine Gas

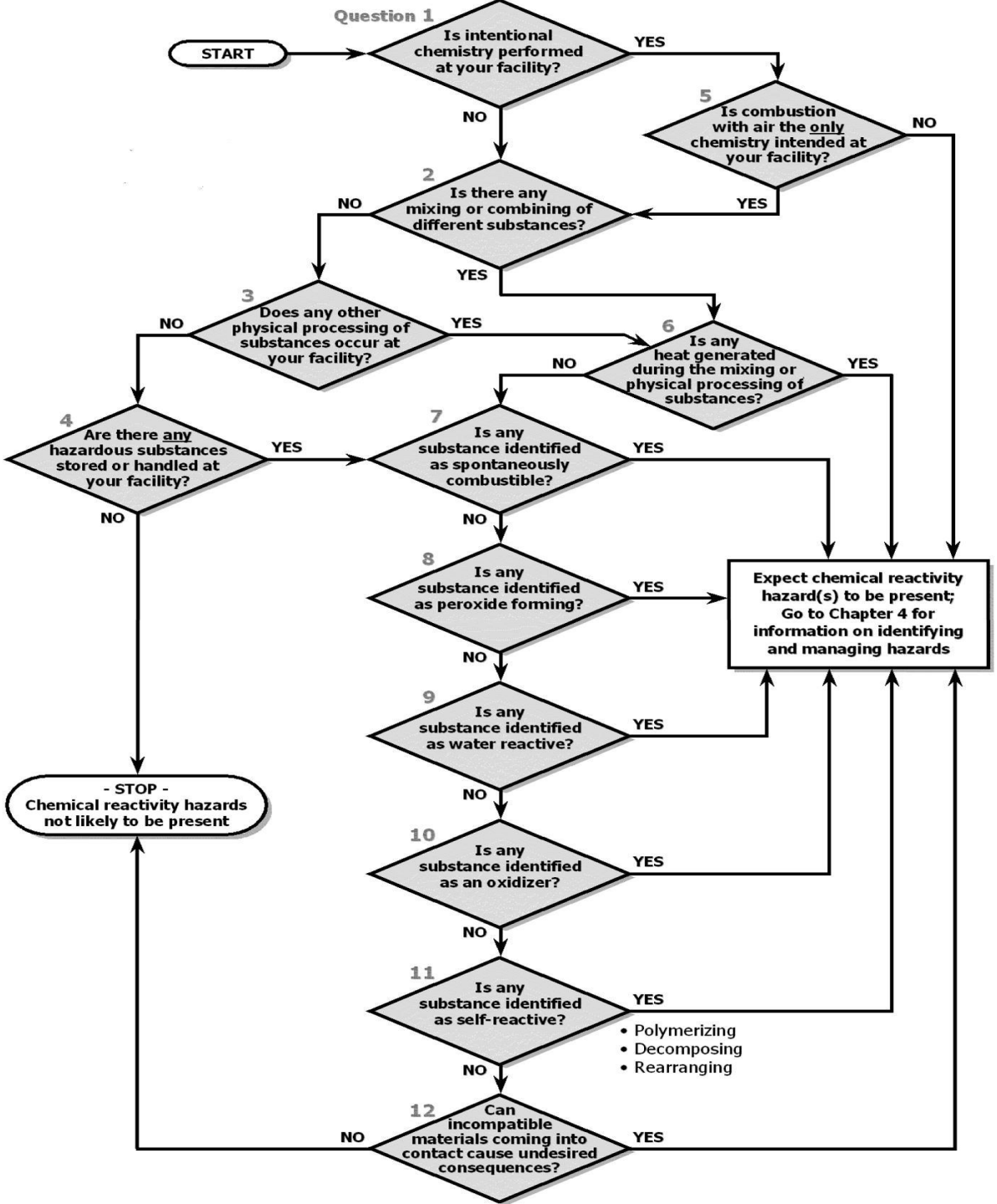
Swimming Pool Chemical Storage

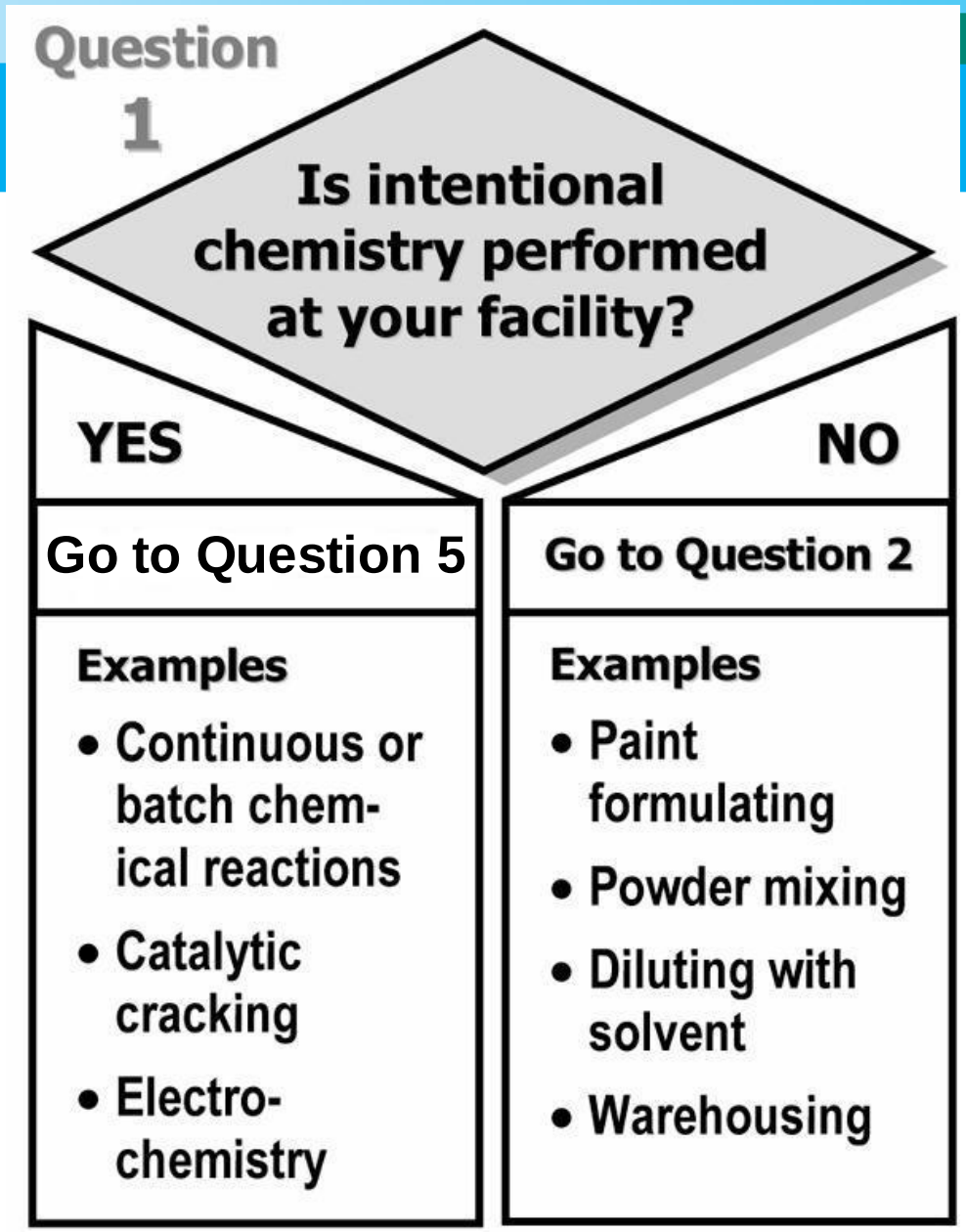
- Secure
- Area should be posted with signs
- Well ventilated
- Away from sunlight
- Dry
- Store in original labeled containers
- Store away from acids
- Spills should be cleaned up immediately according to manufacturer’s procedures

Laboratories

- Small quantities of chemicals
- Wide variety of chemicals
- Usually highly trained and employees

Chemical Reactivity Risk Evaluation




Question 1
Is intentional chemistry performed at your facility?
YES
NO
Go to Question 5
Go to Question 2
Examples
• Continuous or batch chemical reactions
• Catalytic cracking
• Electrochemistry
Examples
• Paint formulating
• Powder mixing
• Diluting with solvent
• Warehousing

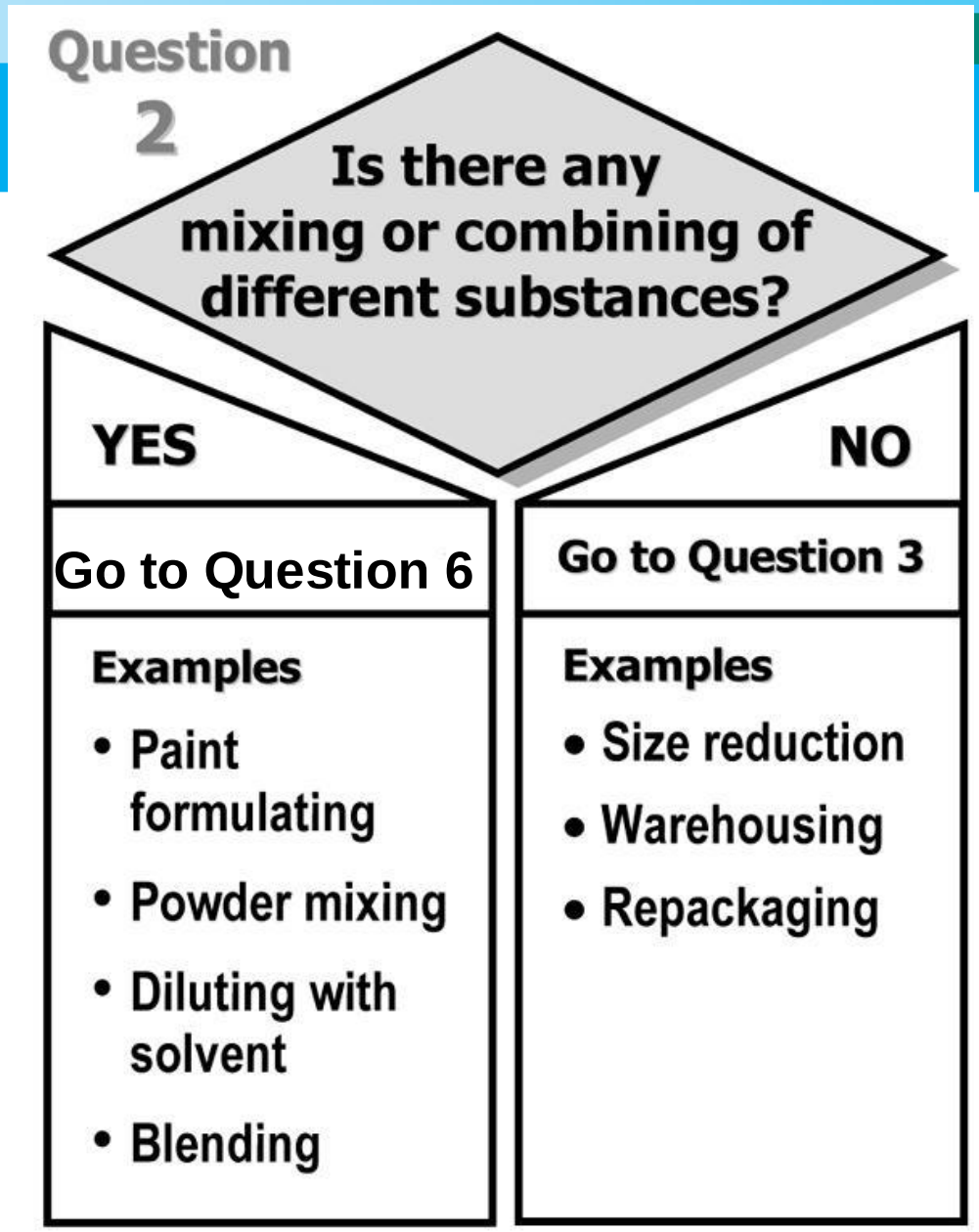
Indicators of Intentional Chemistry

- Products have different chemical formulas than the starting materials
- Gases are given off
- Solid is formed from liquid or gaseous starting materials
- A catalyst or initiator is used
- Heat is generated or must be added to the process

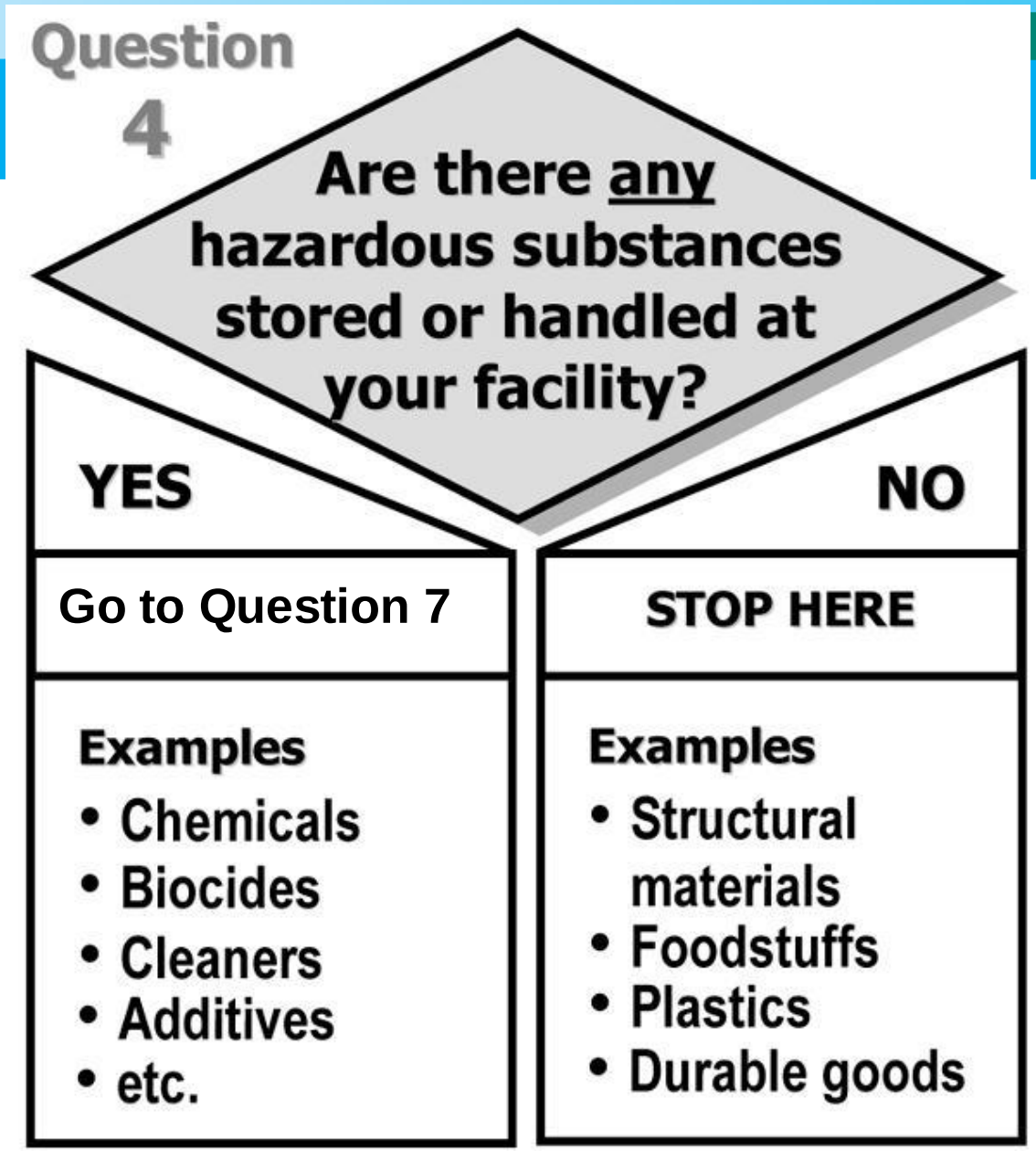
Problems with Intentional Chemistry

- Wrong materials added
- Improper amounts of materials added
- Inadequate cleaning of equipment
- Materials added in wrong sequence
- Materials added to fast or too slow
- Contaminated feed materials
- Improper temperature of feed materials
- Air leaks
- Insufficient agitation
- Heat transfer inadequate
- Off-gas vent blocked or not open

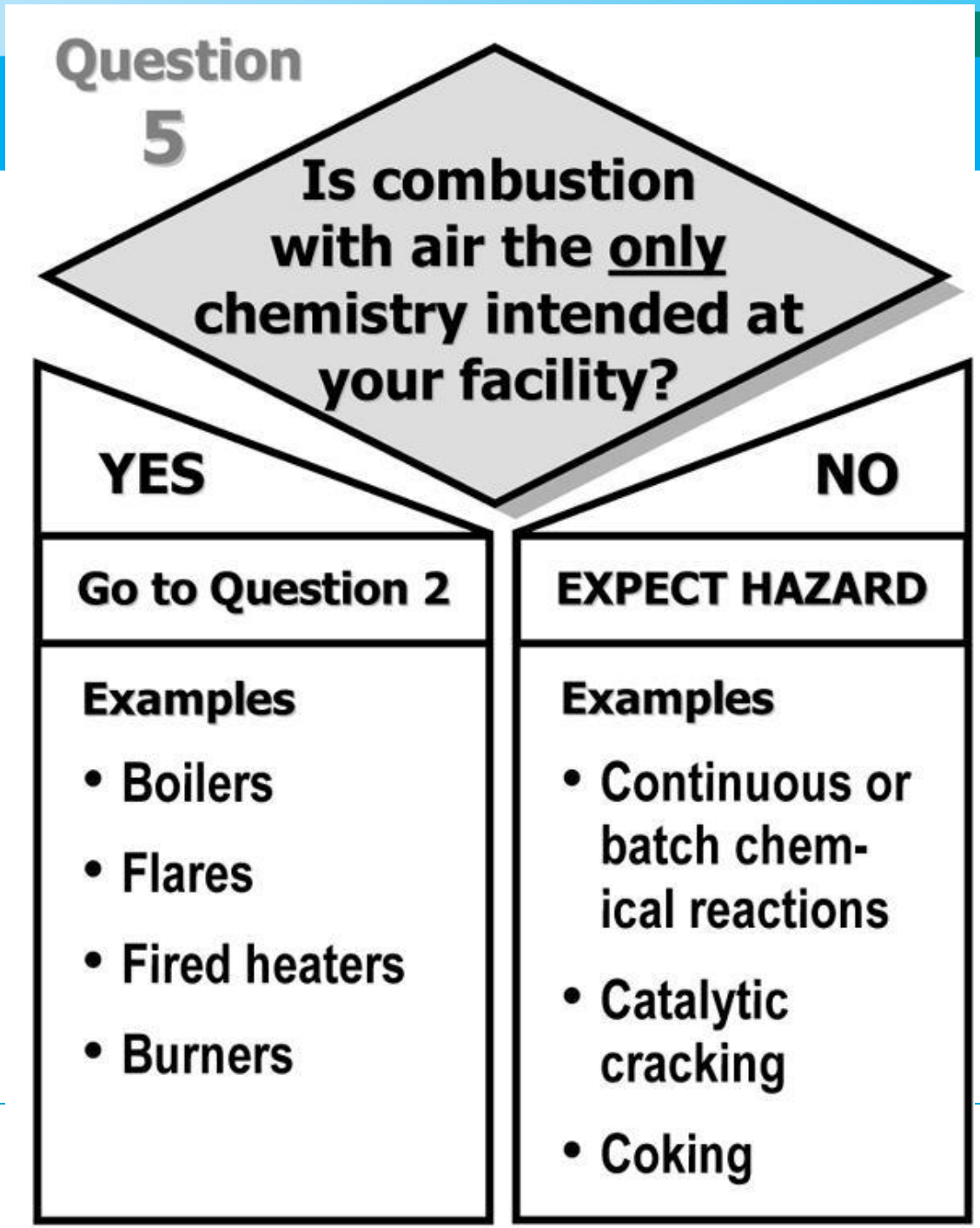
Chemical Reaction Vessel

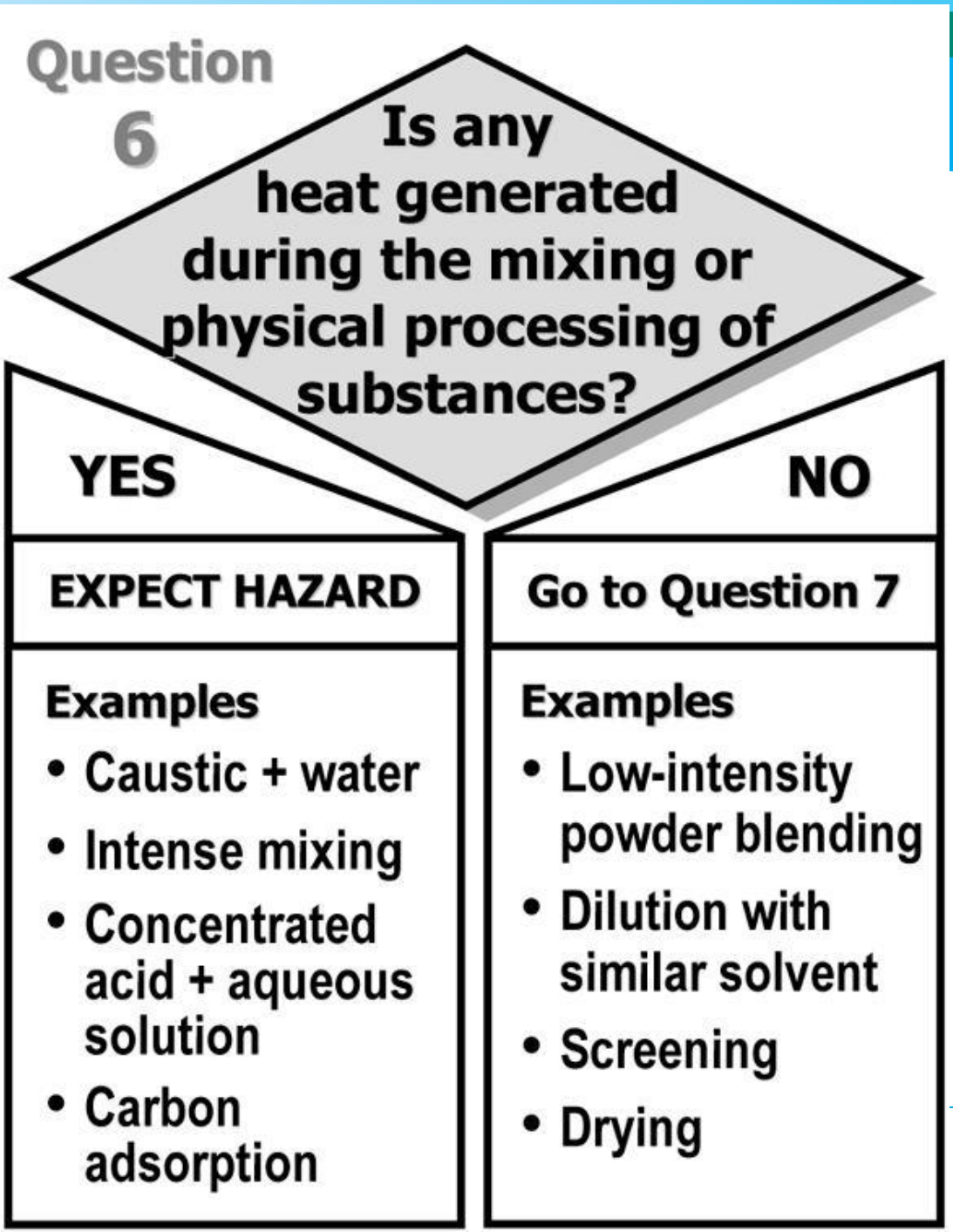

Question 2
Is there any mixing or combining of different substances?
YES
NO
Go to Question 6
Go to Question 3
Examples
• Paint formulating
• Powder mixing
• Diluting with solvent
• Blending
Examples
• Size reduction
• Warehousing
• Repackaging

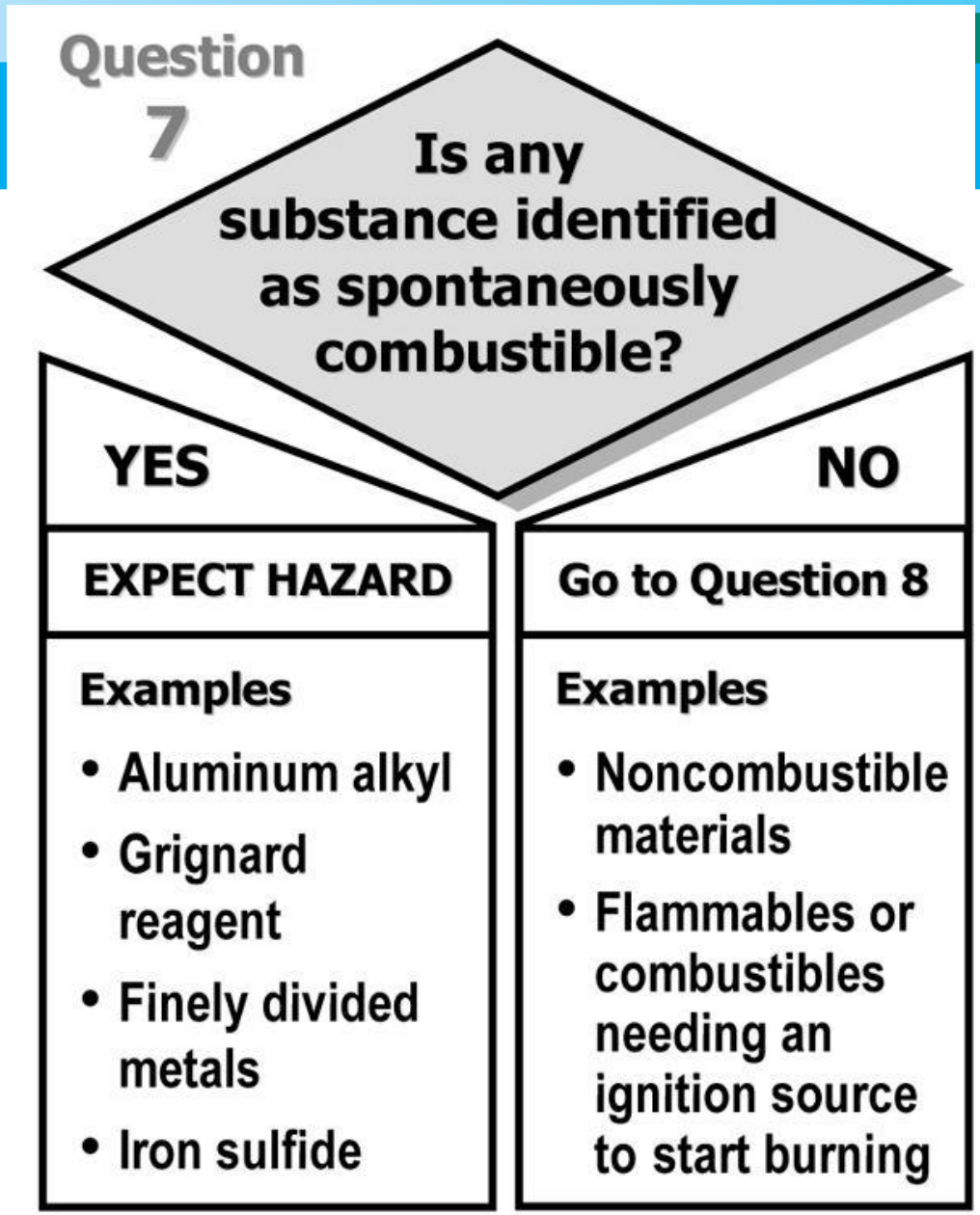

Question 3
Does any other physical processing of substances occur at your facility?
YES
NO
Go to Question 6
Go to Question 4
Examples
• Size reduction
• Heating/drying
• Absorption
• Distillation
• Screening
Examples
• Receiving
• Tank storage
• Warehousing
• Repackaging
• Shipping

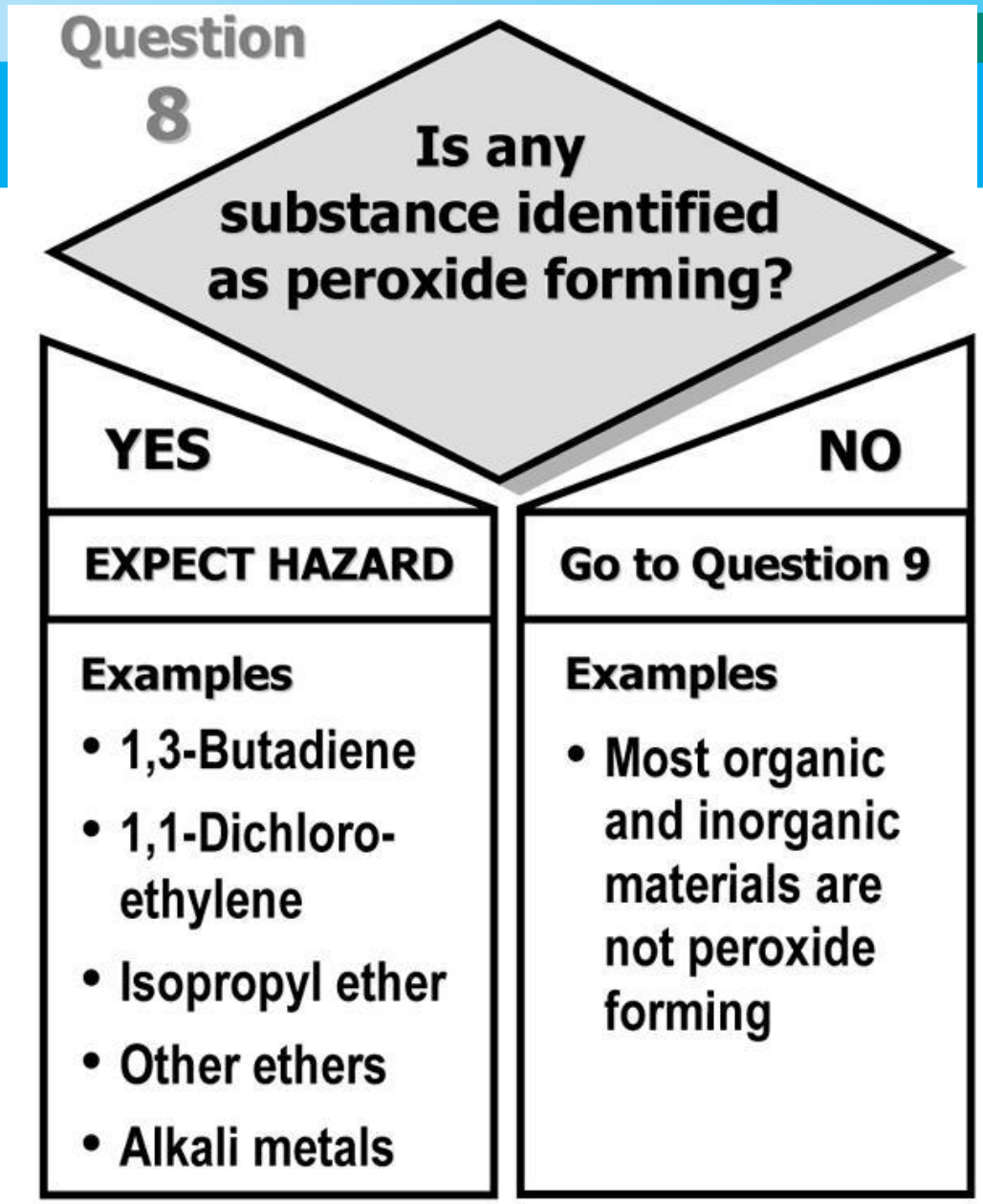

Question 4
Are there any hazardous substances stored or handled at your facility?
YES
NO
Go to Question 7
STOP HERE
Examples
• Chemicals
• Biocides
• Cleaners
• Additives
• etc.
Examples
• Structural materials
• Foodstuffs
• Plastics
• Durable goods

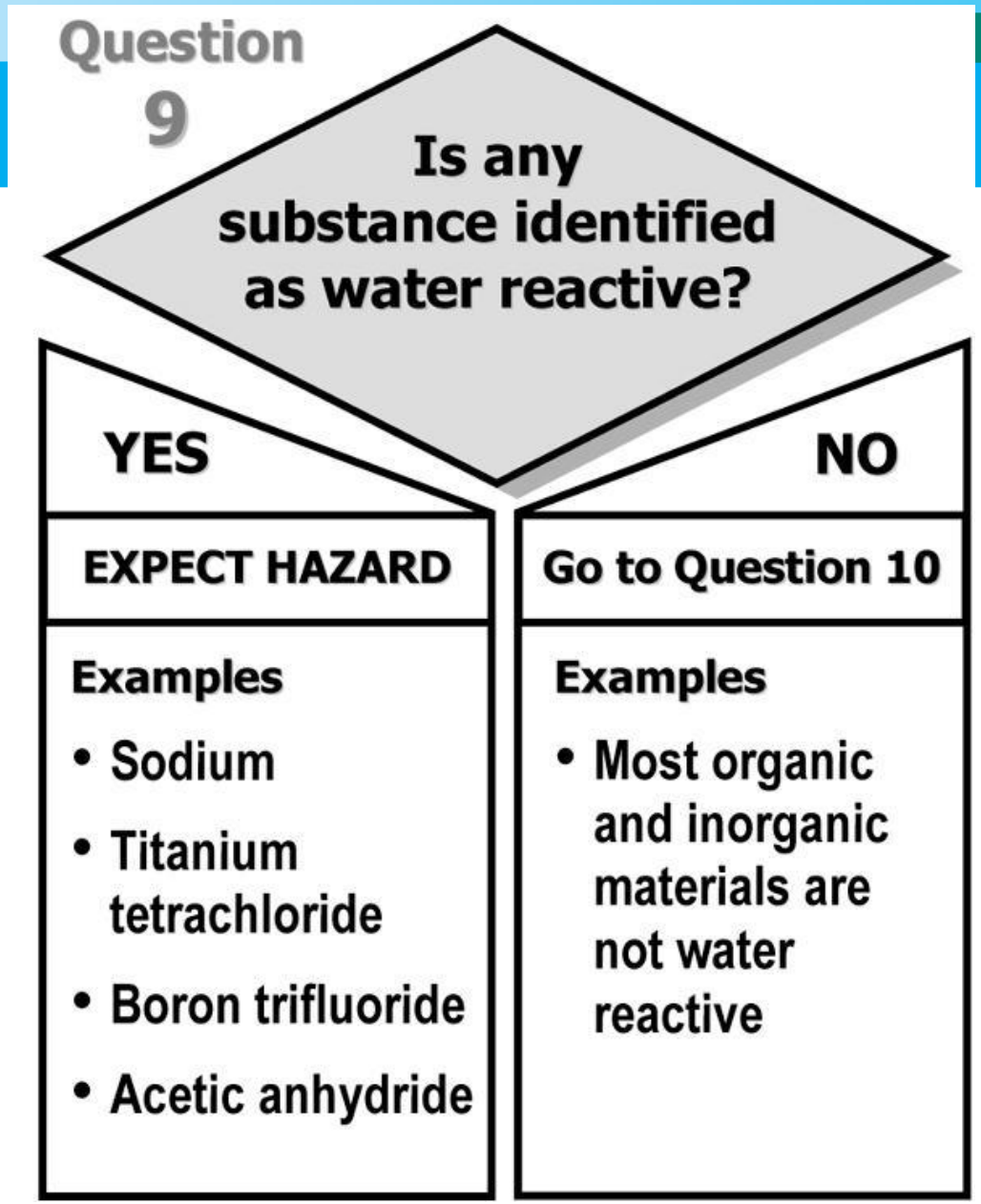
Chemical Storage

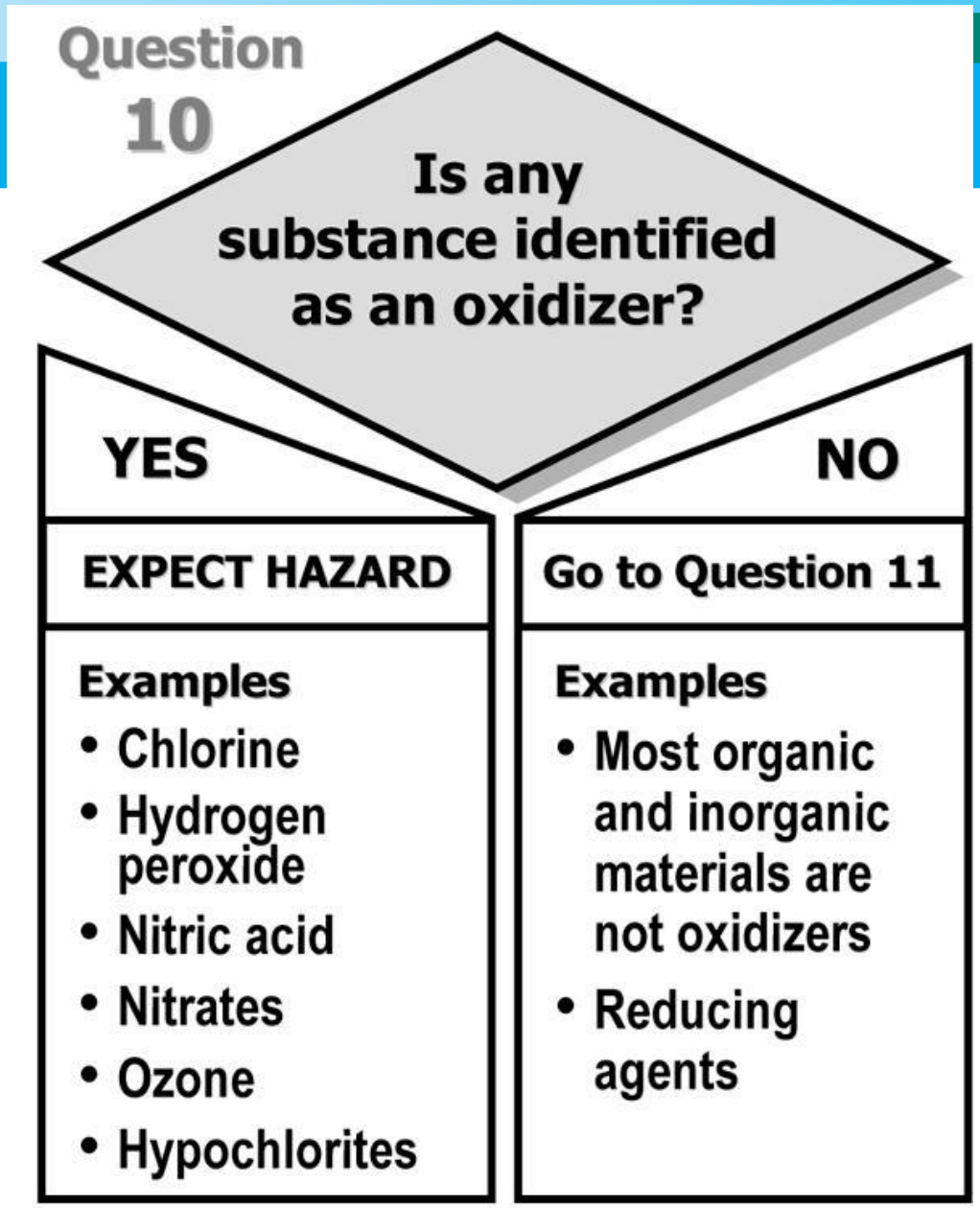

Question 5
Is combustion with air the only chemistry intended at your facility?
YES
NO
Go to Question 2
EXPECT HAZARD
Examples
• Boilers
• Flares
• Fired heaters
• Burners
Examples
• Continuous or batch chem-ical reactions
• Catalytic cracking
• Coking

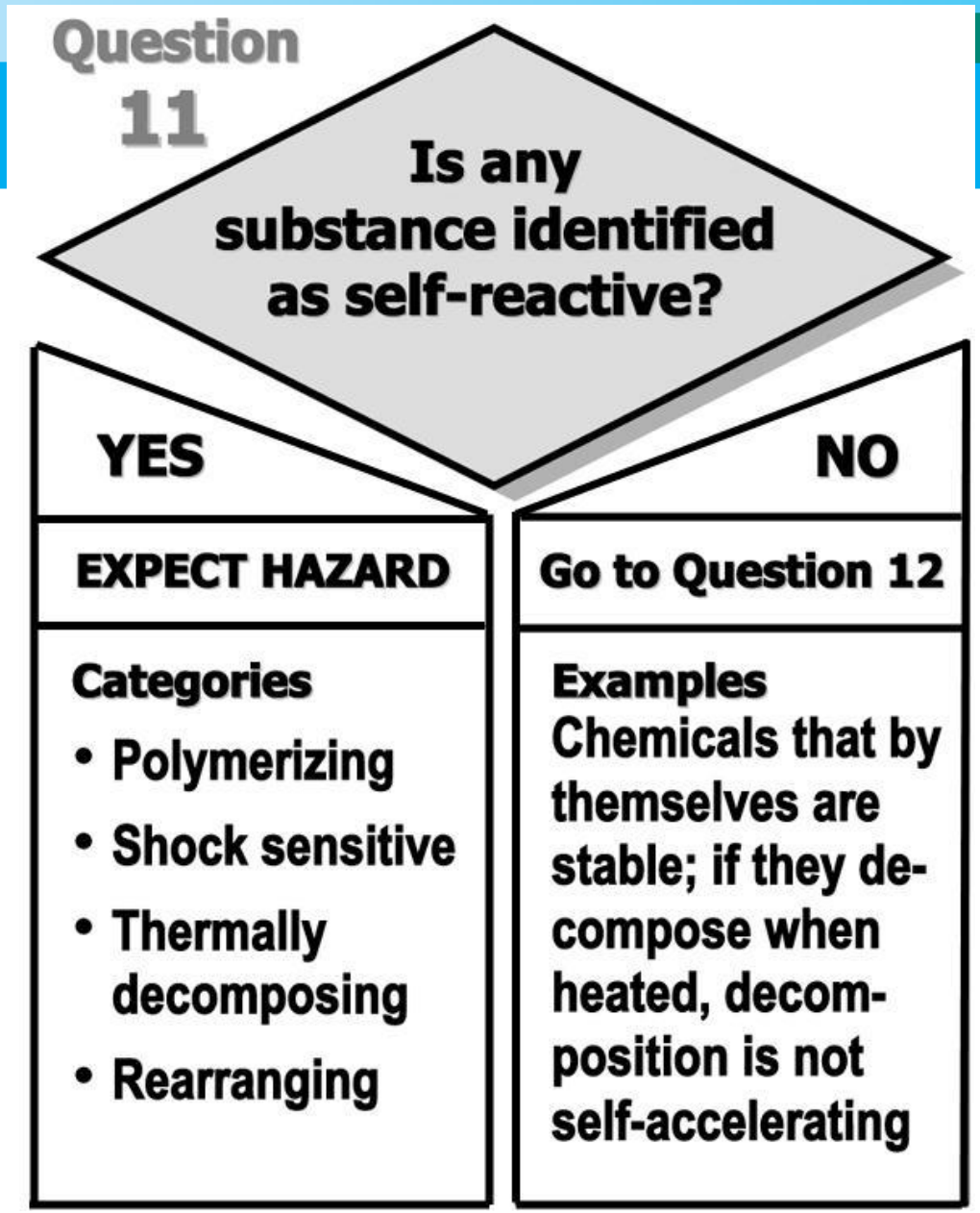

Question 6
Is any heat generated during the mixing or physical processing of substances?
YES
NO
EXPECT HAZARD
Go to Question 7
Examples
• Caustic + water
• Intense mixing
• Concentrated acid + aqueous solution
• Carbon adsorption
Examples
• Low-intensity powder blending
• Dilution with similar solvent
• Screening
• Drying

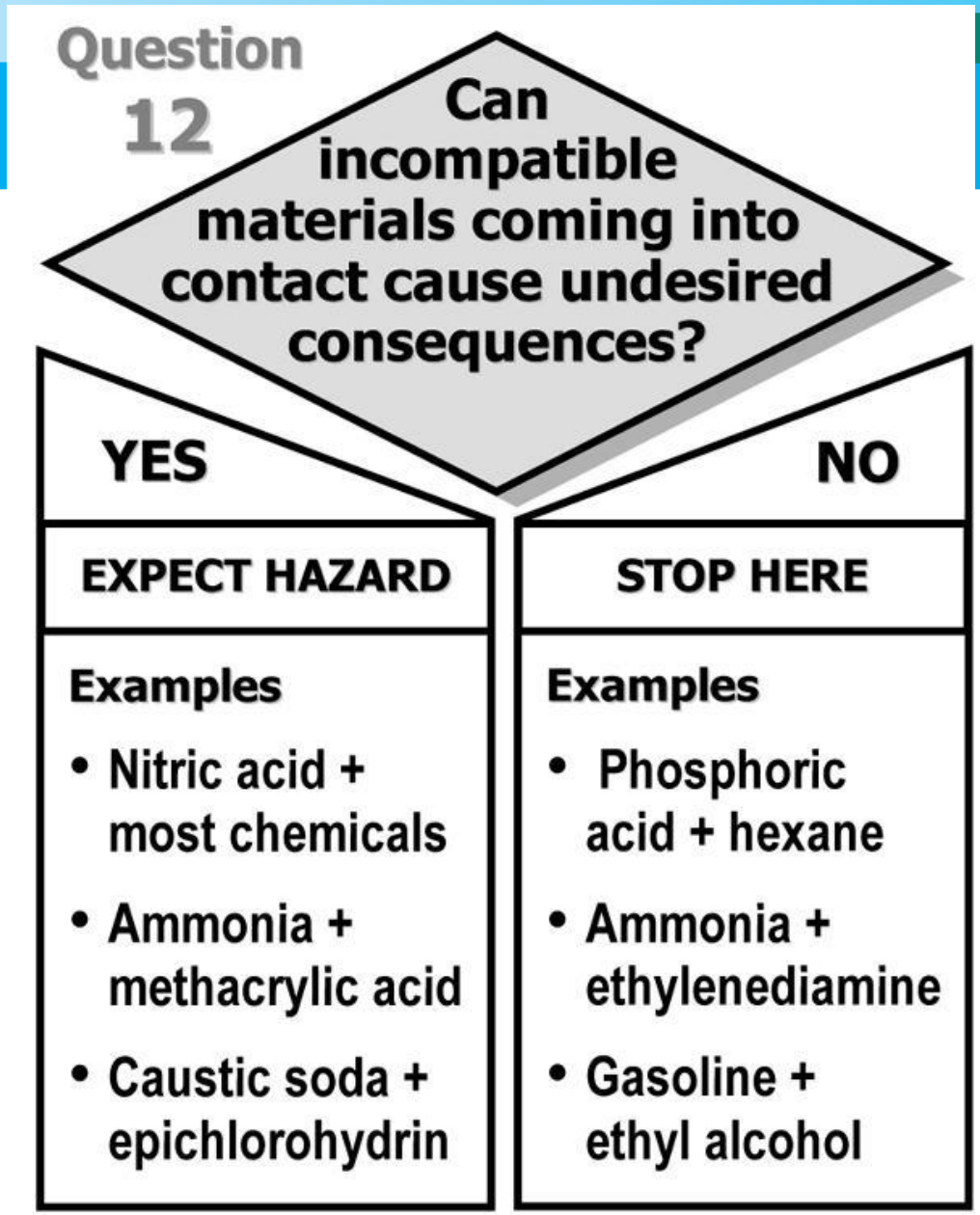

Question 7
Is any substance identified as spontaneously combustible?
YES
NO
EXPECT HAZARD
Go to Question 8
Examples
• Aluminum alkyl
• Grignard reagent
• Finely divided metals
• Iron sulfide
Examples
• Noncombustible materials
• Flammables or combustibles needing an ignition source to start burning


Question 8
Is any substance identified as peroxide forming?
YES
NO
EXPECT HAZARD
Go to Question 9
Examples
• 1,3-Butadiene
• 1,1-Dichloro-ethylene
• Isopropyl ether
• Other ethers
• Alkali metals
Examples
• Most organic and inorganic materials are not peroxide forming


Question 9
Is any substance identified as water reactive?
YES
NO
EXPECT HAZARD
Go to Question 10
Examples
• Sodium
• Titanium tetrachloride
• Boron trifluoride
• Acetic anhydride
Examples
• Most organic and inorganic materials are not water reactive


Question 10
Is any substance identified as an oxidizer?
YES
NO
EXPECT HAZARD
Go to Question 11
Examples
• Chlorine
• Hydrogen peroxide
• Nitric acid
• Nitrates
• Ozone
• Hypochlorites
Examples
• Most organic and inorganic materials are not oxidizers
• Reducing agents


Question 11
Is any substance identified as self-reactive?
YES
NO
EXPECT HAZARD
Go to Question 12
Categories
• Polymerizing
• Shock sensitive
• Thermally decomposing
• Rearranging
Examples
Chemicals that by themselves are stable; if they decompose when heated, decomposition is not self-accelerating


Question 12
Can incompatible materials coming into contact cause undesired consequences?
YES
NO
EXPECT HAZARD
STOP HERE
Examples
• Nitric acid + most chemicals
• Ammonia + methacrylic acid
• Caustic soda + epichlorohydrin
Examples
• Phosphoric acid + hexane
• Ammonia + ethylenediamine
• Gasoline + ethyl alcohol

Chemical Spills/Waste

- Assume all chemicals are reactive
- Many fires start in dumpsters/waste containers due to mixing of incompatible chemicals
- Some reactions are immediate
- Many reactions may take hours or more
- Waste segregation by type
- Spill procedures and training
- HAZMAT procedures

Incompatible Materials Evaluation

Step one: Determine if there are Undesirable Consequences

- Toxic gas generation
- Corrosive gas or liquid generation
- Flammable gas generation
- Formation of shock-sensitive or explosive materials
- Explosion
- Fire
- Off-gas generation that can rupture containers
- Sufficient heating to cause runaway reaction

Incompatible Materials Evaluation

Step two: Identify Mixing Scenarios

- Leaking containers
- Pumping into wrong storage tank, vessel
- Cross connected line left open
- Material mislabeled or unlabeled
- Wrong material selected by operator
- Waste materials combined in tank or container
- Waste material combined in sewer
- Contaminated raw material
- Residue from previous batch in equipment
- Cleaning materials left in process equipment
- Fire or explosion

Incompatible Materials Evaluation

Step Three:

Provide Controls to Prevent Mixing

- Training
- Segregation
- Engineering Controls

Chemical Storage Principles

- Segregation
- Protection from Physical Damage
- Hazard Identification
- Fire Control

Storage Guidelines

- Ensure containers are labeled
- Segregate incompatibles by hazard class
- Do not store alphabetically
- Store flammables according to GC property guidelines
- Do not store chemicals above eye level
- Do not overcrowd shelves
- Avoid storing chemicals on floor
- Liquids should be stored in unbreakable packaging

Chemical Segregation Scheme

- Compressed Gases- Flammable
- Compressed Gases- Oxidizing
- Acids
- Bases
- Flammable Liquids
- Flammable Solids
- Oxidizers
- Reducers
- Water-Reactive
- Peroxide Forming Chemicals
- Poisons/Toxins
- Carcinogens

Chemical Incompatibility Chart

	Acids Inorganic	Acids Oxidizing	Acids Organic	Alkalis Bases	Oxidizers	Poisons Inorganic	Poisons Organic	Water Reactives	Organic Solvents
Acids Inorganic			X	X		X	X	X	X
Acids Oxidizing			X	X		X	X	X	X
Acids Organic	X	X		X	X	X	X	X	
Alkalis Bases	X	X	X				X	X	X
Oxidizers			X				X	X	X
Poisons Inorganic	X	X	X				X	X	X
Poisons Organic	X	X	X	X	X	X			
Water Reactives	X	X	X	X	X	X			
Organic Solvents	X	X		X	X	X			

Loss Control Evaluation of Chemicals

- Improper storage of incompatibles
- Leaking or deteriorating containers
- Spilled chemicals
- Temperature extremes
- Lack of or low lighting levels
- Blocked exits or aisles
- Security of storage area
- Trash accumulation
- Evidence of smoking
- Adequate ventilation
- Hazard communication program
- Employee training
- Waste handling procedures
- HAZMAT procedures
- Intentional chemistry performed
- Fire extinguishers
- Sprinkler system
- Warning signs
- Labeling
- MSDSs

Loss Control Evaluation of Chemicals

Loss Control Evaluation of Chemicals

Chemical Storage Cabinets

Storage Cabinets

Chemical Handling/Dispensing

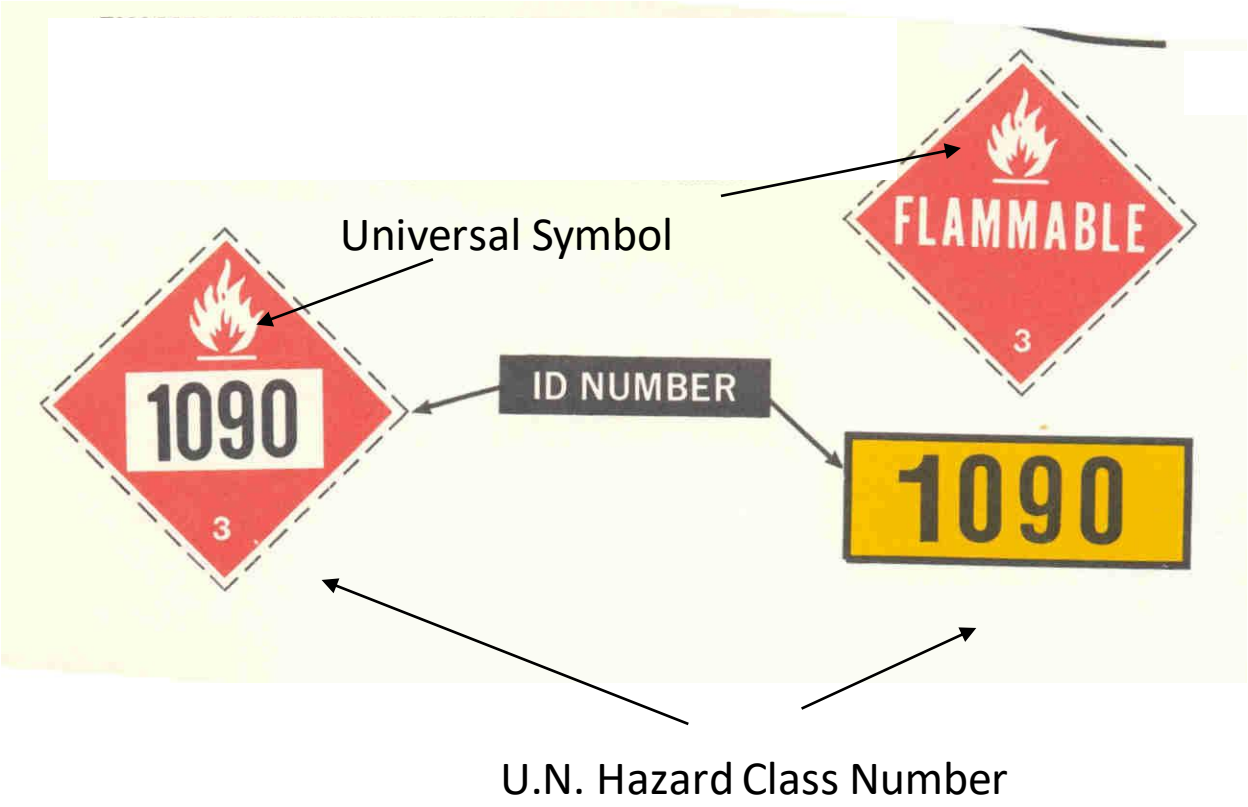
Painting Area

DOT Labels

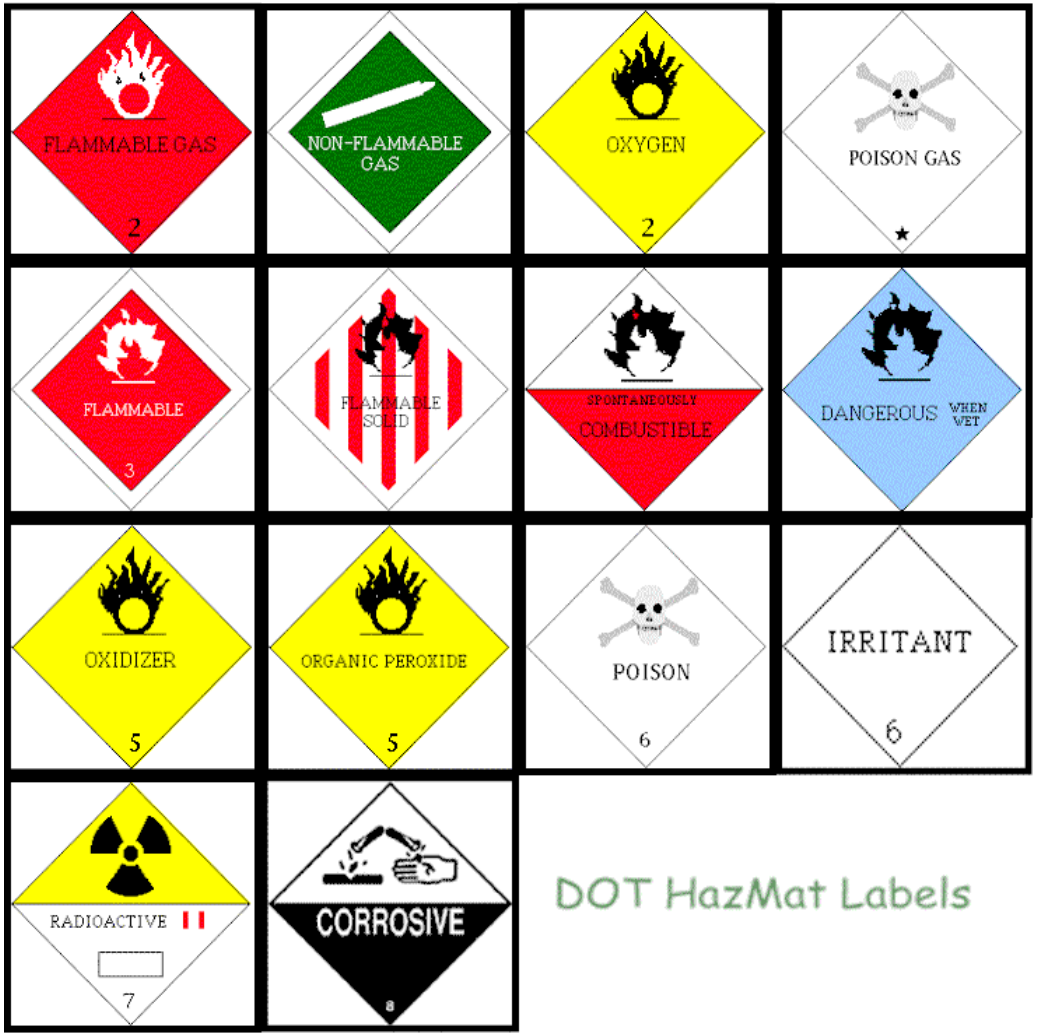
- Hazardous materials fall under the labeling requirements of U.S. DOT for placarding both for bulk transport and nonbulk transport
- DOT has assigned each hazardous material or group of materials a unique four digit ID number for cross reference by hazardous response personnel
- The labels are color coded and may also include a single digit Hazard Class Number and a universal symbol

DOT Labels

DOT labels are the type we most often see on containers in the field



DOT Labels



DOT HazMat Labels

DOT Labels

- Class 1 = Explosives
- Class 2 = Gases
- Class 3 = Flammable Liquids
- Class 4 = Flammable Solids
- Class 5 = Oxidizers
- Class 6 = Poisons & Infectious
- Class 7 = Radioactive
- Class 8 = Corrosives
- Class 9 = Miscellaneous

DOT Labels

Class 1- Explosives

- Division 1.1- Explosives with a mass explosion hazard
- Division 1.2- Explosions with a projection hazard
- Division 1.3- Explosives that are a fire hazard
- Division 1.4- Explosives with no significant blast hazard
- Division 1.5- Very insensitive explosives

Class 4- Flammable solids, Spontaneously combustible materials and materials dangerous when wet

- Division 4.1 Flammable solids
- Division 4.2 Spontaneously combustible materials
- Division 4.3 Materials that are dangerous when wet

Class 5- Oxidizers and Organic Peroxides

- Oxidizers
- Organic Peroxides

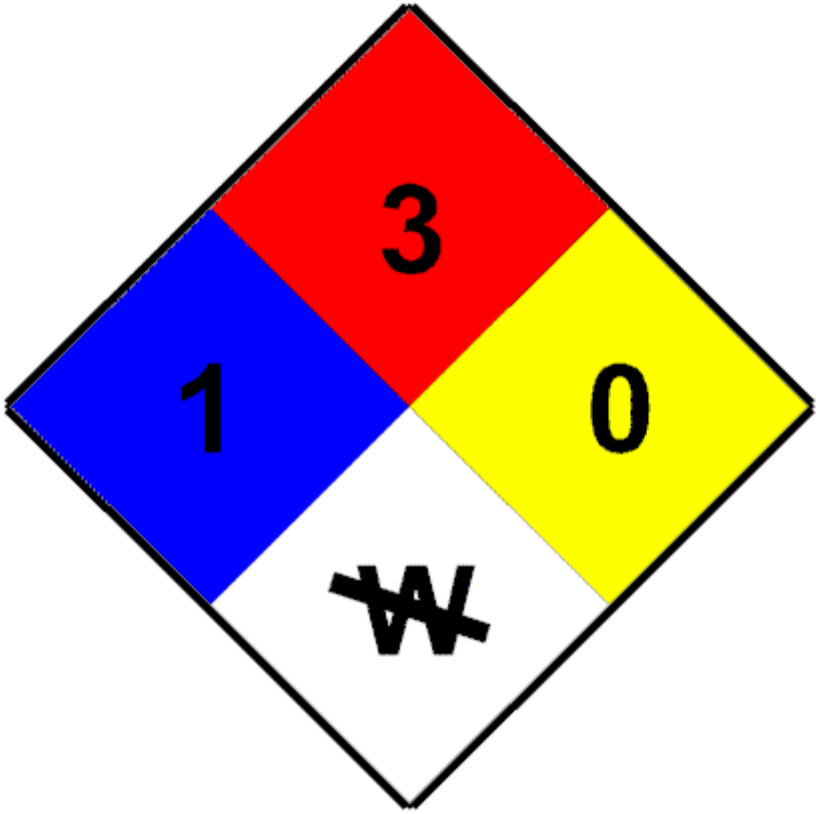
DOT Labels


1.4
EXPLOSIVE
1
1.5
BLASTING AGENT
1
EXPLOSIVE
1
1.6
EXPLOSIVE
1

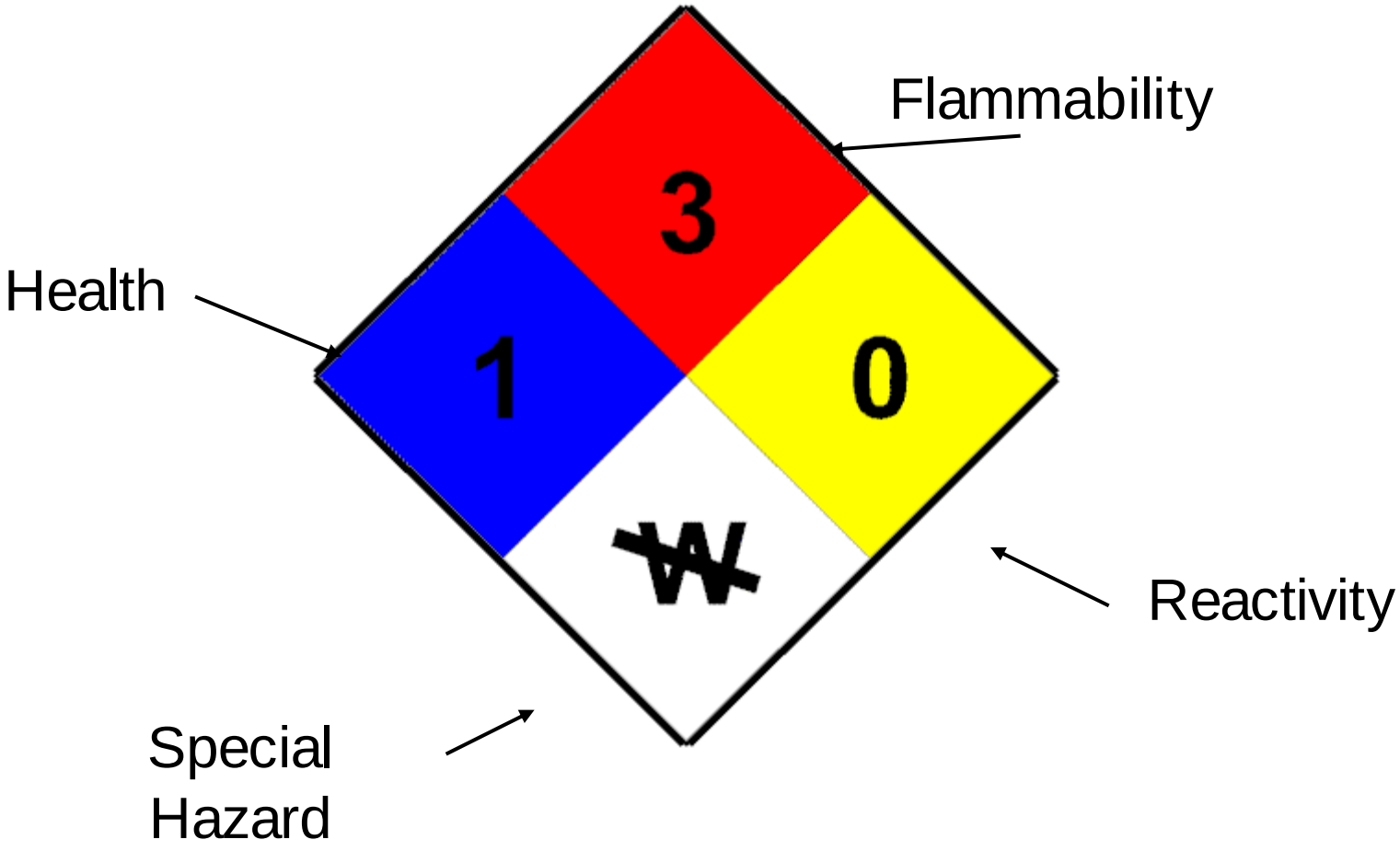
DOT Labels


DANGEROUS WHEN WET
4
SPONTANEOUSLY COMBUSTIBLE
4
ORGANIC PEROXIDE
5.2
OXIDIZER
5.1

NFPA Labels



NFPA Labels



NFPA Labels

- NFPA 704
- Hazards rating based upon exposure hazards during fires
- Reactivity rating based on reactions with water

NFPA Labels

Health

- 4- Materials that can cause death or serious chronic injury with very short exposure
- 3- Materials that can cause serious temporary or chronic injury with short exposure
- 2- Materials that can cause temporary injury or possible chronic injury with intense exposure
- 1- Materials that can cause irritation but only minor chronic injury
- 0- Materials that cause no hazard beyond those of ordinary combustibles in a fire situation

NFPA Labels

Flammability

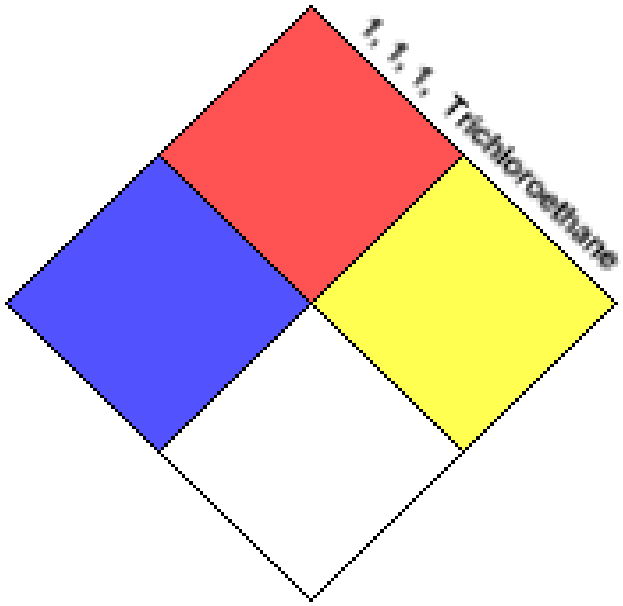
- 4- Materials that rapidly or completely vaporize at atmospheric pressure and normal temperature and burn readily
- 3- Liquids and solids that can be ignited under almost all ambient temperature conditions
- 2- Materials that must be moderately heated before ignition occurs
- 1- Materials that must be preheated before ignition occurs
- 0- Materials that will not burn

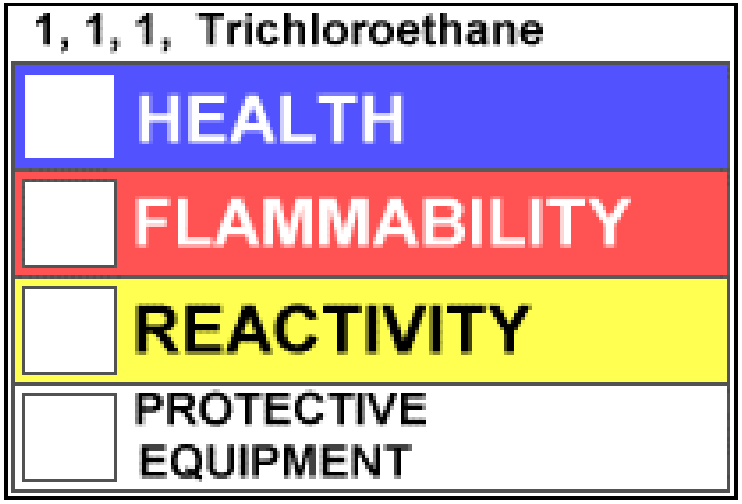
NFPA Labels

Reactivity

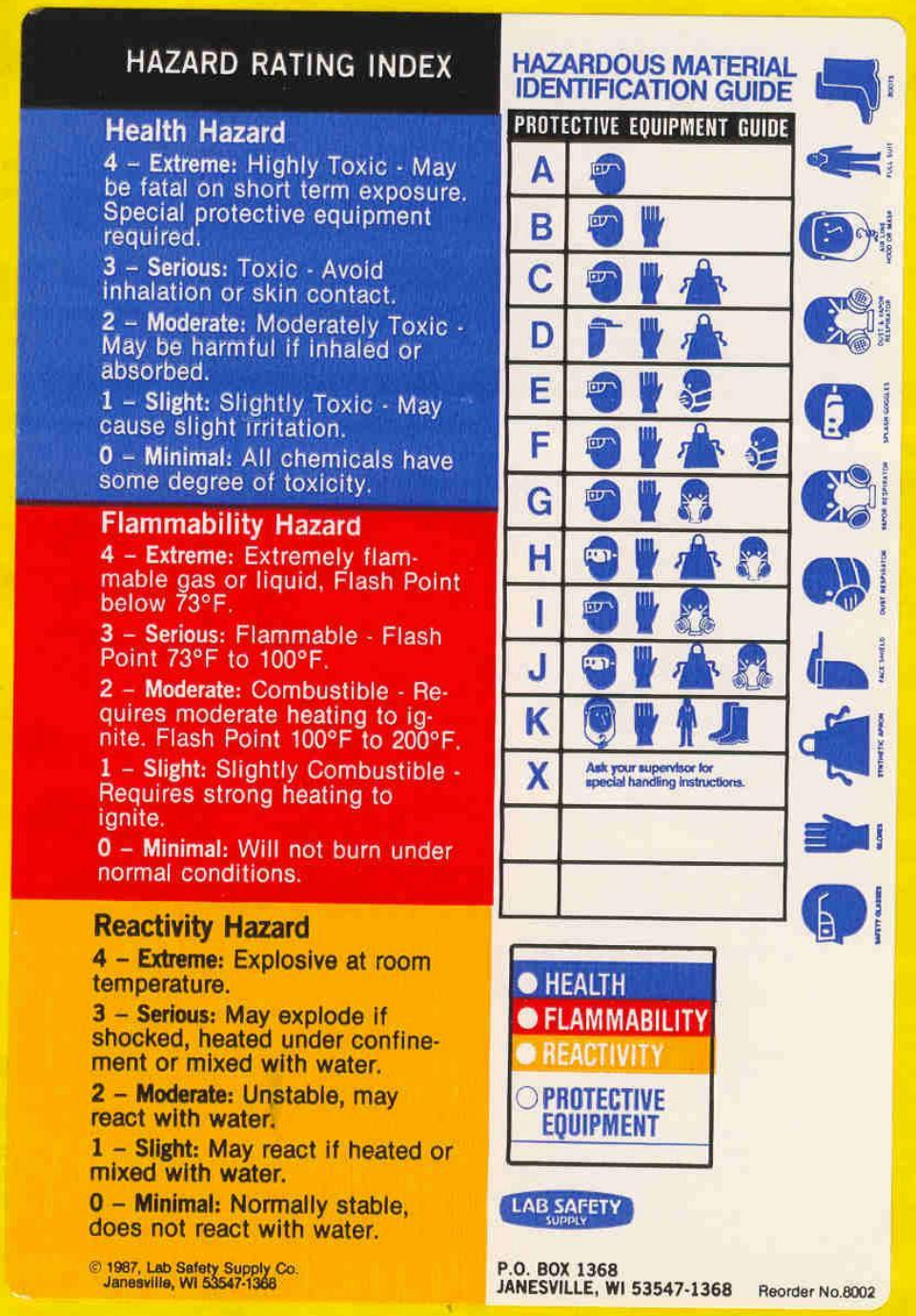
- 4- Materials that are readily capable of detonation or explosive decomposition at normal temperatures and pressures
- 3- Materials that are capable of detonation or explosive decomposition but require a strong initiating source or must be heated under confinement, or explosively react with water
- 2- Materials that readily undergo violent chemical change at elevated temperature or pressure, or react violently with water
- 1- Materials that are normally stable but can become unstable at elevated temperatures or pressures
- 0- Materials that are normally stable even under fire exposure and are not reactive with water

HMIG (Hazardous Material Information Guide)





HMIG Labels


HAZARD RATING INDEX
Health Hazard
4 – Extreme: Highly Toxic - May be fatal on short term exposure. Special protective equipment required.
3 – Serious: Toxic - Avoid inhalation or skin contact.
2 – Moderate: Moderately Toxic - May be harmful if inhaled or absorbed.
1 – Slight: Slightly Toxic - May cause slight irritation.
0 – Minimal: All chemicals have some degree of toxicity.
Flammability Hazard
4 – Extreme: Extremely flammable gas or liquid, Flash Point below 73°F.
3 – Serious: Flammable - Flash Point 73°F to 100°F.
2 – Moderate: Combustible - Requires moderate heating to ignite. Flash Point 100°F to 200°F.
1 – Slight: Slightly Combustible - Requires strong heating to ignite.
0 – Minimal: Will not burn under normal conditions.
Reactivity Hazard
4 – Extreme: Explosive at room temperature.
3 – Serious: May explode if shocked, heated under confinement or mixed with water.
2 – Moderate: Unstable, may react with water.
1 – Slight: May react if heated or mixed with water.
0 – Minimal: Normally stable, does not react with water.
© 1987, Lab Safety Supply Co.
Janesville, WI 53547-1368
HAZARDOUS MATERIAL IDENTIFICATION GUIDE
PROTECTIVE EQUIPMENT GUIDE
A
B
C
D
E
F
G
H
I
J
K
X
Ask your supervisor for special handling instructions.
HEALTH
FLAMMABILITY
REACTIVITY
PROTECTIVE EQUIPMENT
LAB SAFETY SUPPLY
P.O. BOX 1368
JANESVILLE, WI 53547-1368
Reorder No.8002

Housekeeping Issues

Housekeeping & Storage

Labeling

Chemical Storage/Reactivity Red Flags

- Peroxide
- Oxidizer
- Catalyst
- Accelerator
- Activator
- Polymerization
- Reducer
- Chromate
- Dichromates
- Nitrate
- Perchlorate
- Nitric acid
- Chlorates
- Permanganates
- Hypochlorates
- Persulfate
- Water reactive
- Nitro
- Azides
- Curing agent
- Hardener
- Initiator
- Promoter
- Acids
- Bases
- Unstable
- Pyrophoric

10 Loss Control Questions

1. Are hazardous substances stored or handled at the facility?
2. Have materials been evaluated for potential reactivity hazards or incompatibility if they are accidentally mixed together?
3. Is intentional chemistry performed?
4. Is there mixing of different substances?
5. Is heat generated during mixing or processing?
6. Are any spontaneously combustible materials, peroxides, water reactive materials, oxidizers or self-reactive (polymerizable) materials used or stored?
7. Are incompatible chemicals segregated?
8. Are storage containers properly labeled and identified?
9. Are storage containers in good condition?
10. Are employees properly training in Hazard Communication and proper chemical handling and storage procedures?

Other Sources of Information

- OSHA – Many resources are available under “chemical reactivity hazards” in the topics index
- Essential Practices for Managing Chemical Reactivity Hazards- Center for Chemical Process Safety- Download from OSHA’s website
- Organic Peroxides- E&S PC-30-11
- Chlorinated Swimming Pool Sanitizers- E&S PC-30-02
- Contact the HO EH Specialist

Post-test

What are the 4 principles for good chemical storage?

Match the following chemicals to the appropriate reactivity hazard:

___Peroxides	A- Air Sensitive
___Acrylic Resins	B- Spontaneous Peroxide Formation
___Metal Dusts	C- Strong Oxidizers
___Ethers	D- Polymerization Hazard
___Hydrogen	E- Reducer

Explain why intentional chemistry processes are a major concern from a potential loss standpoint.

List 10 things that should be reviewed when evaluating chemical storage areas.