BLR's Safety Training Presentations

Reactive Chemicals

29 CFR 1910.1200

Background for the Trainer:

Although the Occupational Safety and Health Administration (OSHA) does not have specific regulations regarding reactive chemicals, the safe use of all chemicals in the workplace, including reactives, is regulated by OSHA's Hazard Communication Standard 29 CFR 1910.1200.

Speaker's Notes:

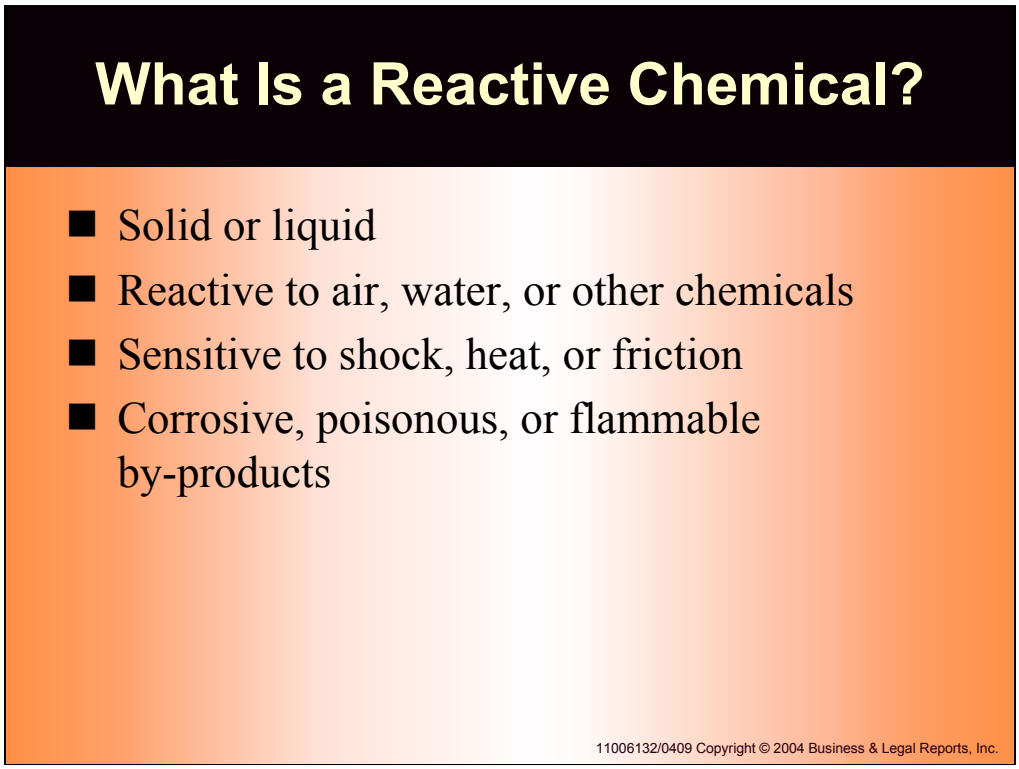
- Chemical reactivity presents serious hazards to workers when the hazard is not thoroughly understood and controlled.
- When intentional or unintentional chemical reactions have gotten out of control, the result has been fires, explosions, or releases of toxic fumes or gases. These incidents have sometimes resulted in employee injuries and fatalities.
- Since chemical reactions are key to the chemical manufacturing industry, it is important that we learn to safely conduct these reactions and handle these chemicals.
- In this training session, we will learn to recognize hazards of working with reactive chemicals as well as how to safely control reactive chemicals.

Goals

- Hazards and types of reactive chemicals
- Managing hazards and emergencies
- Quiz

Speaker's Notes:

- We will start by discussing the hazards and the different types of reactive chemicals.
- Next, we will discuss the steps we can take to control and manage the hazards of working with reactive chemicals as well as how to respond to emergencies that involve them.
- Finally, we will wrap up the class with a quiz.

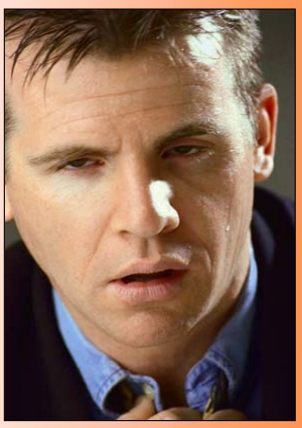


Speaker's Notes:

- Reactive chemicals may be in the form of solid materials, such as granules or powders, or in the form of a liquid.
- These chemicals may be reactive to air, water, or other chemicals such as combustible liquids.
- Reactive chemicals may be sensitive to shock, heat, or friction, and exposure to any of these may result in a fire or explosion.
- Chemical by-products from reactive chemicals may be corrosive, poisonous, or flammable.

Health Hazards

- Burn skin, eyes, nose, throat
- Form acids
- May be poisonous
- Irritate eyes, skin, throat
- Cause dizziness, vomiting
- Cause asphyxiation and death



Speaker's Notes:

- Many reactive chemicals are corrosives and can destroy tissue. Alkali metals (sodium, lithium, potassium) react with body moisture to cause severe burns to skin, eyes, nose, and throat.
- White phosphorus reacts with air to form phosphoric acid, which is severely corrosive.
- Azides may be poisonous, in addition to being unstable, sensitive to heat, shock, and friction.
- Metal peroxides can be irritating to the eyes, nose, and respiratory tract. Hydrazines, which are oxidizers, may also irritate eyes, skin, and respiratory tract. They are suspected carcinogens and mutagens (harmful to reproductive organs).
- Nitrates may cause dizziness, vomiting, convulsions, and death.
- Chlorates irritate the eyes, nose, and respiratory tract. In confined spaces, free chlorine can cause asphyxiation and death.

Fire Hazard

- Friction
- Absorption of moisture
- Spontaneous chemical changes
- Retained heat
- Readily ignited

Background for the Trainer:

- Review the MSDS of the reactive chemical(s) in your workplace to determine how they are most likely to react and become a fire hazard.

Speaker's Notes:

Reactive chemicals can be a serious fire hazard and can cause fire through:

- Friction, such as when physically processed by being mixed or transferred.
- Absorption of moisture, which may cause some water reactive materials to begin to heat up.
- Spontaneous chemical changes, which often generate heat and can result in spontaneous combustion.
- Retained heat from manufacturing or processing, which may cause more reactions to occur, generating more heat and potentially starting a chain reaction that could become a fire.
- Ignition and burning so vigorously and persistently that they create a serious hazard.

Determine Chemical Reactivity Hazards

- Intentional chemistry
- Mixing of different substances
- Physical processing
- Hazardous substance storage
- Combustion with air
- Heat generated

Speaker's Notes:

Ask the following questions to determine if your facility has chemical reactivity hazards and how serious those hazards are. We will discuss some of these questions in this presentation.

- Is intentional chemistry performed at your workplace? For example, does your company intentionally mix chemicals that react to form different substances?
- Is there any mixing or combining of different substances? For example, does your company mix chemicals that do not react, but rather are just mixed together?
- Does any other physical processing of substances occur? Does your company conduct any mixing, heating, or other physical processing of chemicals?
- Are any hazardous substances stored or handled at your workplace?
- Is combustion with air the only chemistry intended? For example, using propane or natural gas to fuel a heater is considered combustion with air.
- Is any heat generated during the mixing or physical processing of substances? Do chemical reactions in your workplace generate heat?

Speaker's Notes:

In order to determine if your facility has chemical reactivity hazards and how serious those hazards are, you must determine whether your facility has:

- Any substance identified as spontaneously combustible
- Any substance identified as peroxide forming
- Any water-reactive substances
- Any substance identified as an oxidizer
- Any substance identified as self-reactive
- Any materials that are incompatible with each other, if they come into contact with each other, and if they do contact each other, the consequences of this contact.

Intentional Chemistry

- Exothermic and endothermic reactions
- Losing control of the intended reaction
- Heat generating
- Adding heat
- Abnormal situations—too much heat

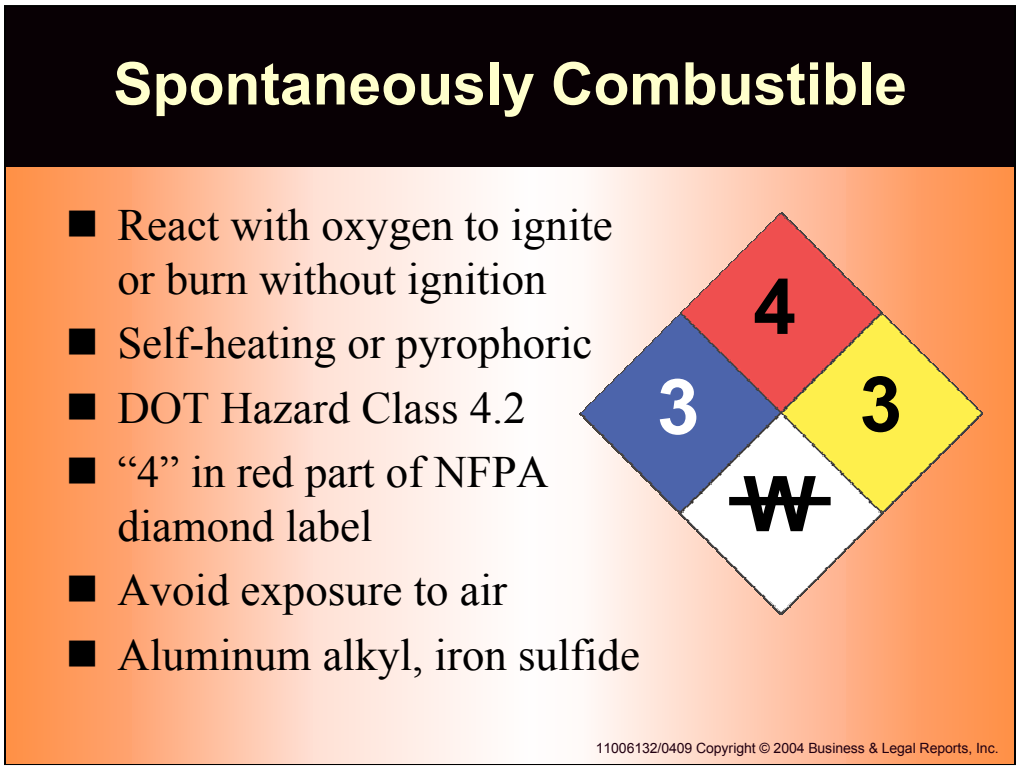
Background for the Trainer:

- Discuss intentional chemical reactions that take place in your workplace.

Speaker's Notes:

Intentional chemistry means processing substances so that a chemical reaction is meant to take place.

- Exothermic reactions are chemical reactions that liberate heat. Endothermic means a reaction that absorbs heat, i.e., heat must be added for the reaction to continue. Since energy is being put into the endothermic reaction, the final products will have greater internal energy than the starting materials, so the products themselves may pose a chemical reactivity hazard. In addition, the endothermic reaction may be reversible under certain conditions and thus, may result in a potentially dangerous exothermic reaction.
- Many different hazard scenarios are possible with intentional chemistry. All of them relate to losing containment or control of the intended reaction, starting another reaction, or side reactions or series of reactions that are not intended or expected.
- An important question to consider is whether the mixing or physical processing of substances generates heat; for example, a mixture will get warm or hot upon combining the ingredients, or will get warm or hot if cooling was lost. Heat can be generated by heat of solution, heat of adsorption, mechanical energy, or other physical heat effects.
- This is different from adding heat during a mixing or physical processing operation. However, recognize that materials or mixtures that were not apparently reactive at one temperature can become dangerously reactive at another temperature.
- Abnormal situations can occur in which too much heat is generated (or too little cooling occurs), and a substance or mixture gets hotter than intended. Consequently, an unintended chemical reaction may be initiated at the higher temperature that may generate even more heat, create toxic or flammable gases, or be explosive. The heat that initiates secondary unintended reactions might be added by nonchemical means.



Background for the Trainer:

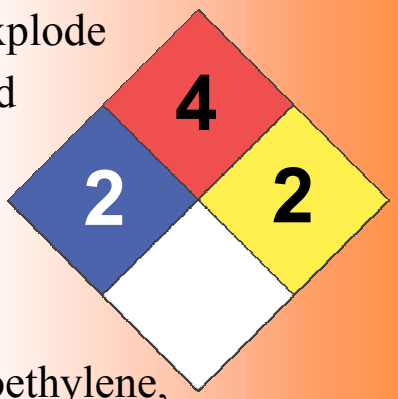
- Discuss any spontaneously combustible materials used or stored in your workplace.

Speaker's Notes:

- Spontaneously combustible substances will react readily with the oxygen in the atmosphere, igniting and burning even without an ignition source. Ignition may be immediate, or may take minutes or hours.
- Self-heating is a process that may require a few minutes or many hours before the substance finally ignites and bursts into flame. Pyrophoric materials ignite spontaneously on short exposure to air under ordinary ambient conditions.
- The potential of pyrophoric materials to exhibit this behavior is usually well-known because of the extreme care required for their safe handling. Pyrophoric and spontaneously combustible substances should be identified as DOT (Department of Transportation) Hazard Class 4.2 materials for shipping purposes and labeled SPONTANEOUSLY COMBUSTIBLE.
- When the NFPA diamond is used for container or vessel labeling of pyrophoric substances, the red (top) quadrant would have a rating of 4, indicating the highest severity of flammability hazard.
- Since exposure of a spontaneously combustible material to air has obvious consequences, loss of containment or other means of air exposure is usually the most important issue regarding what can go wrong. It should be noted that pyrophoric materials often exhibit one or more other reactivity hazards as well, such as water reactivity.
- Examples of pyrophoric or spontaneously combustible materials include aluminum alkyl, finely divided metals, and iron sulfide.

Peroxide Formers

- React with oxygen, may explode
- Inhibitor or stabilizer added
- Usually labeled by another characteristic
- Avoid prolonged storage or opening container
- 1,3-butadiene, 1,1-dichloroethylene, ethers, alkali metals

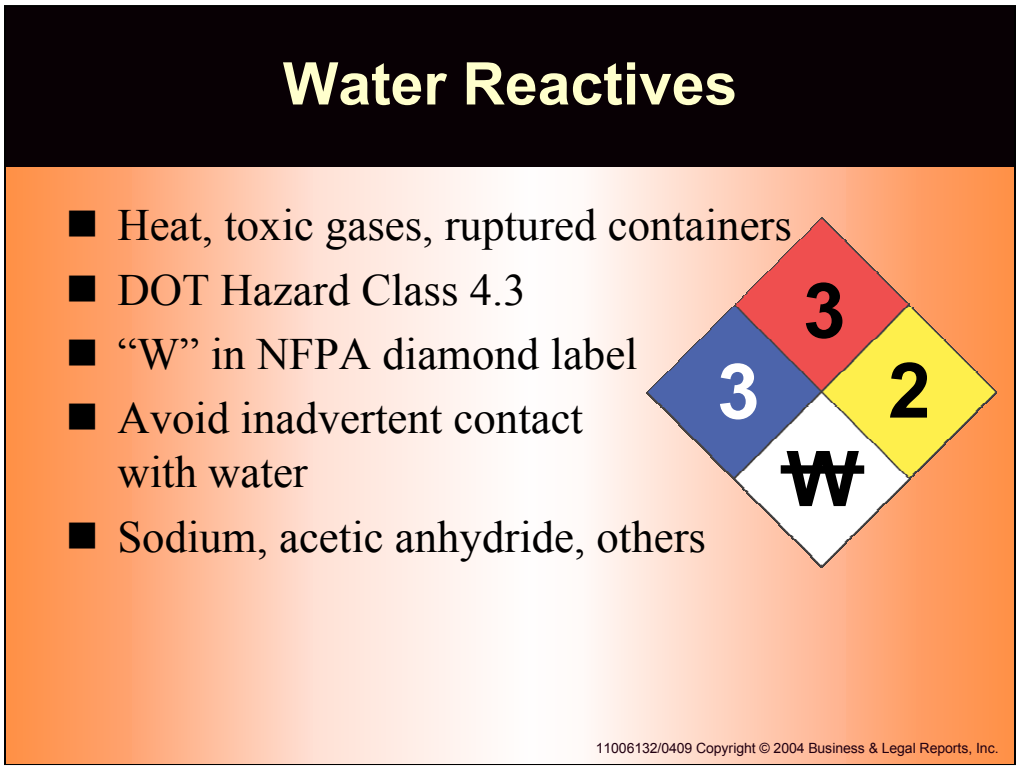


Background for the Trainer:

- Discuss any peroxide-forming materials used or stored in your workplace.

Speaker's Notes:

- Peroxide formers are substances that will react with the oxygen in the atmosphere to form unstable peroxides, which, in turn, might explosively decompose if concentrated. Peroxide formation, or peroxidation, usually happens slowly over time when a peroxide-forming liquid is stored with limited access to air.
- Substances that are peroxide formers will often have an inhibitor or stabilizer added to prevent peroxidation.
- They are often identified by another characteristic, such as flammability, for storage and shipping purposes.
- Exposure of a peroxide-forming material to air does not have obvious and immediate consequences, so what can go wrong is usually more subtle. One general sequence of events is the formation and concentration of unstable peroxides over time, followed by an event such as the opening or agitation of a container that initiates explosive decomposition of the peroxide. Possible causes of uncontrolled reactions associated with peroxide forming materials include, but are not limited to, material stored beyond shelf life, insufficient stabilizer/inhibitor added, leak or spill of the substance, and opening the container and allowing in air.
- Examples of peroxide-forming chemicals include 1,3-butadiene, 1,1-dichloroethylene, isopropyl ether, other ethers, and alkali metals.



Background for the Trainer:

- Discuss any water-reactive materials used or stored in your workplace.

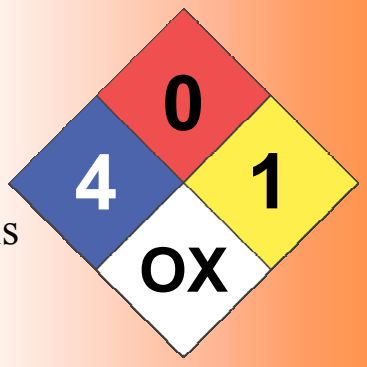
Speaker's Notes:

Water reactives are substances that will chemically react with water.

- Water reactivity can be hazardous. The heat of reaction can cause thermal burns, ignite combustible materials, or initiate other chemical reactions. Flammable, corrosive, or toxic gases are often formed as reaction products. Even slow reactions can generate sufficient heat and off-gases to overpressurize and rupture a closed container.
- Water reactives may be identified as DOT Hazard Class 4.3 materials for shipping purposes and labeled DANGEROUS WHEN WET. However, some water-reactive materials are classified otherwise. Titanium tetrachloride, for example, is DOT Hazard Class 8 (corrosive material) for shipping purposes, and its shipping label is likely to reflect both CORROSIVE and POISON hazards. Acetic anhydride is likewise designated Class 8 and may also be identified as a combustible liquid.
- When the NFPA diamond is used for container or vessel labeling, and the white (bottom) quadrant contains the "W" symbol, the material will react violently or explosively with water. However, if the "W" symbol is not present, the material may still be water reactive, but at a slower rate.
- Inadvertent contact of a water-reactive material with water is obviously the most important safety issue with water-reactive substances. Due to the prevalence of water in living tissues, water-reactive materials are often toxic or corrosive to humans and animals. Some possible causes of uncontrolled reactions include humidity in incoming air or gas, leaking water from cooling coil into process, rainwater, or sprinkler water onto cardboard containers.
- Examples of water reactives include sodium, titanium tetrachloride, boron trifluoride, and acetic anhydride.

Oxidizers

- Yield oxygen or promote combustion
- DOT Hazard Class 5.1
- "OX" in NFPA diamond label
- Avoid combustible materials
- Chlorine, hydrogen peroxide, nitric acid, others



Background for the Trainer:

- Discuss any oxidizers used or stored in your workplace.

Speaker's Notes:

- Oxidizers are any material that readily yields oxygen or that easily reacts to promote or initiate combustion of combustible materials. Most oxidizers are reactive with ordinary combustible liquids or solids. They can also react with many other substances.
- They may be identified as DOT Hazard Class 5.1 materials for shipping purposes and labeled as oxidizers. However, some oxidizers are classified otherwise. Chlorine, for example, is DOT Class 2.3 (gases toxic by inhalation) and labeled as POISON GAS for shipping purposes; it may also be labeled as a corrosive material. Liquid oxygen is Class 2.2 (nonflammable nontoxic compressed gases) but should be labeled as NONFLAMMABLE GAS and OXIDIZER.
- When the NFPA diamond is used for container or vessel labeling, and the white (bottom) quadrant contains "**OX,"** the material possesses oxidizing properties. It should be considered as posing a chemical reactivity hazard.
- Contact of oxidizers with reducing agents, including combustible materials, is the most important issue regarding what can go wrong when handling oxidizing substances. This will increase the burning rate of the combustible materials; it may also cause a fire to spontaneously ignite. Some oxidizers can also undergo self-sustained vigorous or explosive decomposition when contaminated or exposed to heat or shock.
- Examples of oxidizers include chlorine, hydrogen peroxide, nitric acid, nitrates, ozone, and hypochlorites.

Self-Reactive Materials

- Polymerizing, decomposing, rearranging
- DOT Hazard Class 1 or 5.2
- "1" to "4" in yellow part of NFPA diamond label
- Avoid shock, friction, heat

Background for the Trainer:

- Discuss any self-reactive materials used or stored in your workplace.

Speaker's Notes:

Materials that self-react often do so with accelerating or explosive rapidity. There are three forms of self-reaction.

  - Polymerizing occurs when individual molecules called monomers combine to form very large chainlike or crosslinked polymer molecules.
  - Decomposing occurs when larger molecules break apart into smaller, more stable molecules.
  - Rearranging occurs when the atoms in a molecule rearrange themselves into a different molecular structure, such as a different isomer.

- Substances that are DOT Class 1 (Explosives) and Class 5.2 (Organic Peroxides) are likely to be self-reactive. However, some organic peroxide formulations burn with even less intensity than ordinary combustibles and present no chemical reactivity hazard. Many self-reactive materials are classified in other categories; for example, most self-polymerizing materials are labeled as flammable gases or flammable liquids because of their flammability and reactivity.
- When the NFPA diamond is used for labeling containers or vessels of self-reactive materials, the yellow (right) quadrant should have some rating between 1 (lowest) and 4 (highest) inclusive. This indicates the material poses an instability hazard. A nonzero NFPA instability rating is a straightforward means of identifying self-reactive materials.
- For some highly reactive materials, such as shock-sensitive explosives and organic peroxides, mechanical shock, friction, or a spark may be sufficient to start a decomposition reaction. However, for most self-reactive materials, the energy input is in the form of thermal energy or heat.

Incompatible Materials

- Results of uncontrolled reactions
- Potential mixing scenarios
- Determine compatibility
- Nitric acid and most chemicals, others

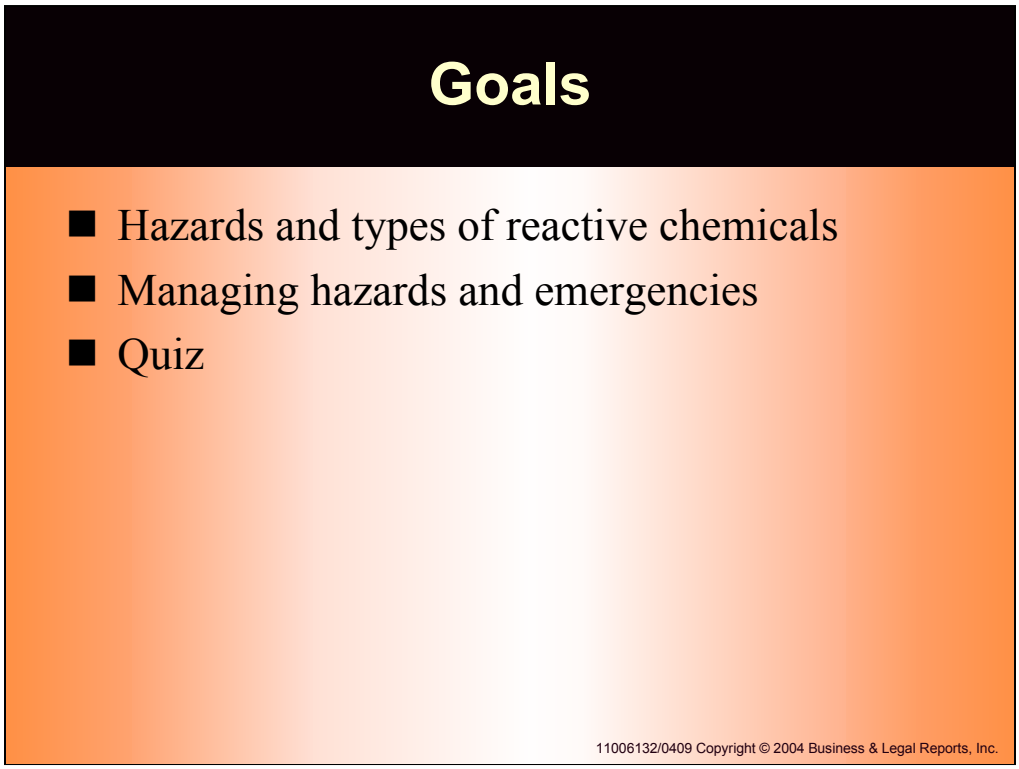
Background for the Trainer:

- Discuss potential incompatible materials in your workplace and potential mixing scenarios.

Speaker's Notes:

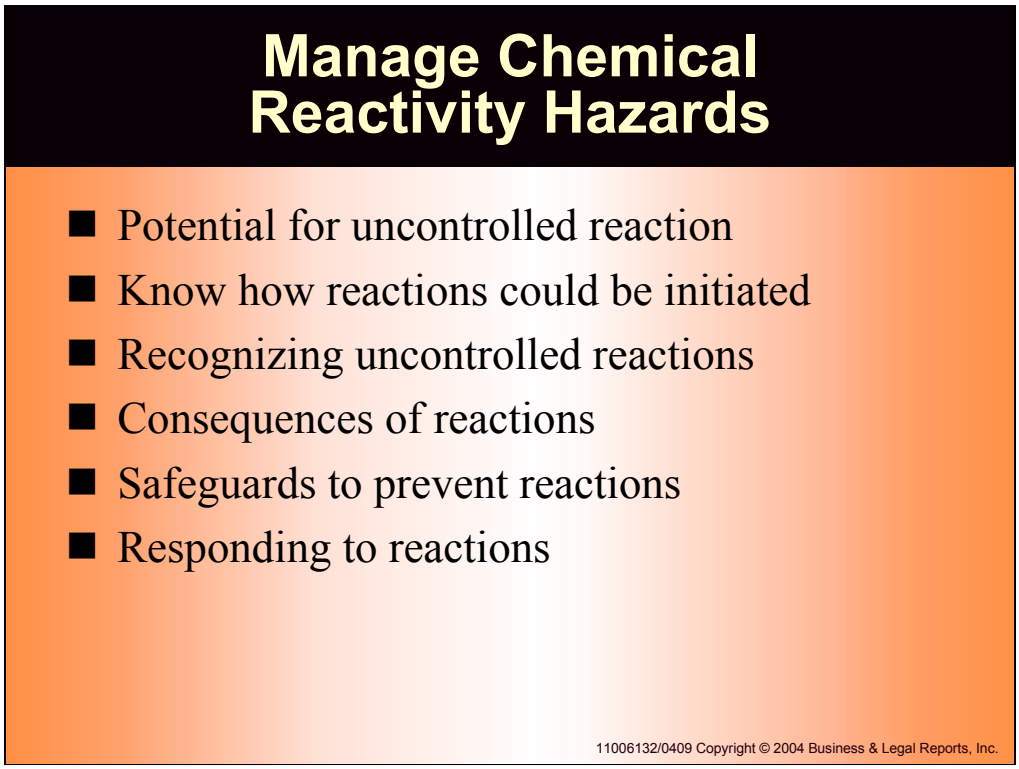
Now we will address the potential for an unintended chemical reaction resulting from incompatible materials contacting one another. Compatibility means the ability of materials to exist in contact without hazardous consequences.

- The result of uncontrolled chemical reactions may include toxic gas, corrosive gas, flammable gas, formation of shock-sensitive or explosive material, explosion, ignition of combustible material, over-pressurization that could rupture a container, or heat generation that could initiate chemical decomposition.
- Depending on the nature of your facility, many different scenarios may be possible for the unintentional mixing or combining of different substances, such as: a leaking liquid contacts adjacent material, material is pumped or transferred to wrong process vessel, material is mislabeled or unlabeled, or the wrong material is selected by an operator to add to a mixture or formulation.
- Determine compatibility of the chemicals in your workplace by developing a compatibility chart. Once you determine which chemicals are incompatible, take the necessary steps to ensure they are stored and processed separately.
- Examples of incompatible materials include nitric acid and most chemicals, ammonia and methacrylic acid, caustic soda, and epichlorohydrin.



Speaker's Notes:

- Do you have any questions regarding the hazards of reactive chemicals and different types of reactive chemicals?
- Now we will discuss the steps we can take to control and manage the hazards of working with reactive chemicals as well as how to respond to emergencies that involve them.



Speaker's Notes:

- In order to manage chemical reactivity hazards, you need to know if the potential exists for uncontrolled chemical reaction(s) in your facility.
- Know how chemical reactions might be initiated, such as by heat, contamination, inadvertent mixing, impact, friction, electrical short, etc.
- Know how to recognize when an uncontrolled reaction is taking place.
- Know what the consequences would be if such a reaction took place, such as toxic gas release, fire, explosion.
- Know what safeguards are in place to prevent uncontrolled reactions from taking place, including how to avoid them altogether with inherently safer design/operations, and how to control them within safe limits using automatic controls and procedures.
- Know how to respond properly if an uncontrolled reaction takes place. Responses might include operator actions, emergency response plans, and plans to alert the community.

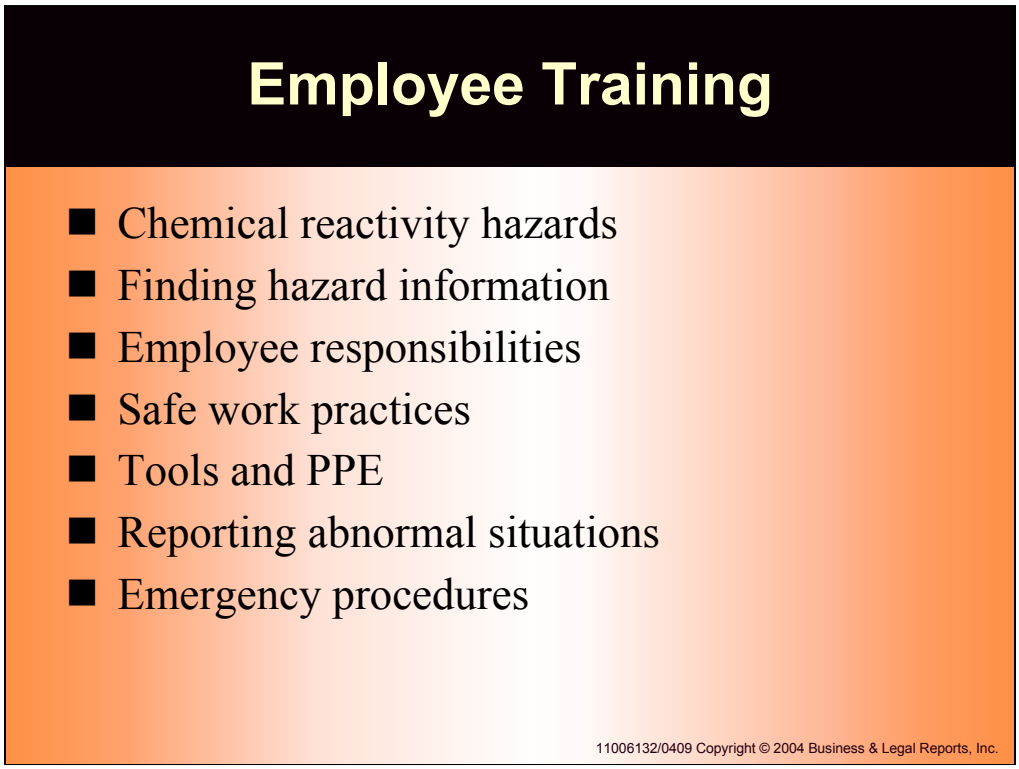
Hazard Management Program

- Active monitoring
- Audits of procedures and practices
- Management of change
- Keeping abreast of new technology
- Corrective action

Speaker's Notes:

Controlling the hazards of reactive chemicals requires constant attention.

- Active monitoring, including: walkaround inspections, informal spot checks, and specific discussions by management to ensure that chemical reactivity hazard management systems and procedures are actually being implemented and followed on a day-to-day basis. Questions should be raised if unexpected changes have been made or unusual circumstances are detected.
- Audits are periodic examinations of procedures and practices. Audits provide management with a tool for measuring facility performance. The general goal of most process safety audit programs is to verify whether a facility's procedures and practices comply with legal requirements, internal policies, company standards and guidelines, and/or accepted industry practices.
- The objective of managing change is to ensure that all changes made to a facility after startup that might introduce a new chemical reactivity hazard, increase the likelihood of an uncontrolled chemical reaction, make safeguards against uncontrolled chemical reactions less effective, or make the consequences of an uncontrolled chemical reaction more severe are identified, evaluated, and addressed so that chemical reactivity incident risks are adequately controlled.
- Companies with strong chemical reactivity hazard management programs should strive to benefit from the latest advances in process safety technology, and keep abreast of technological advances through active participation in professional and trade associations.
- Corrective action includes not only the process of addressing identified deficiencies, weaknesses, or vulnerabilities, but also the processes for corrective action planning and follow-up. The corrective action process includes preparing and distributing an audit report, developing, reviewing, and implementing action plans, and verifying completion.



Speaker's Notes:

- All affected personnel should be informed of chemical reactivity hazards at the facility.
- Employees must know where to find chemical hazard information, including any material safety data sheets (MSDS), container labels, or facility-specific compatibility charts.
- They require training on any responsibilities they are accountable for regarding reactive chemicals, such as proper storage, handling, and processing.
- Workers should also be trained on written operating procedures and safe work practices.
- They should know how to properly use any tools and how to use and wear the personal protective equipment (PPE) required in the performance of their responsibilities.
- Employees should know how to report abnormal situations, near misses, incidents, leaks and spills.
- They also need to be trained on any procedures necessary to respond to or otherwise protect themselves in an emergency.

PPE

- Gloves
- Goggles and face shield
- Chemical-resistant clothing
- Air-supplied respirator

Background for the Trainer:

Bring examples of the PPE that employees in your workplace wear when working with reactive chemicals.

Speaker's Notes:

The handling of many reactive chemicals requires special PPE. PPE should be selected by conducting an assessment that includes a review of the MSDS and the work process involved.

- Chemical-resistant gloves should be worn since moisture from the skin may cause materials to react.
- Splash goggles and a full-face shield may be required to protect the eyes and face.
- Chemically impervious clothing or fire-retardant clothing may be required for handling certain reactive chemicals.
- Certain reactive chemicals require the use of an air-supplied respirator or SCBA (self-contained breathing apparatus) when an operator is handling the material.

Detecting Hazards

- Sight
- Smell
- Air monitoring

Background for the Trainer:

- Discuss any hazard detection information that can be found in the MSDS of the reactive chemical(s) you work with, such as specific smells or visual keys.

Speaker's Notes:

- Use your eyes to look for signs of a reaction, such as ignition, smoke, fume, or bubble, when a chemical is exposed to air or water. If this happens, immediately evacuate to a safe distance and notify emergency personnel.
- Use your nose to detect unusual smells or odors. Some oxidizers have odors (chlorates-chlorine) that may be detected. However, do not rely on smell only, because the sense of smell may be quickly deadened by even small amounts of some gases.
- Air-monitoring equipment may also be used to detect leaks of reactive chemicals.

Investigating Incidents

- Report all incidents and near misses
- Investigate root causes
- Identify unrecognized hazards
- Resolve all recommendations
- Communicate lessons learned

Speaker's Notes:

A chemical reactivity incident or near miss may occur despite all efforts to effectively manage chemical reactivity hazards.

- Report all incidents, including near misses. An essential element of managing chemical reactivity hazards is to appropriately report and investigate every incident or near miss. A near miss is an unplanned sequence of events that could have caused harm or loss if conditions were different or were allowed to progress, but actually did not.
- Investigations identify root causes. By investing the time and effort to determine the root causes and take corrective action, future incidents can be avoided.
- Previously unrecognized hazards can be identified and weaknesses in the facility safeguards and management system can be corrected.
- Investigations identify recommended measures that reduce or eliminate the underlying chemical reactivity hazard, reduce the likelihood of recurrence, or reduce the severity of potential consequences. Effective follow-up actions are made to complete or resolve all recommendations.
- Document the investigation and communicate the lessons learned to all employees.

First Aid

- Skin—flush with water
- Eyes—flush with water for 15 minutes
- Inhalation—move to fresh air
- Ingestion—seek medical attention

Background for the Trainer:

- Discuss any specific first-aid requirements described on the MSDSs of the reactive chemicals you work with.

Speaker's Notes:

These are the general first-aid procedures if overexposed to a reactive chemical. It is also important to review the MSDS for any other first-aid practices specific to the chemical you are working with.

- If you get a reactive chemical on your skin, flush with large quantities of cold water. Keep affected area cold.
- If you get a reactive chemical in your eyes, go to an eyewash station. Hold your eyelids open and flush with large quantities of water for 15 minutes.
- If you feel the symptoms of inhalation of a reactive chemical, leave the area and get fresh air.
- If you accidentally ingest or swallow a reactive chemical, seek medical attention immediately.

Emergency Procedures

- Leave the area
- Notify others of the spill
- Limit access to spill area
- Only trained personnel can clean up large spills

Background for the Trainer:

- Discuss emergency response procedures that are specific to your workplace.

Speaker's Notes:

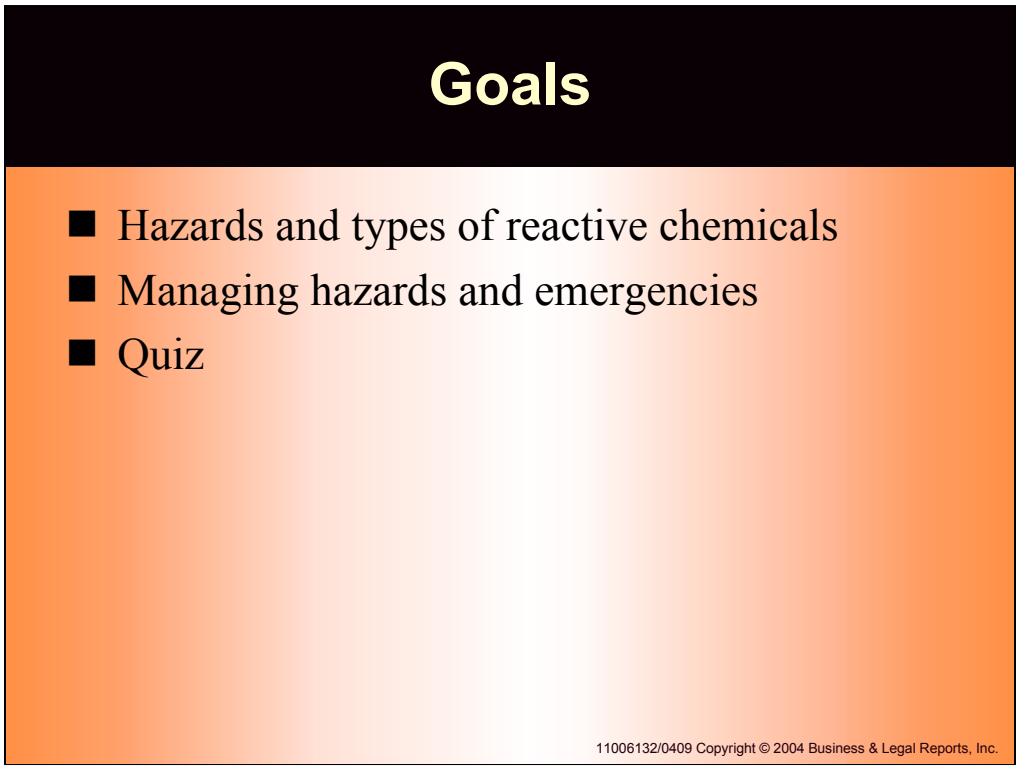
- Leave the area if a hazardous condition exists. Evacuate the area at once if you are not trained to handle the problem or if it is clearly beyond your control. Some small leaks or drips can be absorbed with a rag or absorbent wipe and then disposed of properly. Ask your supervisor how to handle small leaks or drips of reactive chemicals in your work area.
- Immediately notify others of a reactive chemical spill or emergency so they can evacuate the area. Notify your supervisor or lead person as well as your company's emergency response team members. If your company does not have an emergency response team, contact the local fire department by calling 911.
- Limit access to the area affected by the spill. Stay away from the area until the emergency response team determines that it is safe to return. Do not attempt to go near the spill, and keep others away from the spill.
- Only trained personnel can clean up large spills of reactive materials. You should not attempt to clean up a spill unless specifically trained to do so.

Emergency Equipment

- First-aid kit
- Spill response supplies
- Safety showers
- Eyewash stations
- Fire extinguishers

Speaker's Notes:

- Ensure that properly stocked first-aid kits are available nearby and that employees are trained on first-aid procedures.
- Make sure spill response supplies are available in the nearby work area. The supplies should be checked regularly, such as monthly. Also make sure the supplies are appropriate for the types of reactive chemicals in the area.
- Safety showers should be checked weekly to make sure they will work in the case of an emergency.
- Eyewash stations must also be tested weekly. Make sure the water is clean and nozzles are capped.
- Fire extinguishers must be available in the work area in case a chemical reaction gets out of control.



Speaker's Notes:

- Do you have any questions regarding the steps we can take to control and manage the hazards of working with reactive chemicals or how to respond to emergencies that involve reactive chemicals?
- Let's wrap up the class with a quiz.

Summary

- Know the hazards of reactive chemicals
- Identify the different types of reactives
- Wear PPE
- Follow safe handling and storage practices
- Learn emergency procedures

Quiz

1. Name one of the health hazards of reactive chemicals.
2. Name one way reactive chemicals can ignite a fire.
3. What do pyrophoric materials do when they contact air?
4. Why should peroxide formers not be stored longer than their shelf life?
5. What symbol will water-reactive chemicals have in the NFPA label?

Background for the Trainer:

- Remind employees that the quiz is to encourage further discussion and to help you, the trainer, be sure that everyone understands what was discussed.

Quiz (cont.)

6. Give an example of an oxidizer.
7. If you have a self-reactive chemical, what should be avoided?
8. Describe some consequences of an uncontrolled reaction.
9. How can employees help manage hazards of reactive chemicals?
10. If not trained, how should you respond to a spill of reactive materials?

Quiz Answers

1. Burn skin, form acids, poisonous, dizziness, asphyxiation, death
2. Friction, absorb moisture, chemical changes, heat generation
3. React with oxygen to burn without ignition source
4. Form unstable peroxides slowly over time, which may explode
5. "W" in the white diamond section

Quiz Answers (cont.)

6. Chlorine, hydrogen peroxide, nitric acid
7. Shock, friction, heat
8. Toxic gases released, fire, explosion
9. Walkaround inspections, spot checks, report unusual sights or smells
10. Evacuate area, notify others, and stay away