Reactive Chemicals

Why This Training Is Important

Reactive chemicals are substances that can react violently with air, water, or other chemicals to produce heat, fires, explosions, or toxic gases. Chemical reactions can be extremely hazardous if they are not properly controlled. If you work with or around reactive chemicals, you could be injured, or even killed, by an uncontrolled chemical reaction. Your facility and equipment could also be damaged in an explosion or a fire. This is why it is essential that you be able to identify and safely manage reactive chemicals and prevent accidents in your workplace. In this training session, we will discuss what reactive chemicals are, the hazards associated with them, and what you can do to protect yourself and your coworkers when working around reactive chemicals.

What Is A Reactive Chemical?

Let's begin by more clearly defining what we mean by the term reactive chemicals.

- Reactive chemicals can be in the form of a solid material, such as granules or powders, or they can be in the form of a liquid.
- These chemicals can react with air, water, or other chemicals. Reactions can sometimes be very violent.
- Reactive chemicals can also be sensitive to shock, heat, or friction, and exposure to any of these could result in a fire or an explosion.
- Reactive chemical byproducts can be corrosive, poisonous, or flammable, which makes reactive chemicals even more dangerous.

Health Hazards

- Reactive chemicals can also be hazardous to your health. Many reactive chemicals are corrosive and can destroy tissue. For example, alkali metals, like sodium, lithium, and potassium, can react with body moisture to cause severe burns to the skin, eyes, nose, and throat. One reactive chemical,

white phosphorus, reacts with air to form phosphoric acid, which is severely corrosive.

- Reactive chemicals can also be poisonous-azides, for example, which are used in the manufacture of airbags.
- Metal peroxides and chlorates can be irritating to the eyes and respiratory tract. Hydrazines, which are oxidizers, can irritate the eyes, skin, and respiratory tract. These chemicals are also suspected of causing cancer and harming the reproductive organs.
- Some reactive chemicals, such as nitrates, can cause dizziness, vomiting, convulsions, and death.
- And in confined spaces, free chlorine can cause asphyxiation and death.
- The safety data sheet, or SDS, for each reactive chemical explains the specific health hazards you could face.

Fire Hazard

Reactive chemicals can be a serious fire hazard because the substances they react with can cause them to generate heat and ultimately set fire. There are a number of ways this can happen.

- Some chemicals, such as silanes, fine metal powders, and white phosphorus, can heat up when exposed to air and spontaneously ignite.
- Other chemicals, such as sodium, aluminum chloride, and non-metal oxides, are water reactive and can ignite from the heat generated when they come in contact with water or moisture in the air.
- Certain chemicals are very sensitive to heat, light, shock, pressure, and friction, which can occur when chemicals are mixed or transferred. When exposed to these environmental factors, the reactive chemicals can explode.
- Reactive chemicals can also retain heat from manufacturing or processing, which can cause more reactions to occur, generating more heat, and potentially starting a chain reaction that could become a fire.
- When a chemical reaction results in fire, that fire can ignite other materials in the work area and spread rapidly.

Factors That Create Reactivity Hazards

Now that we've covered the general hazards of reactive chemicals, it's time to talk about how you might encounter them in your workplace. Activities that could create reactivity hazards in the workplace include:

- Intentionally mixing chemicals to form different substances;
- Manufacturing processes that involve mixing, heating, or other physical processing of chemicals;
- Storage and handling of hazardous substances in the workplace;
- Processes that involve burning fuels and combustion; *and*
- Processes that generate heat.

Factors That Create Reactivity Hazards (cont.)

Some of the chemicals in your workplace may not even require any intentional mixing or processing to react violently with other substances. Identify any chemicals you work around that are classified as:

- Spontaneously combustible;
- Peroxide-forming;
- Water reactive;
- Oxidizers;
- Self-reactive; or
- Incompatible, which means they can react adversely with one another if they come in contact.

Detecting Hazards

Now let's talk about detecting hazards.

- The best sources of hazard detection information are the safety data sheet, or SDS, and chemical labels. But there are other methods you can use to help detect reactive chemical hazards, as well.
- For example, you can use your eyes to look for signs of a reaction, such

as ignition, smoke, fumes, or bubbles, when the chemical is exposed to air or water. If you see any of these signs of reactivity, immediately evacuate to a safe distance and notify emergency personnel. We'll talk more about emergency procedures in a few minutes.

- You can also use your nose to detect unusual smells or odors. Some oxidizers, for example, have odors that can be detected. But you shouldn't rely exclusively on your sense of smell because it may be deadened even by small amounts of some gases, and not all chemicals have an odor.
- Another way to detect reactive chemical hazards is by using air-monitoring equipment to detect leaks and other problems that could release chemical gases into the air.

Do you know where SDSs are located in your facility? Make sure you have access to the SDSs for any hazardous chemicals stored or used in your work area.

Intentional Reactions

Let's take a closer look at intentional reactions, or chemical reactions that are created on purpose.

- Intentional reactions may involve exothermic or endothermic reactions. Exothermic reactions release heat. Endothermic reactions absorb heat from the surrounding area or a heating source.
- Generation of heat is an important issue to consider. For example, will a mixture get hot when ingredients are combined? Too much heat can be hazardous.
- Adding heat can also be hazardous. Substances or mixtures that were not apparently reactive at one temperature can become dangerously reactive at a higher temperature.
- Many different hazard scenarios are possible with intentional reactions. All of them relate to losing control or containment of the intended reaction or starting another reaction, side reactions, or series of reactions that are not intended or expected.

Think about any processes in your workplace that involve intentional chemical reactions. Are there any unintended reactions that could occur as a result? Familiarize yourself with the chemicals in your work area and their hazards. Be sure to check the SDSs for those chemicals for specific hazard, handling, storage, and other information.

Container Labels

Any containers of hazardous chemicals that enter your workplace must be labeled. It's critical that information about the hazards associated with those chemicals be properly conveyed to you and that the information be easy to understand. That's why there are standardized labeling systems for hazardous chemicals. Let's go over the different chemical labeling systems you may encounter in your workplace. There are three main types of chemical labels you may see.

Select each tab to learn more.

- The Occupational Safety and Health Administration, or OSHA, Hazard Communication Standard, also known as HazCom, requires all chemical containers that enter your workplace to have labels that comply with the Globally Harmonized System of Classification, or GHS. These labels are marked with any number of pictograms, shown as symbols inside a white diamond with a red border, as well as hazard statements and other text to convey the hazards associated with a particular chemical. The exploding bomb pictogram, for example, is meant to convey a reactivity hazard. SDSs are also required to follow the GHS, so the pictograms you see in a chemical's SDS will match what is on the container label.
- You may see tanks or containers with a National Fire Protection Association, or NFPA, label. These diamond-shaped labels have four quadrants in red, blue, yellow, and white, each of which represents different types of hazards. Red represents flammability, blue is for health hazards, yellow is instability, and white is for other hazard types, such as water reactivity. Each quadrant will contain a number to indicate the level of hazard.
- The Department of Transportation, or DOT, has its own requirements for hazardous materials labeling. Chemical containers that are shipped to your workplace will have DOT labels that include a number, a symbol, and sometimes text to indicate the chemical's hazard class.

Now, let's discuss some of the specific types of reactive chemicals you may find in your workplace and what the container labels might look like.

Spontaneously Combustible Substances

- Spontaneously combustible substances react with the oxygen in the air, igniting and burning without any ignition source. For some spontaneously combustible substances, spontaneous heating is slow and could take minutes or hours. Pyrophoric substances, on the other hand, are

spontaneously combustible materials that ignite instantly when exposed to air. They can also be water reactive.

- Spontaneously combustible materials must be identified as DOT Hazard Class 4.2 for shipping purposes and labeled SPONTANEOUSLY COMBUSTIBLE.
- On NFPA diamond labels for spontaneously combustible substances, the red quadrant at the top of the diamond would have a rating of 4, indicating the highest severity of flammability hazard. NFPA labels also display numbers ranging from 0 for no hazard to 4 for extremely hazardous. Note that the GHS works in the opposite way-there are hazard numbers ranging from 1 to 4, with 1 being the most hazardous and 4 being the least hazardous. Under GHS, there is no 0. Remember this to avoid confusion.
- Because exposure to air is very hazardous, you must always ensure that these substances are properly contained to prevent contact with air. Oxidizers (OX) promote combustion in other materials, causing a fire hazard.
- Examples of spontaneously combustible substances include aluminum alkyl, finely divided metals, and iron sulfide.

Do you work with any spontaneously combustible materials? Consult the SDS for these materials to identify their specific hazards and how to safely handle them.

Peroxide Formers

- Peroxide formers are substances that will react with oxygen in air to form unstable peroxides that can explode.
- To prevent peroxide formation, these substances often have an inhibitor or stabilizer added.
- It's important to note that peroxide formers may not be labeled as such. They are often identified by another hazardous characteristic, such as flammability.
- Peroxide formers should not be stored beyond their safe shelf life. Otherwise, the formation and concentration of unstable peroxides over time, followed by an event such as opening or agitating the container, could cause an explosion. Other possible accident scenarios include leaks or spills, opening containers and allowing air to get in, or insufficient inhibitors or stabilizers.
- Examples of peroxide-forming chemicals include 1,3-butadiene; 1,1-dichloroethylene; isopropyl ether; other ethers; and alkali metals.

Are there any peroxide formers used or stored in your workplace? How are they labeled? Check the SDSs for these chemicals to determine the specific hazards they pose and how to safely handle them.

Water Reactives

- Water reactives are chemicals that react vigorously with water. The heat of this reaction can cause burns, ignite combustible materials, or initiate other chemical reactions. Flammable, corrosive, and toxic gases are often formed during the reaction. Even slow reactions can generate enough heat and gases to rupture a closed container.
- Water reactives may be identified as DOT Hazard Class 4.3 for shipping and labeled DANGEROUS WHEN WET. However, some water reactives may be classified and labeled as corrosives or poisons.
- In the NFPA label, the white quadrant at the bottom contains the "W" symbol. Just remember that even if the "W" isn't present, the material might still be water reactive, just at a slower rate. Check the SDS.
- When handling or storing these reactives, avoid inadvertent contact with water. Even humidity in the air can cause a reaction if it comes in contact with a water reactive chemical.
- Examples of water reactive chemicals include sodium, titanium, tetrachloride, boron trifluoride, and acetic anhydride.

Do you work with any water-reactive chemicals on the job? How are they labeled? Be sure to check the SDSs for chemical-specific information.

Oxidizers

- Oxidizers are materials that readily yield oxygen or that easily react to promote or initiate fire. Most oxidizers can react with ordinary flammable and combustible liquids or solids. They can also react with many other substances.
- They may be identified as DOT Hazard Class 5.1, but they can also be classified as toxic or corrosive. Chlorine, for example, is labeled as DOT Hazard Class and labeled POISON GAS. Liquid oxygen is Class and labeled NONFLAMMABLE GAS and OXIDIZER.
- In the NFPA label, the white quadrant contains the "OX" symbol for materials that are oxidizers.
- When handling or storing oxidizers, avoid contact with any combustible or

flammable materials.

- Examples of oxidizers include chlorine, hydrogen peroxide, nitric acid, nitrates, ozone, and hypochlorites.
- Under OSHA, GHS flame over circle pictogram corresponds to oxidizers.

Do you work with any oxidizers? How are they labeled? Look at the SDSs for these chemicals to find specific information about hazards and precautions you need to take.

Self-Reactive Materials

Materials that self-react often do so with explosive force and speed. There are three forms of self-reaction:

- Polymerizing occurs when individual molecules combine to form larger molecules. Decomposing occurs when large molecules break apart into smaller, more stable molecules. And rearranging occurs when the atoms of molecules rearrange themselves into a different molecular structure.
- Substances that are DOT Hazard Class 1, explosives, or 5.2, organic peroxides, are likely to be self-reactive. However, some self-reactives are classified as flammable gases or liquids, as well.
- In the NFPA label, the yellow quadrant on the right should have a rating between 1, the lowest hazard, and 4, the highest. Remember, the GHS system works in the opposite way-GHS has hazard numbers ranging from 1 to 4, with 1 being the most hazardous and 4 being the least hazardous. Under GHS, there is no 0.
- For some highly self-reactive chemicals, such as shock-sensitive explosives and organic peroxides, mechanical shock, friction, sparks, or heat could be enough to start a decomposition reaction.

Are there any self-reactive chemicals in your workplace? Remember to follow any procedures your employer has implemented for handling these chemicals.

Select **"*Types of Reactive Chemicals"*** from ***Resources*** for a summary of the characteristics and labels of the chemicals we've just discussed.

Incompatible Materials

There is also the risk of chemical reactions resulting from incompatible materials coming in contact with one another.

- The result of such contact could be an uncontrolled reaction that might include the release of toxic, corrosive, or flammable gases; a fire or an

explosion; rupture of containers; the formation of shock-sensitive or explosive chemicals; or heat generation that could cause other reactions.
- Potential scenarios in which incompatible chemicals could come in contact include situations such as a leaking liquid contacting an incompatible chemical stored nearby; materials pumped or transferred into the wrong process vessel; materials mislabeled or unlabeled; or the wrong material selected to add to a mixture or formulation.
- You should always consult a compatibility chart to make sure incompatible chemicals are stored and processed separately.
- Examples of incompatible materials include nitric acid and most chemicals and ammonia and methacrylic acid.

Do you take precautions to keep incompatible chemicals separate? Select "***Chemical Segregation and Storage"*** from ***Resources*** to see what types of chemicals are incompatible.

Hazard Management Program

Now that we've discussed the hazards of reactive chemicals and how to identify them, let's move on to talk about controlling reactive chemical hazards. Your employer's hazard management program strives to protect your safety and prevent incidents involving reactive chemicals by ensuring the following:

- Active monitoring of the facility through walkaround inspections, informal spot-checks, and specific discussions to ensure that chemical reactivity hazard management systems and procedures are actually being implemented and followed on a day-to-day basis;
- Periodic audits to examine procedures and practices to ensure the organization complies with regulatory requirements, established standards and policies, and accepted industry practices;
- Effective management of change to ensure that all changes made in the facility that could introduce new reactivity hazards are identified, evaluated, and addressed to control risks;
- The use of new technology so that the organization can benefit from the latest advances in process safety technology; *and*
- Taking immediate corrective action whenever deficiencies, weaknesses, or vulnerabilities in the program are identified.

Are you familiar with your organization's hazard management program? Ask

your supervisor if you would like to see a copy of the program.

PPE

One way to manage chemical reactivity health hazards, of course, is to wear proper personal protective equipment, or PPE, to prevent exposures. The handling of many reactives requires special PPE. The SDS for a reactive chemical will tell you what type of PPE is necessary.

- Wear chemical-resistant gloves, as many reactive chemicals are poisonous, corrosive, or irritating to skin. Furthermore, when handling water-reactive chemicals, moisture from your skin could cause a reaction, so you want to avoid skin contact for that reason.
- Wear splash goggles and a full-face shield to protect eyes from toxic, corrosive, or irritating chemicals.
- Chemical-resistant or fire-retardant clothing may also be required when handling certain reactive chemicals.
- Certain reactive chemicals might also require the use of an air-supplied respirator.

Investigating Incidents

Despite all your employer's best efforts to detect and manage hazards, occasionally a chemical reactivity incident or near miss could occur. If this happens, report it right away.

- To manage chemical reactivity hazards effectively, your employer will investigate every incident or near miss to determine what went wrong and how to fix it. Investigations identify root causes of hazardous conditions.
- They also point to previously unrecognized hazards and weaknesses in our safeguards and management system that can be corrected.
- Additionally, investigations identify the best measures to reduce or eliminate the underlying chemical reactivity hazard. Even when the hazard can't be totally eliminated, you can still reduce the severity of potential consequences in the future if you understand the things that go wrong today.
- Your employer will document all the findings of its investigations and will share what has been learned with you so that together, you and your coworkers can all take effective action to prevent future incidents.

First Aid

In the event of an incident, you might also need to give first aid to coworkers or yourself if you are trained in first aid. Again, the best place to find specific information about proper first-aid procedures is the SDS for the reactive chemical you're working with.

- Generally speaking, however, there are certain protocols you can keep in mind. If you get a non-water-reactive chemical on your skin, flush the area immediately with large quantities of cold water, and keep the affected area cold until you can get medical assistance.
- If you get non-water-reactive chemicals in your eyes, go immediately to an eyewash station. Hold your eyelids open, and flush with large quantities of water for 15 minutes. Then seek medical attention.
- If you think you might have inhaled chemical fumes or vapors, leave the area immediately and get to fresh air. Get medical attention.
- If you accidentally swallow a reactive chemical, seek medical attention immediately.

Do you know proper first-aid procedures for the reactive chemicals you work with? If not, check the SDSs so that you'll be prepared.

Emergency Procedures

In an emergency involving reactive chemicals, the best thing to do is leave the area immediately if you're not trained to handle the problem or if it's clearly beyond your control.

- Immediately notify others of a reactive chemical spill or other emergency situation so that they, too, can evacuate the area.
- And be sure to notify your supervisor and the company's emergency response team as well.
- Once safely out of the area, you can help by keeping others out.
- Stay away until the emergency response team tells you it's safe to return.
- Remember, only specially trained and equipped personnel are authorized to clean up large spills of reactive chemicals. Some small leaks or drips can be absorbed with a rag or absorbent wipe, which can then be disposed of properly. But you should not attempt to clean up a larger spill unless you are authorized to do so. Become familiar with your employer's specific procedures for spill cleanup.

Emergency Equipment

The last item on our agenda today is emergency equipment. Make sure you know where to find-and how to use-emergency equipment such as:

- First-aid kits;
- Spill response supplies, if you're authorized to use them;
- Safety showers;
- Eyewash stations; *and*
- Fire extinguishers, if you're authorized to use them.

Do you know the location of emergency equipment in your work area? It's essential that you do so you can find it quickly in an emergency.

Key Points to Remember

Here are the main points to remember from this session on reactive chemicals:

- Reactive chemicals can be extremely hazardous and have to be handled with great care. They can ignite, explode, release toxic gases, or present other serious hazards.
- There are different types of reactive chemicals that pose their own risks. Be familiar with the reactive chemicals used and stored in your workplace.
- A chemical's label and its SDS are the best sources of information pertaining to hazards, exposure controls, and first-aid measures.
- And finally, never try to handle or attempt to clean up a spill of a reactive chemical if you are not trained and authorized to do so. In the event of a reactive chemical emergency, evacuate the area and notify your supervisor.