Hazardous materials:

flammable solids, oxidising agents and organic peroxides

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Fire fighting of organic peroxides must be done from a safe area

This is the fourth article in our series on responding to specific classes of hazardous materials (hazmat). I have decided to include two classes in this month's article namely (1) flammable solids, which also includes substances liable to spontaneously combust and substances which, in contact with water, emit flammable gases and (2) oxidising agents and organic peroxides.

Flammable solids

Flammable solids are amongst the most common hazardous materials yet a relatively small percentage is included in the United Nations (UN) hazardous substances classification. The first classification includes flammable solids, self-reactive substances and desensitised explosives such as the types that are wetted down with sufficient water, alcohol or plasticiser to suppress their explosive properties eg trinitrotoluene, nitroglycerine mixture.

Readily combustible solids include solids that are capable of causing a fire through friction (safety matches) and celluloid. Also included are self-reactive materials that are thermally unstable and are prone to undergoing a strong exothermic decomposition even without the presence of oxygen. Materials that meet the UN transport regulations definition of explosive, oxidiser or organic peroxide are excluded from this classification.

The second classification of flammable solids includes those solids that are liable to spontaneous combustion. These include substances that are liable to spontaneous heating under normal transport conditions or will have an exothermic reaction when it comes in contact with air.

Spontaneously combustible solids include (1) pyrophoric materials, which are materials that are capable of igniting, without being exposed to any external ignition source, within five minutes of being exposed to air eg UN 1854 barium alloys and (2) those self-heating materials that exhibit spontaneous ignition or can self-heat to temperatures of 200 degrees Celsius during a 24-hour period in the presence of air but without any external energy supply eg UN 2002 celluloid.

The third classification includes substances that emit flammable gases when they come into contact with water. Examples of this classification includes aluminium phosphide, which releases phosphine gas and calcium carbide, which emits acetylene when in contact with water and sodium.

Health hazards

The primary health risk of exposure to flammable solids is the inhalation of dust powder particles of certain types of these materials. Particles such as sodium metals react with the moisture in the lungs to form a caustic solution that will damage sensitive lung tissue. There is a further risk of chemical burns when certain metallic dusts come into contact with body moisture. It is therefore important for responders to stay clear of any smoke columns that may contain by-products of the burning metal.

Managing the incident

The most important operational consideration would be to make sure that you know what the reaction of the substance will be before deciding to apply any extinguishing agent. Make sure that the relevant safety data information for the product is at hand and that the correct extinguishing or controlling agent is available in sufficient quantities before starting the operation.

A flammable solid spill can be relatively easily managed by covering the spilled product with tarps or heavy plastic sheeting and to ensure that it does not come into contact with water. Regardless of the condition of the product ie fire or dust, always ensure that responders have adequate respiratory protection available.

Most actions involving flammable solids will be based on letting the incident stabilise through fire or just exercising control over the spilled product and could be handled relatively easily.

A dust propagation will increase the surface area of a combustible solid and enhance the ease of ignition. A flammable gas-air mixture can form within certain limits and the resulting explosion will be similar to a gas explosion. Although dust explosions are rare, they can propagate an enormous energy release.

Preventing a possible dust explosion in a flammable solid environment will require a strict control of the environment where the spillage occurred. Firstly, all ignition sources need to be eliminated. Try to avoid or limit disturbing the dust and attempt to control the dust concentrations. This can be done by using hoselines to 'water down' the particles of a product that is non-water reactive.

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Oxidising agents and organic peroxides

The best known oxidising agent we know is air, which is necessary for all combustion to take place. There are, however, a number of other substances that are able to propagate large volumes of oxygen thereby accelerating a burning process and, if uncontrolled, have disastrous results.

Oxidising agents are generally defined as "substances that supply oxygen to another substance" or "substances that supply any supporter of combustion to another substance". The first definition would be more relevant to our purposes, however, large quantities of other supporters of combustion such as chlorine, fluorine and bromine, may also be encountered and should therefore form part of the preparedness planning for fire department hazmat teams.

In order for a product to be classified as an oxidising agent, it must conform to the following criteria:

- It must itself contain oxygen and
- It must be capable of supplying oxygen to another substance

Sodium chlorate is a good example of a powerful oxidising agent while although calcium carbonate and calcium sulphate contain at least as much oxygen as sodium chlorate, they are not capable of transferring their oxygen to another substance.

Oxidising agents can further be classified into organic and inorganic oxidising agents. The most common of these is the inorganic. Although they are classified as ▶

Know the properties of the products you are dealing

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non-flammable, certain types (sodium chlorate and ammonium nitrate) will decompose rapidly and present a major risk when stored or transported in an enclosed area in large quantities.

Products classified as organic oxidising agents are organic peroxides, which are commonly used as catalysts in the manufacture of plastics ie dibenzol peroxide, methyl ethyl ketone peroxide. Where inorganic oxidising agents are non-flammable and only provide the one side of the fire triangle ie oxygen, organic peroxides are also capable of burning and therefore provide two sides of the triangle ie oxygen and fuel.

Hazards

The main fire hazard related to inorganic oxidising agents is when the agent comes into contact with flammable materials. The oxidising agent will slowly provide oxygen to the fuel at first. This exothermic reaction will cause the temperature to rise gradually until it reaches its ignition temperature and then starts to burn. As when highly concentrated hydrogen peroxide comes into contact with wood, the spontaneous combustion occurs almost immediately. Other spontaneous combustion reactions can take slightly longer eg glycerol coming into contact with potassium permanganate and finally the well-known example of rags soaked in linseed oil being exposed to atmospheric oxygen can take quite a while to combust.

The risk is not only limited to spontaneous combustion but can manifest when a fuel starts to burn in the presence of an oxidising agent. The fire is then not reliant on ambient atmospheric oxygen to burn but is fed by the oxidising agent, which ensures the presence of oxygen in a highly concentrated form eg if a cellulose material such as a wooden floor or shelving becomes impregnated with an oxidising agent such as sodium nitrate.

The heat energy generated through the self-decomposition of an organic peroxide such as methyl ethyl ketone peroxide exceeds 50 degrees Celsius. Others are significantly lower and must be stored in refrigerated conditions. These peroxides, if heated, can become sensitive to heat, shock and friction. Due to the instability of these products, they are normally stored in a diluted state by adding a chemically inert material; generally at 50 percent relations. This is also how they will in all possibility be encountered. Even in this state, certain products can still ignite and burn fiercely.

In addition to its fire risk, several concentrated oxidising agents also hold a corrosive and toxic risk. The skin and eyes are specific areas which could be affected.

Responding to the incident

Incidents involving organic peroxides and oxidising agents will require a full hazmat team response and access to a comprehensive database of the products you might encounter.

The most important consideration will be to appreciate the unpredictability of the product involved. As with most hazmat incidents, approach the incident in a defensive mode. Be alert for possible violent container failure eg peracetic acid could detonate if its concentration exceeds 56 percent; this could happen if the container is stored incorrectly and the product is allowed to evaporate.

If it is possible, efforts must be made to separate the affected product from the fuels. Water streams can be used to cool down containers and consider ventilation if the containers are in a confined area. If the product is involved in a fire, the choice of extinguishing agent must be carefully considered. The challenges that certain water reactive products may provide must be an important consideration. Also take into account the potential environmental impact of any fire fighting operations.

Fire fighting of organic peroxides must be done from a safe area. The surrounding area should be evacuated of all non-essential personnel. Placement of ground monitors should also be considered.

There is also the danger of mixing combustible products with water containing dissolved oxidising agents, which might spontaneously combust later on after the water evaporates.

In closing

Incidents involving flammable solids, oxidising agents and organic peroxides will not happen often. It is generally fairly easy to identify the sites where these incidents might take place.

Transport route response planning will also give you an indication of what hazardous materials might be travelling through your area of jurisdiction. As mentioned a few times in this article, knowing the properties of the products you are dealing with and understanding their reactivity with water, air and other elements is what will give you the critical advantage when responding to this type of hazmat incident.