

# Spontaneous Combustible Substances: a Database Update

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## **Executive Summary**

A database of spontaneous combustible substances is under development. Over 100 substances commonly found in the chemical processing industry have been included to date. Spontaneous combustion includes the several related phenomena such as spontaneous heating/ignition, spontaneous oxidation, pyrophoric gases, pyrophoric liquids, pyrophoric nonmetals, pyrophoric metals, and moisture reactive metals.

Among the information included in the database are:

- General information on spontaneous combustion
- Range of conditions for spontaneous combustion
- Avoidance techniques
- Mitigation procedures
- References to detail studies
- Case histories of incidents involving various spontaneously combustible materials

This database will be made available on the Mary Kay O'Connor Process Safety Center web site, with encouragement for others to add their experiences in the spirit of sharing safety information.

## **Introduction**

With the exponential growth of information available on the Internet, the spread of incorrect, partially erroneous, misleading, and incomplete information has also increased. To combat this growth of mis-information, the Mary Kay O'Connor Process Safety Center is attempting to create islands of information for the student, safety professional in industry, and the process safety researcher.

As an adjunct to the Mary Kay O'Connor Process Safety Center research program on certain pyrophoric materials, a database on spontaneously combustible substances is being developed. The purpose of this project is to gather information into one rational database the major resources on the subject of spontaneously combustible materials.

## **Scope of Database**

The focus of this database is materials that can be designated as spontaneously combustible. Spontaneously combustible materials differ from readily flammable materials in that flammables will ignite within a specified time period (a few minutes) and burn rapidly when exposed to specific ignition sources such as hot surfaces, hot gases, electric sparks, adiabatic compression.

Spontaneously combustible materials can inflame even in the absence of what are normally regarded as ignition sources. Generally spontaneously combustible materials are considered to be a sub-class of flammable solids and liquids. This is especially true when the heat-generating reaction in certain spontaneously combustible materials is one involving bacterial action.

Further sub-classification of spontaneously combustible materials include pyrophoric materials, which will ignite spontaneously on exposure to air.

Not covered in this database are water reactive materials and hypergolic reactions with oxidants other than air.

## **Information Contained in the Database**

A section on definitions is key to understanding the materials within the technology of Spontaneously Combustible Materials

A list of references on the subject of Spontaneously Combustible Materials is contained within the database. Reference to Handbooks, Conference Proceedings, and special subject texts are listed. Abstracts and keywords of technical articles are included, with an on going program to gather copies of pertinent references within the Mary Kay O'Connor Process Safety Center library.

## **Classification of Spontaneously Combustible Materials**

In order to define the common conditions of spontaneously combustible materials, the following classes have been of

- Spontaneous Heating/Ignition of Liquid Hydrocarbons
- Spontaneous Heating/Ignition of Organic Materials
- Spontaneous Heating/Ignition of Coal
- Pyrophoric Gases
- Pyrophoric Liquids
- Pyrophoric Metals
- Pyrophoric Nonmetallic Solids

## **Information Contained in Each Classification Of Spontaneously Combustible Materials**

Within each classification, the general conditions that promote spontaneous combustion are described. In addition to specific data on each material, information on mitigation and control, extinguishing fires, topics on storage and material transfer, and special process hazards. A unique feature of the database is the accumulation of case histories documenting instances of spontaneous combustion.

### **Examples of Information Available within the Database**

#### **◆ Spontaneous Heating/Ignition of Liquid Hydrocarbons**

Some hydrocarbons are capable of spontaneous heating and ignition under proper conditions. Spontaneous heating of hydrocarbons usually involves a combustible liquid hydrocarbon in contact with combustible materials. An example of this would be combustible rags impregnated with oils or solvents. Some solid hydrocarbons, such as coal, can react directly with atmospheric oxygen. Whether spontaneous heating leads to ignition depends on several items:

- The rate at which heat is generated and removed from the material being oxidized
- The ignition temperature of the fibrous combustible material, hydrocarbon, or any gases liberated by oxidation
- The specific area of the hydrocarbon exposed to an oxidizer
- The amount of moisture present in the atmosphere and the fibrous material.

For spontaneous ignition to occur, the rate of heat being generated through oxidation must exceed the rate of heat removal by conduction, convection, and radiation (thermal). As the temperature of the material begins to rise, the rate of heat generation will often increase. The result is a "runaway" reaction that ultimately causes ignition. If the rate of heat removal exceeds the rate of generation, the material will cool and will not ignite. The rate of heat removal may be increased through physical contact with a thermally conductive surface, by rotating piles of combustibles to cool hot spots, and by circulating inert gases through the piles to cool hot spots and displace oxygen.

The ignition temperature of the materials is obviously of concern and varies widely among materials. Much more stringent controls must be placed on materials that have lower ignition temperatures and those which liberate explosive gases. Although most materials with high ignition temperatures are of lesser concern, some are more explosive than those with lower ignition temperatures. Material Safety Data Sheets (MSDSs) are a source for information such as ignition temperature, vapor pressure, toxicity, and reactivity.

The specific area of a combustible substance is a measure of the surface area of the material exposed to an oxidizing atmosphere per gram of material and is expressed in units of  $\text{cm}^2/\text{g}$ . Materials which have a high specific area are more prone to heat and ignite spontaneously. For example, combustible liquids on fibrous material pose a

spontaneous fire hazard. This is because the fibers of the material allow the liquid to spread out over a larger surface area, allowing more contact with oxygen. Therefore, porous combustible materials are more likely to ignite than tightly packed solid materials.

It is important to keep potentially spontaneously heating compounds as dry as possible. High ambient temperatures compound moisture problems. As the ambient temperature rises, the rate of spontaneous heat generation will also rise. High ambient temperatures also reduce the rate of heat removal, bringing the hydrocarbon closer to its ignition temperature.

With these facts in mind, the following housekeeping steps will help minimize the threat of spontaneous heating and ignition of hydrocarbon or other organic compounds:

- Keep potentially spontaneously heating materials in a cool environment. The heat transfer resulting from a cooler atmosphere or circulating air will lower the temperature of the materials.
- Know all of the chemicals and their potential self-heating hazards and their ignition temperatures. Consult the chemical manufacturer's MSDSs.
- Reduce the amount of fibrous materials used with combustible liquid hydrocarbons. Fibers allow liquid hydrocarbons to increase in specific areas, thereby increasing the likelihood of self-heating.
- Keep combustible materials away from existing spontaneous heating hazards. Many fires have been started as the result of a self-heating material coming in contact with a combustible with a low ignition temperature. This practice is also important from a fire loss minimization aspect.
- Keep appropriate fire extinguishing equipment near potential areas of ignition. Type A extinguishing agents are appropriate for most non-hazardous, combustible materials (rags, wood, textiles), whereas a Type B agent is necessary in the presence of quantities of combustible liquids. Extinguishing agents for metal fires are discussed in a later section.

#### ◆ Spontaneous Heating/Ignition of Organic Materials

Spontaneous combustion may occur in piles of moist organic material where heat is generated in the early stages by the respiration of bacteria, molds, and microorganisms. A high moisture content is required for vigorous activity. Furthermore heating is generally controlled by maintaining the moisture content below a predetermined level. This type of heating can only raise the material to the temperature range of 50 to 75°C (122 to 167 °F), where the living organisms die. Beyond this point, oxidation reactions must take over if ignition is to occur. The existence of biological heating requires careful control of moisture, air supply, and nearby combustible or flammable materials. If a "hot spot" in a pile of organic material comes in contact with a highly flammable liquid or gas, a fire or explosion may occur. Heat generated by biological action may also act as a catalyst for other reactions that occur only at elevated temperatures.

The likelihood of biological heating may be reduced by the following measures:

- Provide adequate ventilation of the organic material to remove moisture, heat, and dust particles.
- Limit the storage time of the organic material using a "first in, first out" rule of thumb.

Circulate large quantities of organic materials to disperse areas of localized heating.

### ◆PYROPHORIC GASES

There are several kinds of pyrophoric gases that should be included in any discussion of pyrophoricity. Many of these are used in manufacturing microelectronics. All of the gases presented here have three (3) things in common:

1. they can ignite immediately upon exposure to air,
2. they are all nonmetallic hydrides, and
3. many other compounds which contain these gases in their molecular structure are also pyrophoric.

#### ◆◆Arsine

Arsine ( $\text{AsH}_3$ ), also known as arsenic hydride, is a colorless, highly toxic gas with a distinctive garlic-like odor. It is heavier than air and is a blood and nerve poison. Arsine will generally not ignite in air unless at elevated temperatures, but it can be detonated by a suitably powerful initiation (heat source, shock wave, electrostatic discharge). Arsine may also exist in other compounds. The ignition temperature of many of these arsine-containing compounds is lower than that of arsine, causing them to ignite in air even at low temperatures (below  $0^\circ\text{C}$ ,  $32^\circ\text{F}$ ). All arsine compounds should be considered pyrophoric until they are properly characterized.

#### ◆◆Silane

Silane ( $\text{SiH}_4$ ), also known as silicon tetrahydride, is a colorless gas with a putrid odor. It and its compounds (e.g., di-silane) can ignite in air and also react violently with chlorine. The presence of other hydrides as impurities causes ignition to occur in air. However, 99.95% pure silane generally ignites in air only when emerging at very high gas velocities, whereas mixtures of up to 10% silane may not ignite. Hydrogen liberated from its reaction with air (atmospheric oxygen) often ignites explosively. Silanes react violently with chlorine and bromine. All silanes should be considered pyrophoric until they are properly characterized. Halon should not be used as an extinguishing agent on silane fires.

#### ◆◆Extinguishing Pyrophoric Gas Fires

Pyrophoric gases may spontaneously explode at high gas release rates. For fires involving flammable gases, the best procedure is to stop the flow of the gas before attempting extinguishment of the fire. To extinguish the fire while allowing continued flow of the gas is extremely dangerous; an explosive cloud of gas/air mixture may be created that, if ignited, may cause far more damage than the original fire. Extinguishing the flame using

carbon dioxide or dry chemical may be desirable to allow immediate access to valves to shut off the flow of gas, but this must be done carefully. In many cases, it will be preferable to allow continued burning, while protecting exposures with water spray, until the flow of gas can be stopped. Since many pyrophoric gases react violently with halogens, Halons should not be used as extinguishing agents.

#### ◆◆Pyrophoric Gas Storage and Dispensing Areas

Pyrophoric gas cylinders in storage or dispensing areas should be provided with the following safeguards:

- a. Pyrophoric storage and dispensing areas should be located exterior to the building, or in an approved shelter as specified in NFPA 318, *Standard for the Protection of Clean Rooms*.
- b. When used in a manifold or dispensing rack system, pyrophoric gas cylinders should be separated from each other by a steel plate 6 mm (1/4 in.) thick, extending 76 mm (3 in.) beyond the footprint of the cylinder. The steel plate should extend from the top of the purge panel to 305 mm (12 in.) below the cylinder valve.
- c. Mechanical or natural ventilation at a minimum of .00047 m<sup>3</sup>/sec per .09 m<sup>2</sup> (1.0 cu ft/minute per sq ft) of storage and dispensing area should be provided.
- d. Cylinders located in cabinets should be provided with mechanical ventilation at a minimum of 0.762 m/s [200 ft per min (fpm)] across the cylinder neck and the purge panel. The ventilation system should be provided with an automatic emergency back-up source of power to operate at full capacity.
- e. Remote manual shutdown of process gas flow should be provided outside each gas cabinet or near each gas panel. The dispensing area should have an emergency shutdown for all gases that can be operated at a minimum distance of 4.6 m (15 ft) from the dispensing area.
- f. Gas cabinets and cylinders not located in shelters or bunkers containing silane or silane mixes should be provided with a security chain link fence to prevent unauthorized entry and to reduce the impact of an explosion at the perimeter. The area should also be separated from structures in accordance with Table 1. Gas cabinets and cylinders located in shelters containing silane or silane mixes should comply with the Table 1 without regard to shelter walls.
- g. When gas cabinets are used, only single cylinder cabinets should be used for pyrophoric chemicals and pyrophoric mixes.
- h. Gas cabinets should be provided with sprinklers to protect cylinders from exposure to external fires.

## ◆◆PYROPHORIC LIQUIDS

### ◆◆Hydrazine Properties

Hydrazine is a colorless oily liquid resembling water in appearance and possesses a weak, ammonia-like odor. Its chemical formula is  $N_2H_4$ . Commercially it is available as an anhydrous (without water) liquid and in aqueous solutions. Hydrazine is most well known for its use as a rocket fuel, but is also used in manufacturing agricultural chemicals, explosives, and plastics. It fumes in air and reacts with all oxidizing agents. Hydrazine is *hypergolic*, meaning that it reacts explosively upon contact with many oxidizing agents. The flash point of hydrazine is 38 degrees C (100 degrees F). Its autoignition temperature is 270 °C (518 °F) on a glass surface but may be as low as 23°C (74 °F) when in contact with a strong oxidizing agent. Hydrazine forms flammable mixtures with air from 4% to 100% by volume and decomposes when heated. Hydrazine ignites in air at room temperature when exposed to metal oxide surfaces and in a wide variety of porous materials.

### ◆◆Storage and Handling of Hydrazine

Storage in a detached building is preferred. Inside storage should be in a standard flammable liquids storage warehouse, room, or cabinet. An emergency water reservoir or sprinklers should be provided for fire extinguishment. Hydrazine should be stored separately from metal oxides, acids, and all oxidizing agents. Hydrazine is highly toxic and may be fatal if inhaled or absorbed through the skin. It is also corrosive and may cause severe eye and skin burns. Protective clothing that prevents penetration of hydrazine and positive pressure self-contained breathing apparatus must be worn when working with hydrazine.

### ◆◆Extinguishing Hydrazine Fires

Fires involving hydrazine may produce irritants and toxic gases such as nitrogen oxides. Fires should not be approached without protective clothing and positive pressure respirators. Hydrazine fires should be approached from upwind to avoid hazardous vapors and toxic decomposition products. Flooding amounts of water should be applied as a fog or spray. Water should be sprayed on fire-exposed containers of hydrazine to keep them cool. Fires should be fought from a protected location or at a maximum possible distance. Flooding amounts of water may be necessary to prevent re-ignition.

## PYROPHORIC NONMETALLIC SOLIDS

### ◆◆PHOSPHORUS

There are two different compounds of phosphorus. These are commonly known as white (or yellow) phosphorus, and red phosphorus. Red phosphorus is not considered pyrophoric. However, red phosphorus ignites easily and produces phosphine (a pyrophoric gas) during combustion.

Pyrophoric (white, or yellow) phosphorus is a colorless to yellow, translucent, nonmetallic solid. It ignites spontaneously on contact with air at or above 30 °C (86 °F).

Phosphorous is explosive when mixed with oxidizing agents. Fumes from burning phosphorus are highly irritating but only slightly toxic except in very high concentrations. Like red phosphorus, white phosphorus also produces phosphine during combustion.

When storing, protect containers against physical damage. Phosphorus should always be kept underwater, or under an inert atmosphere, separated from oxidizing agents and combustible materials. When shipping, keep phosphorus under water in hermetically sealed cans inside wooden boxes, under water in drums, or in tank motor vehicles or tank cars under water or blanketed with an inert gas.

Phosphorous fires should be deluged with water until the fire is extinguished and the phosphorus has solidified. The solidified phosphorus should then be covered with wet sand, clay, or ground limestone.

### ◆PYROPHORIC METALS

Nearly all metals will burn in air under certain conditions. Some are oxidized rapidly in the presence of air or moisture, generating sufficient heat to reach their ignition temperatures. Others oxidize so slowly that heat generated during oxidation is dissipated before the metal becomes hot enough to ignite. Certain metals, notably magnesium, titanium, sodium, potassium, lithium, zirconium, hafnium, calcium, zinc, plutonium, uranium, and thorium, are referred to as combustible metals because of the ease of ignition when they reach a high specific area ratio (thin sections, fine particles, or molten states). However, the same metals in massive solid form are comparatively difficult to ignite.

Some metals, such as aluminum, iron, and steel, that are not normally thought of as combustible, may ignite and burn when in finely divided form. Clean, fine steel wool, for example, may be ignited. Particle size, shape, quantity, and alloy are important factors to be considered when evaluating metal combustibility. Combustibility of metallic alloys may differ and vary widely from the combustibility characteristics of the alloys' constituent elements. Metals tend to be most reactive when in finely divided form, and some may require shipment and storage under inert gas or liquid to reduce fire risks.

Hot or burning metals may react violently upon contact with other materials, such as oxidizing agents and extinguishing agents used on fires involving ordinary combustibles or flammable liquids. Temperatures produced by burning metals can be higher than temperatures generated by burning flammable liquids. Some metals can continue to burn in carbon dioxide, nitrogen, water, or steam atmospheres in which ordinary combustibles or flammable liquids would be incapable of burning.

Properties of burning metal fires cover a wide range. Burning titanium produces little smoke, while burning lithium smoke is dense and profuse. Some water-moistened metal powders, such as zirconium, burn with near explosive violence, while the same powder wet with oil burns quietly. Sodium melts and flows while burning; calcium does not. Some metals (e.g., uranium) acquire an increased tendency to burn after prolonged



exposure to moist air, while prolonged exposure to dry air makes it more difficult to ignite.

The toxicity of certain metals is also an important factor in fire suppression. Some metals (especially heavy metals) can be toxic or fatal if they enter the bloodstream or their smoke fumes are inhaled. Metal fires should never be approached without proper protective equipment (clothing and respirators).

A few metals, such as thorium, uranium, and plutonium, emit ionizing radiation that can complicate fire fighting and introduce a radioactive contamination problem. Where possible, radioactive materials should not be processed or stored with other pyrophoric materials because of the likelihood of widespread radioactive contamination during a fire. Where such combinations are essential to operations, appropriate engineering controls and emergency procedures should be in place to prevent fires or quickly suppress fires in the event the controls fail.

Because extinguishing fires in combustible metals involves techniques not commonly encountered in conventional fire fighting operations, it is necessary for those responsible for controlling combustible metal fires to be thoroughly trained prior to an actual fire emergency.

The following material discusses the properties of various combustible metals, conditions in which they become pyrophoric, storage and handling practices, processing hazards, and methods of extinguishing fires involving these kinds of metals.

### ◆◆MAGNESIUM Properties

The ignition temperature of massive magnesium is very close to its melting point of about 650 °C (1,202 °F). However, ignition of magnesium in certain forms may occur at temperatures well below 650 °C (1,200 °F). For example, magnesium ribbons and shavings can be ignited under certain conditions at about 510 °C (950 °F), and finely divided magnesium powder can ignite well below 482 °C (900 °F).

Metal marketed under different trade names and commonly referred to as magnesium may be one of a large number of different alloys containing magnesium, but also significant percentages of aluminum, manganese, and zinc. Some of these alloys have ignition temperatures considerably lower than pure magnesium, and certain magnesium alloys will ignite at temperatures as low as 427 °degrees C (800 °degrees F). Flame temperatures of magnesium and magnesium alloys can reach 1,371 °degrees C (2,500 °degrees F), although flame height above the burning metal is usually less than 300 mm (12 in.).

As is the case with all combustible metals, the ease of ignition of magnesium depends upon its size and shape. The specific area of a combustible substance is the surface area of the substance exposed to an oxidizing atmosphere per gram of the substance and is

usually expressed in  $\text{cm}^2/\text{g}$ . A combustible substance that has a high specific area is more prone to oxidize, heat, and ignite spontaneously. Thin, small pieces, such as ribbons, chips, and shavings, may be ignited by a match flame whereas castings and other large pieces are difficult to ignite even with a torch because of the high thermal conductivity of the metal. In order to ignite a large piece of magnesium, it is usually necessary to raise the entire piece to the ignition temperature.

Scrap magnesium chips or other fines (finely divided particles) may burn as the result of ignition of waste rags or other contaminants. Chips wet with water, water soluble oils, and oils containing more than 0.2% fatty acid may generate hydrogen gas. Chips wet with animal or vegetable oils may burn if the oils ignite spontaneously. Fines from grinding operations generate hydrogen when submerged in water, but they cannot be ignited in this condition. Grinding fines that are slightly wetted with water may generate sufficient heat to ignite spontaneously in air, burning violently as oxygen is extracted from the water with the release of hydrogen.

#### ◆◆Storage and Handling of Magnesium

The more massive a piece of magnesium, the more difficult it is to ignite, but once ignited, magnesium burns intensely and is difficult to extinguish. The storage recommendations in NFPA 480, *Standard for the Storage, Handling, and Processing of Magnesium* (hereinafter referred to as NFPA 480) take these properties into consideration. Recommended maximum quantities of various sizes and forms to be stored in specific locations are covered in this standard. Storage buildings should be noncombustible, and the magnesium should be segregated from combustible material as a fire prevention measure.

With easily ignited lightweight castings, segregation from combustible materials is especially important. In the case of dry fines (fine magnesium scrap), storage in noncombustible covered containers in separate fire resistive storage buildings or rooms with explosion venting facilities is preferable. For combustible buildings or buildings containing combustible contents, NFPA 480 recommends automatic sprinkler protection to assure prompt control of a fire before the magnesium becomes involved.

Because of the possibility of hydrogen generation and of spontaneous heating of fines wet with coolants (other than neutral mineral oil), it is preferable to store wet scrap fines outdoors. Covered noncombustible containers should be vented.

#### ◆◆Process Hazards of Magnesium

In machining operations involving magnesium alloys, sufficient frictional heat to ignite the chips or shavings may be created if the tools are dull or deformed. If cutting fluids are used (machining of magnesium is normally performed dry), they should be of the mineral-oil type that have a high flash point. Water or water-oil emulsions are hazardous, since wet magnesium shavings and dust liberate hydrogen gas and burn more violently than dry material when ignited. Machines and the work area should be frequently cleaned and the waste magnesium kept in covered, clean, dry steel or other noncombustible drums which should be removed from the buildings at regular intervals. Magnesium dust

clouds are explosive if an ignition source is present. Grinding equipment should be equipped with a water-spray-type dust precipitator. NFPA 480 requires these types of precipitators to be vented to prevent hydrogen buildup resulting from magnesium reacting with the water spray. NFPA 480 also places restrictions on the mass flow rate of magnesium into the precipitator as well as the amount of magnesium sludge accumulated in the precipitator. The equipment should be restricted to magnesium processing only. Molten magnesium in the foundry presents a serious fire problem if not properly handled. Sulfur dioxide or melting fluxes are commonly used to prevent oxidation or ignition of magnesium during foundry operations. The action of sulfur dioxide is to exclude air from the surface of the molten magnesium; it is not an extinguishing agent. Fluxes perform both functions.

Pots, crucibles, and ladles that may contact molten magnesium must be kept dry to prevent steam formation or a violent metal-water reaction. Containers should be checked regularly for any possibility of leakage or weak points. Steel lined runoff pits or pits with tightly fitting steel pans should be provided, and the pans must be kept free of iron scale. Leaking metal contacting hot iron scale results in a violent thermite reaction. Use of stainless steel pans or linings will eliminate this possibility.

Heat treating ovens or furnaces, where magnesium alloy parts are subjected to high temperatures to modify their properties, present another special problem. Temperatures for heat treating needed to secure the desired physical properties are often close to the ignition temperatures of the alloys themselves, and careful control of temperatures in all parts of the oven is essential. Hot spots leading to local overheating are a common cause of these fires. Large castings do not ignite readily, but fins or projections on the castings, as well as chips or dust, are more readily subject to ignition. For this reason, castings should be thoroughly cleaned before heat treating. Magnesium castings in contact with aluminum in a heat treating oven will ignite at a lower temperature than when they are placed on a steel car or tray.

Magnesium should not be heat treated in nitrate salt baths. Certain commonly used molten mixtures of nitrates and nitrites can react explosively with magnesium alloys, particularly at temperatures over 538 °C (1,000 °F).

#### ◆◆ Extinguishing Magnesium Fires

Magnesium and its alloys present special problems in fire protection. Magnesium combines so readily with oxygen that under some conditions water applied to extinguish magnesium fires may be decomposed into its constituent elements, oxygen and hydrogen. The oxygen combines with the magnesium and the released hydrogen adds to the intensity of the fire. None of the commonly available gaseous extinguishing agents (CO<sub>2</sub>), for example) are suitable for extinguishing magnesium fires. The affinity of magnesium for oxygen is so great that it will burn in an atmosphere of carbon dioxide. Magnesium may also burn in an atmosphere of nitrogen to form magnesium nitride. For these reasons, the common extinguishing methods which depend on water, water solutions, or inert gas are not effective on magnesium chip fires. Halogen - containing extinguishing agents (the Halons) react violently with burning magnesium because the

chlorine or other halogen combines with the magnesium. However, flooding with noble gases (e.g., helium or argon) will extinguish burning magnesium.

The method of extinguishing magnesium fires depends largely upon the form of the material. Burning chips, shavings, and small parts must be smothered and cooled with a suitable dry extinguishing agent (e.g., graphite and dry sodium chloride). Where magnesium dust is present, care must be taken to prevent a dust cloud from forming in the air during application of the agent because this may result in a dust explosion. Fires in massive magnesium can be fought without difficulty if attacked in their early stages. It may be possible to remove surrounding material, leaving the small quantity of magnesium to burn itself out harmlessly. Considering the importance of prompt attack on magnesium fires, automatic sprinklers are desirable because they provide automatic notification and control of fire. While the water from the sprinklers may have the immediate effect of intensifying magnesium combustion, it will serve to protect the structure and prevent ignition of surrounding combustible material. An excess of water applied to fires in solid magnesium (avoiding puddles of molten metal) cools the metal below the ignition temperature after some initial intensification, and the fire goes out rapidly. By contrast, the fire may be intensified but not controlled with only a small, finely divided water spray.

Magnesium fires in heat treating ovens can best be controlled with powders and gases developed for use on such fires. By using melting fluxes to exclude air from the burning metal, fires in heat treating furnaces have been successfully extinguished. Boron trifluoride gas is an effective extinguishing agent for small fires in heat treating furnaces. Cylinders of boron trifluoride can be permanently connected to the oven or mounted on a suitable cart for use as portable equipment. Boron trifluoride is allowed to flow into the oven until the fire is extinguished, or, where large quantities of magnesium are well involved before discovery or where the furnace is not tight, the boron trifluoride will control the fire until flux can be applied to extinguish the fire.

#### ◆◆ Water on Magnesium Fires

Although water in small quantities accelerates magnesium fires, rapid application of large amounts of water is effective in extinguishing magnesium fires because of the cooling effect of water. Automatic sprinklers will extinguish a typical shop fire where the quantity of magnesium is limited. However, water should not be used on any fire involving a large number of magnesium chips when it is doubtful that there is sufficient water to handle the large area. (A few burning chips can be extinguished by dropping them into a bucket of water.) Small streams from portable extinguishers will violently accelerate a magnesium chip fire.

Burning magnesium parts such as castings and fabricated structures can be cooled and extinguished with coarse streams of water applied with standard fire hoses. A straight stream scatters the fire, but coarse drops (produced by a fixed nozzle operating at a distance or by use of an adjustable nozzle) flow over and cool the unburned metal. Some temporary acceleration normally takes place with this procedure, but rapid extinguishment follows if the technique is pursued. Well-advanced fires in several

hundred pounds (100 lb equals 45 kg) of magnesium scrap have been extinguished in less than 1 minute with two 37.5 mm (1-1/2 in.) fire hoses. Water fog, on the other hand, tends to accelerate rather than cool such a fire. Application of water to magnesium fires must be avoided where quantities of molten metal are likely to be present; the steam formation and possible metal-water reactions may be explosive.

## ◆ **Metals Not Normally Combustible**

### ◆◆ **Aluminum**

The usual forms of aluminum have a sufficiently high ignition temperature so that its burning is not a factor in most fires. However, very fine chips and shavings are occasionally subject to somewhat the same type of combustion as described for magnesium. Powdered or flaked aluminum in its pure form can ignite spontaneously in air and can be explosive in air.

### ◆◆ **Iron and Steel**

Iron and steel are not usually considered combustible; in a massive form (as in structural steel, cast iron parts, etc.), they do not burn in ordinary fires. Steel in the form of fine steel wool or dust may be ignited in the presence of heat from, for example, a torch, yielding a form of sparking rather than actual flaming in most instances. Fires have been reported in piles of steel turnings and other fine scrap which presumably contained some oil and were perhaps also contaminated by other materials that facilitated combustion. Spontaneous ignition of water-wetted borings and turnings in closed areas, such as ship hulls, has also been reported. Pure iron has a melting point of 1,535 °C (2,795 °F). Ordinary structural steel has a melting point of 1,430 °C (2,606 °F).

## ◆ **ACCIDENT CASE STUDIES**

### ◆◆ **Silane Gas Cabinet Fire**

A 6.1 x 9.1 m (20 x 30 ft) room with concrete block walls was used for distribution of process gases to clean room areas. Silane cylinders were located in 12-gauge metal gas cabinets. The ventilation system for the cabinets was in the process of being upgraded and the cabinets were protected by automatic sprinklers.

The silane cylinder involved was installed about 30 minutes prior to the incident. Employees in the area heard a loud "pop" from the process gas distribution room. Upon investigation, they found the windows of the cabinet broken, the doors open, and fire coming from the cylinder valve. The sprinkler activated properly and confined the fire to the cylinder head.

The escaping silane was caused by an improper connection of the cylinder to the distribution piping. There was evidence that the connection was cross-threaded, allowing the leakage. The flow of silane could not be shut off because of damage to the cylinder

manifold connections. The fire continued to burn for about 8-1/2 hours until all silane in the cylinder had been consumed.

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