

METRIC

DOE-HDBK-1081-94
December 1994

DOE HANDBOOK

PRIMER ON SPONTANEOUS HEATING AND PYROPHORICITY



U.S. Department of Energy
Washington, D.C. 20585

FSC-6910

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FOREWORD

The *Primer on Spontaneous Heating and Pyrophoricity* is approved for use by all DOE Components. It was developed to help DOE facility contractors prevent fires caused by spontaneous combustion. Spontaneously combustible materials include those that ignite because of a slow buildup of heat (spontaneous heating) and those that ignite instantly in air (pyrophoricity). The scientific principles of combustion and how they affect materials known to be spontaneously combustible are explained. The fire hazards of specific spontaneously heating and pyrophoric materials are discussed as well as techniques to prevent their ignition. Suitable fire extinguishing agents are included for most materials as well as safety precautions for storage and handling.

The Department of Energy (DOE) Primers are a set of fundamental handbooks on safety-related topics of interest in the DOE Complex. The Primers are written as an educational aid for operations and maintenance personnel. The Primers attempt to supply information in an easily understandable form which will help them perform their duties in a safe and reliable manner. Persons trained in other technical areas may also find the Primers useful as a guide or as a reference source for further investigation.

The DOE Primer series draws heavily upon the subject-specific Primers and training materials previously developed by DOE sites (Savannah River, Rocky Flats, and Mound) and is intended for distribution to all DOE contractors. Information is also drawn from the applicable volumes of the *DOE Fundamentals Handbook* series developed by the DOE Office of Nuclear Safety Policy and Standards. References to other material sources are indicated in the text where applicable and a bibliography is included.

Beneficial comments in the form of recommendations and any pertinent data that may be of use in improving this document should be addressed to

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by using the U.S. Department of Energy Standardization Document Improvement Proposal Form (DOE F 1300.3) appearing at the end of this document or by letter.

Key words: Combustion, Fire, Spontaneous, Ignition, Heating, Pyrophoricity, Temperature, Hypergolic, Extinguishing Agent, Hydrocarbons, Organic, Heating, Specific Area, Liquids, Gases, Metals, Oxidizer

OVERVIEW

The *Department of Energy Primer on Spontaneous Heating and Pyrophoricity* was prepared as an information resource for personnel who are responsible for operation of the Department's nuclear facilities. An understanding of spontaneous heating and pyrophoricity hazards is necessary for DOE facility personnel to operate and maintain facilities and facility support systems in a safe manner.

The *Primer on Spontaneous Heating and Pyrophoricity* contains an introduction and sections on the following topics:

- Principles of Combustion
- Spontaneous Heating/Ignition of Hydrocarbons and Organics
- Pyrophoric Gases and Liquids
- Pyrophoric Nonmetallic Solids
- Pyrophoric Metals
- Accident Case Studies.

The information contained in this Primer is by no means all-encompassing. However, enough information is presented to provide the reader with a fundamental knowledge level sufficient to recognize most spontaneous combustion hazards and how to prevent ignition and widespread fires. This Primer is provided as an information resource only, and is not intended to replace any fire protection or hazardous material training.

The Department of Energy wishes to acknowledge the contributions of all those who supplied literature and technical expertise for this Primer. Much of the information contained in this Primer was obtained from the 17th Edition of the National Fire Protection Association (NFPA) Handbook, 1991, and the 2nd Edition of Chemistry of Hazardous Materials, by E. Meyer, 1989.

**Department of Energy
Handbook**

**PRIMER ON
SPONTANEOUS HEATING AND
PYROPHORICITY**

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INTRODUCTION

The purpose of this Primer is to provide operations and maintenance personnel with the information necessary to identify and prevent potential spontaneous combustion hazards. Throughout the history of industry and the DOE Complex, fires caused by spontaneously heating and pyrophoric materials have occurred, sometimes causing personal injury and significant damage to facilities. By its very nature, spontaneous heating and pyrophoricity are among the most insidious types of fire hazards. Many times there is no outward evidence of the potential for fires caused by these phenomena. An understanding of the principles of spontaneous heating and pyrophoricity is necessary for instituting fire prevention measures.

Upon completion of this Primer, the reader should be able to do the following:

- Identify the three required elements of the Fire Triangle necessary to support combustion
- Define the following terms: combustion, oxidation, spontaneous heating, pyrophoricity, hypergolic, and specific area
- Describe the effects that atmospheric oxygen, moisture, heat transfer, and specific area have on spontaneous heating and ignition
- Identify five metals and three gases known to be pyrophoric
- Identify acceptable methods of long-term storage of spontaneously heating and pyrophoric materials
- Identify measures for preventing fires caused by spontaneous heating and pyrophoricity
- Identify references for obtaining further information on oxidizers, pyrophoric materials, hypergolic substances, and fire extinguishing agents
- Identify proper extinguishing agents for various spontaneously igniting materials
- Describe the importance of good housekeeping in limiting fire damage

Some materials ignite instantly when exposed to air or other oxidizing atmosphere. Other materials such as coal may take weeks to ignite. This difference in time until ignition is the difference between pyrophoricity and spontaneous heating and will be explained in detail later in the text.

DEFINITIONS

Combustion	- Burning of gas, liquid, or solid in which the fuel is rapidly oxidized, producing heat and often light
Hypergolic	- Property of a material which describes its ability to spontaneously ignite or explode upon contact with an oxidizing agent
Ignition temperature	- Temperature at which an element or compound will catch fire in air (atmospheric oxygen)
Oxidization	- Removal electrons from an atom or molecule, usually by chemical reaction with oxygen
Oxidizing agent	- Chemical substance that gives up oxygen easily, removes hydrogen from another substance, or attracts electrons
Pyrophoricity	- Spontaneous combustion of a material upon exposure to air (atmospheric oxygen)
Specific area	- Amount of surface area per unit weight of a material, usually expressed in cm ² /g
Spontaneous combustion	- Ignition of a combustible material caused by the accumulation of heat from oxidation reactions
Spontaneous heating	- Slow oxidation of an element or compound which causes the bulk temperature of the element/compound to rise without the addition of an external heat source

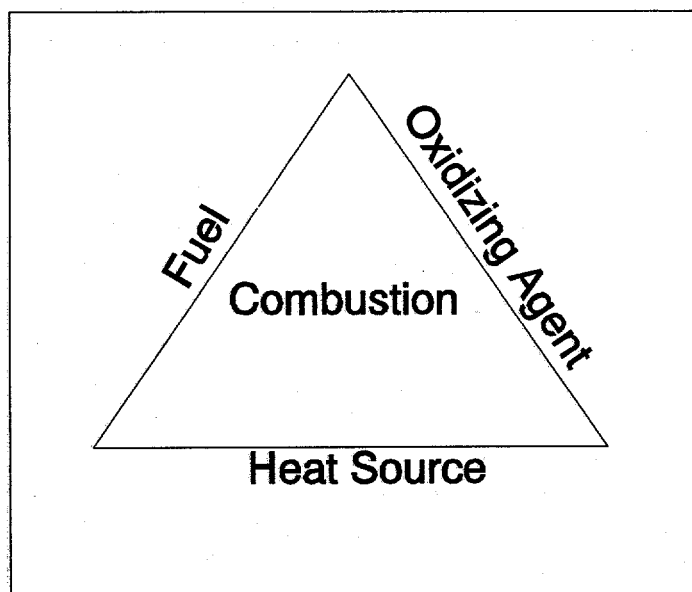


Figure 1. Fire triangle.

relative hazards and classifications of oxidizing agents may be found in Appendix B and in NFPA 43A, *Code for the Storage of Liquid and Solid Oxidizing Materials*.

Fuel

A fuel is the substance that reacts with the oxidizing agent during combustion. Fuels can be solids, liquids, gases, and even metals. Familiar fuels are coal, firewood, and gasoline. For the purpose of this document, the discussion of fuels will be limited to those that are known to combust spontaneously.

Heat Source

Normally, a heat source such as a flame or spark is required to ignite a mixture of a fuel and oxidizing agent. That is, heat must be added or the fuel and oxidizing agent will not react. The reactions that are the subject of this document are special instances where no heat source is required to ignite the fuel. These fuels react so readily with oxygen that a heat source is not required for ignition. Ignition for these fuels occurs as a result of spontaneous heating or pyrophoricity.

Spontaneous Combustion

Spontaneous combustion is the ignition of a combustible material caused by the accumulation of heat from oxidation reactions. Fires started by spontaneous combustion are caused by the following mechanisms:

PRINCIPLES OF COMBUSTION

Combustion

Combustion (burning, or fire) falls into a class of chemical reactions called *oxidation*. Oxidation may be defined as the chemical combination of a substance with oxygen or, more generally, the removal of electrons from an atom or molecule. Oxidation reactions are almost always exothermic, or release heat.

Many materials react with oxygen to some degree. However, the rates of reactions differ between materials. The difference between slow and rapid oxidation reactions is that the latter occurs so rapidly that heat is generated faster than it is dissipated, causing the material being oxidized (fuel) to reach its *ignition temperature*. Once the ignition temperature of a material is reached, it will continue to *burn* until the fuel or oxygen is consumed. The heat release during combustion is usually accompanied by a visible flame. However, some materials, such as charcoal, smolder rather than produce a flame.

A familiar slowly occurring oxidation reaction is the rusting of iron. Such a reaction releases heat so slowly that the temperature hardly increases more than a few degrees above the temperature of the surroundings. These slow reactions do not cause fires and are not considered combustion.

The Fire Triangle

Generally, there are three items necessary to support combustion:

1. Oxidizing Agent
2. Fuel
3. Heat Source.

These are depicted pictorially in Figure 1, commonly called the Fire Triangle. The Fire Triangle shows that for combustion to occur, fuel, an oxidizing agent, and a heat source must all be present in the same place at the same time. If any one of the legs of the triangle are removed, the fire will be extinguished.

Oxidizing Agents

An oxidizing agent (or oxidizer) is a chemical substance that gives up oxygen easily, removes hydrogen from another substance, or attracts electrons. By far the most common oxidizing agent is the oxygen in the earth's atmosphere. However, there are many chemical compounds that also act as oxidizing agents. Some of these agents react with fuels more readily and violently than oxygen. Further information on the

1. Spontaneous Heating
2. Pyrophoricity
3. Hypergolic reactions.

Spontaneous Heating

Spontaneous heating is the slow oxidation of an element or compound which causes the bulk temperature of the element or compound to rise without the addition of an external heat source. Spontaneous heating may be the result of direct oxidation of hydrocarbons (for example, oils, coal, and solvents) or it may occur because of the action of microorganisms in organic materials. A more detailed discussion on spontaneous heating is included in the next section.

Pyrophoricity

Pyrophoric substances ignite instantly upon exposure to air (atmospheric oxygen). A pyrophoric substance may be a solid, liquid, or gas. Most materials are not pyrophoric unless they are in a very finely divided state. Although there are some pyrophoric liquids and gases, most pyrophoric materials are metals. Information concerning specific pyrophoric liquids, gases, nonmetals, and metals are provided in later sections. It should be noted that pyrophoricity is a special case of a *hypergolic* reaction because the oxidizing agent is restricted to atmospheric oxygen. Hypergolic reactions are described in the following paragraph.

Hypergolic Reactions

Where pyrophoricity is concerned only with the spontaneous combustion of a material when exposed to air (atmospheric oxygen), a hypergolic reaction describes a material's ability to spontaneously ignite or explode upon contact with *any* oxidizing agent. The remainder of this document will be concerned only with spontaneous heating and pyrophoricity.

Note: Many of the fuels identified in this handbook react violently or explosively with the oxidizing agents identified in Appendix B and NFPA 43A because of hypergolic reactions.

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SPONTANEOUS HEATING/IGNITION OF HYDROCARBONS AND ORGANICS

Spontaneous Heating/Ignition of 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 (cm^2/g , defined below) 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 which 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 which 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 cm^2/g . Materials which have a high specific area are more prone to heat and ignite spontaneously. For example, it was mentioned earlier that 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.

These principles are illustrated in Figure 2. Although coal is used as the example in Figure 2, the principles depicted apply to all materials which are known to heat spontaneously (including pyrophoric liquids, gases, metals, and other solids).

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 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 nonhazardous, 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, and heating is generally controlled by maintaining the moisture content below a predetermined level. This type of heating can only

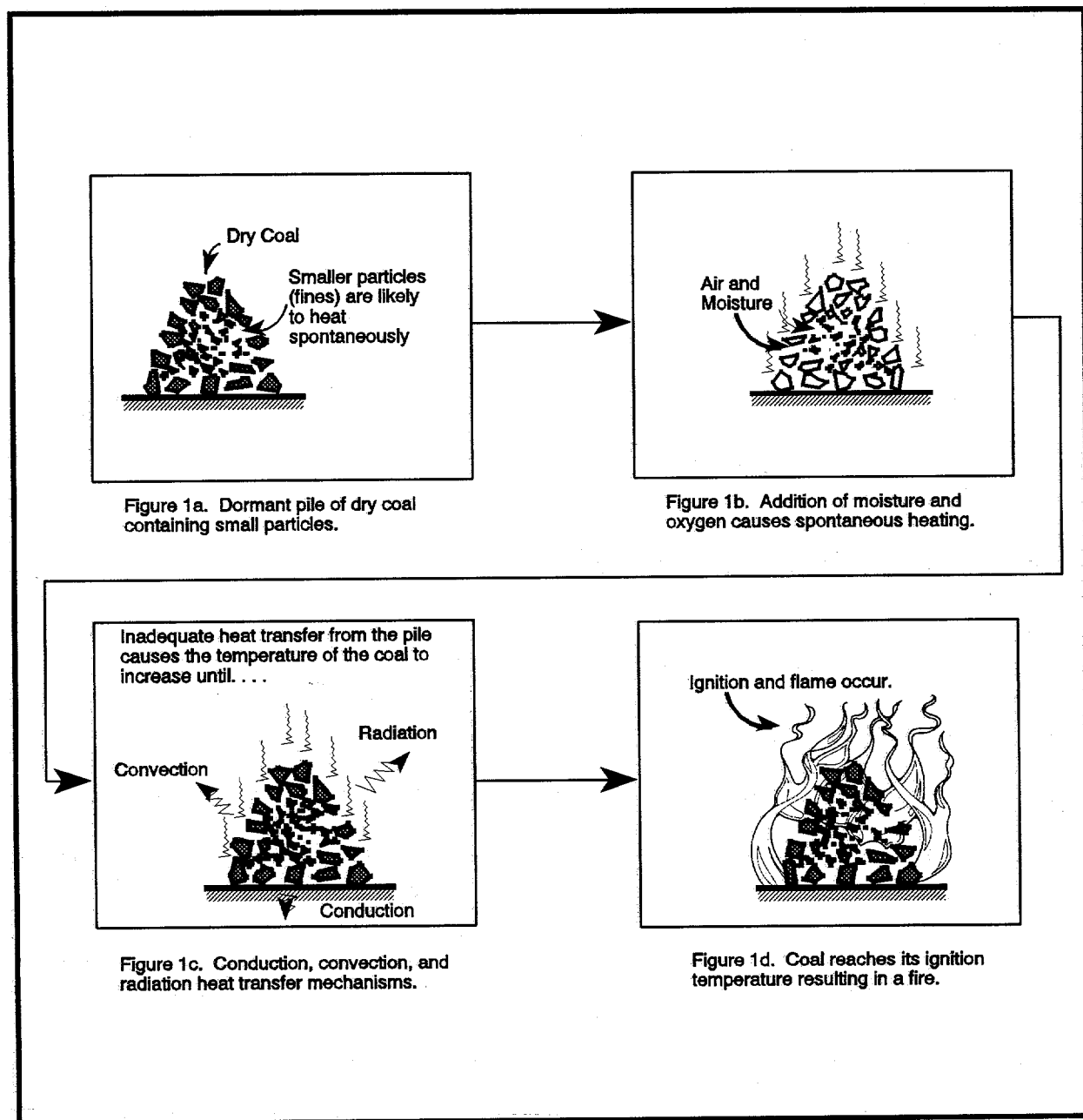


Figure 2. The evolution of a fire caused by spontaneous heating.

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 which 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.

Appendix A lists many organic materials known to heat spontaneously and measures to prevent their ignition.

Spontaneous Oxidation and Heating of Coal

Coal presents hazards between the time it is mined and its eventual consumption in boilers and furnaces. Below are listed some of the characteristics of spontaneous fires in coal. These characteristics can be used to evaluate the potential for coal fires and as guidelines for minimizing the probability of a fire.

1. The higher the inherent (equilibrium) moisture, the higher the heating tendency.
2. The lower the ash free Btu, the higher the heating tendency. The higher the oxygen content in the coal, the higher the heating tendency.
3. Sulfur, once considered a major factor, is now thought to be a minor factor in the spontaneous heating of coal. There are many very low-sulfur western subbituminous and lignite coals that have very high oxidizing characteristics and there are high sulfur coals that exhibit relatively low oxidizing characteristics.
4. The oxidation of coal is a solid/gas reaction, which happens initially when air (a gas) passes over a coal surface (a solid). Oxygen from the air combines with the coal, raising the temperature of the coal. As the reaction proceeds, the moisture in the coal is liberated as a vapor and then some of the volatile matter that normally has a distinct odor is released. The amount of surface area of the coal that is exposed is a

direct factor in its heating tendency. The finer the size of the coal, the more surface is exposed per unit of weight (specific area) and the greater the oxidizing potential, all other factors being equal.

5. Many times, segregation of the coal particle sizes is the major cause of heating. The coarse sizes allow the air to enter the pile at one location and react with the high surface area fines at another location. Coals with a large top size [e.g., 100 mm (≥ 4 in.)], will segregate more in handling than those of smaller size [50 mm (≥ 2 in.)].
6. It is generally believed that the rate of reaction doubles for every 8 to 11°C (15 to 20°F) increase in temperature.
7. Freshly mined coal has the greatest oxidizing characteristic, but a hot spot in a pile may not appear before one or two months. As the initial oxidization takes place, the temperature gradually increases and the rate of oxidization accelerates.
8. There is a critical amount of airflow through a portion of a coal pile that maximizes the oxidation or heating tendencies of coal. If there is no airflow through a pile, there is no oxygen from the air to stimulate oxidation. If there is a plentiful supply of air, any heat generated from oxidation will be carried off and the pile temperature will reach equilibrium with the air temperature; this is considered a ventilated pile.
9. When there is just sufficient airflow for the coal to absorb most of the oxygen from the air and an insufficient airflow to dissipate the heat generated, the reaction rate increases and the temperatures may eventually exceed desirable limits.

Coal Storage

Coal should be stored in properly designed bunkers, silos, bins, or in outside piles. The most important aspects of coal storage are minimizing the flow of air through the pile, using the "first-in, first out" rule of thumb, and minimizing the amount of finely divided coal in the pile. "Hot spots" should be removed or exposed to the atmosphere to allow cooling. Coal should be compacted if possible to reduce the amount of air in the pile. Water may be used to cool hot spots, but should be used with caution on large areas of hot coal to prevent accumulations of hazardous amounts of water. Coal should not be stored in outside piles located over utility lines (water, gas, etc.).

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PYROPHORIC GASES AND LIQUIDS

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 3 things in common: a) they can ignite immediately upon exposure to air, b) they are all nonmetallic hydrides, and c) many other compounds which contain these gases in their molecular structure are also pyrophoric.

Arsine

Arsine (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°C , 32°F). All arsine compounds should be considered pyrophoric until they are properly characterized.

Diborane

Diborane (B_2H_6) is a highly toxic, colorless gas with a repulsive but sweet odor; it is highly reactive and flammable. It forms flammable mixtures with air over a wide range (flammable limits, 0.9% and 98%). The ignition temperature of diborane is between 38 and 52°C (100 and 125°F). Diborane will ignite spontaneously in moist air at room temperature. It reacts spontaneously with chlorine and forms hydrides with aluminum and lithium, which may ignite spontaneously in air. It reacts with many oxidized surfaces as a strong reducing agent, and reacts violently with vaporizing liquid-type extinguishing agents.

Storage should be in a detached, refrigerated (less than 20°C , 68°F), and well-ventilated place. Boranes should be separated from halogens and other oxidizing agents and checked periodically for decomposition. Protect against electrical spark, open flames, or any other heat source. A dry nitrogen purge should be used in any transfer. Waste material should be completely hydrolyzed with water before disposal. Combustible solutions should be burned as a means of disposal. There are no special shipping requirements for diborane other than steel pressure cylinders.

Fire fighting should be done from an explosion-resistant location. Use water from unmanned monitors or hoseholders to keep fire-exposed containers cool. If it is necessary to stop the flow of gas, use water spray to protect personnel effecting shut-off. Halon should not be used as an extinguishing agent on diborane fires.

Phosphine

Phosphine (PH_3) is a highly toxic colorless gas. This chemical is very dangerous, with an ignition temperature of 212°F , often igniting spontaneously. Phosphine gas readily combines with nitrates, halogens, and metals to form very explosive and volatile compounds. Specifically, phosphine reacts violently with air, BCl_3 , Br_2 , Cl_2 , ClO , $\text{Hg}(\text{NO}_3)_2$, NO , N_2O , NCl_3 , $-\text{NO}_3$, N_2O , HNO_2 , O_2 , $(\text{K}+\text{NH}_3)$, and AgNO_3 . In addition, at elevated temperatures, phosphine decomposes, emitting highly toxic fumes of PO_x , which react vigorously with oxidizing materials. It possesses the characteristic putrefying odor of a mixture of garlic and decaying fish. Prolonged exposure to very low concentrations will cause chronic poisoning, characterized by anemia, bronchitis, gastro-intestinal disturbances, and visual, speech, and motor difficulties.

Silane

Silane (SiH_4), also known as silicon tetrahydride, is a colorless gas with a putrid odor. It and its compounds (e.g., disilane Si_2H_6) can ignite in air and react violently with chlorine (Cl_2). The presence of other hydrides as impurities causes ignition always to occur in air. However, 99.95% pure silane ignites in air unless 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 m³/s per .09 m² (1.0 ft³/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 .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 pyrophorics and pyrophoric mixes.
- h. Gas cabinets should be provided with sprinklers to protect cylinders from exposure to external fires.

Table 1. Recommended distances of pyrophoric gas cylinders from fences and walls.

	Distance to Fence in Ft	Distance to Wall in Ft
Unconfined Cylinders	6	9
Single Cylinder Cabinets	12	12

NFPA 70, *National Electrical Code*, should be consulted for explosion proofing of electrical equipment near flammable gas storage areas.

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°C (100°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

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 reignition.

PYROPHORIC NONMETALLIC SOLIDS

Phosphorus

There are two different compounds of phosphorus (P_4). These are commonly known as white (or yellow) phosphorus, and red phosphorous. 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.

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PYROPHORIC METALS

This section covers the pyrophoricity of combustible metals. Properties of various combustible metals are discussed as well as the conditions in which they become pyrophoric.

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 quiescently. 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 650°C (1,202°F). (See Table 2.) 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 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°C (800°F). Flame temperatures of magnesium and magnesium alloys can reach 1,371°C (2,500°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. As noted earlier, 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 cm²/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.

Table 2. Melting, boiling, and ignition temperatures of pure metals in solid form.¹ (From NFPA Handbook, 17th Edition).

Pure metal	Temperature					
	Melting point		Boiling point		Solid metal ignition	
	°F	°C	°F	°C	°F	°C
Aluminum	1,220	660	4,445	2,452	1,832 ^{2,3}	555 ^{2,3}
Barium	1,337	725	2,084	1,140	347 ²	175 ²
Calcium	1,548	824	2,625	1,440	1,300	704
Hafnium	4,032	2,223	9,750	5,399	--	--
Iron	2,795	1,535	5,432	3,000	1,706 ²	930 ²
Lithium	367	186	2,437	1,336	356	180
Magnesium	1,202	650	2,030	1,110	1,153	623
Plutonium	1,184	640	6,000	3,315	1,112	600
Potassium	144	62	1,400	760	156 ²	69 ²
Sodium	208	98	1,616	880	239 ⁴	115 ⁴
Strontium	1,425	774	2,102	1,150	1,328 ²	720 ²
Thorium	3,353	1,845	8,132	4,500	932 ²	500 ²
Titanium	3,140	1,727	5,900	3,260	2,900	1,593
Uranium	2,070	1,132	6,900	3,815	6,900 ^{2,5}	3,815 ^{2,5}
Zinc	786	419	1,665	907	1,652 ²	900 ²
Zirconium	3,326	1,830	6,470	3,577	2,552 ²	1,400 ²

1. Variation of test conditions may produce different results.

2. Ignition in oxygen.

3. Spontaneous ignition in moist air.

4. Above indicated temperature.

5. Below indicated 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

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

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 (CO₂, 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.

Titanium

Properties

Titanium, like magnesium, is classified as a combustible metal, but again the size and shape of the metal determine to a great extent whether or not it will ignite. Castings and other massive pieces of titanium are not combustible under ordinary conditions. Small chips, fine turnings, and dust ignite readily and, once ignited, burn with the

release of large quantities of heat. Tests have shown that very thin chips and fine turnings could be ignited by a match and heavier chips and turnings by a Bunsen burner. Coarse chips and turnings 0.79 by 2.7 mm (1/32 by 3/28 in.) or larger may be considered as difficult to ignite, but unless it is known that smaller particles are not mixed with the coarser material in significant amounts, it is wise to assume easy ignition is possible.

Finely divided titanium in the form of dust clouds or layers does not ignite spontaneously (differing in this respect from zirconium, plutonium, and certain other metals). Ignition temperatures of titanium dust clouds in air range from 332 to 588°C (630 to 1,090°F), and of titanium dust layers from 382 to 510°C (720 to 950°F). Titanium dust can be ignited in atmospheres of carbon dioxide or nitrogen. Titanium surfaces that have been treated with nitric acid, particularly with red fuming nitric acid containing 10 to 20% nitrogen tetroxide, become pyrophoric and may be explosive.

The unusual conditions under which massive titanium shapes will ignite spontaneously include contact with liquid oxygen, in which case it may explode on contact. It has been found that under static conditions spontaneous ignition will take place in pure oxygen at pressures of at least 2,413 kPa (350 psi). If the oxygen was diluted, the required pressure increased, but in no instance did spontaneous heating occur in oxygen concentrations less than 35%. Another requirement for spontaneous heating is a fresh surface which oxidizes rapidly and exothermically in an oxygen atmosphere.

Storage and Handling

Titanium castings and ingots are so difficult to ignite and burn that special storage recommendations for large pieces are not included in NFPA 481, *Standard for the Production, Processing, Handling, and Storage of Titanium*. Titanium sponge and scrap fines, on the other hand, do require special precautions, such as storage in covered metal containers and segregation of the container from combustible materials. Because of the possibility of hydrogen generation in moist scrap and spontaneous heating of scrap wet with animal or vegetable oils, a yard storage area remote from buildings is recommended for scrap that is to be salvaged. Alternate recommended storage locations are detached scrap storage buildings and fire resistive storage rooms. Buildings and rooms for storage of scrap fines should have explosion vents.

Process Hazards

Contact of molten metal with water is the principal hazard during titanium casting. To minimize this hazard, molds are usually thoroughly predried and vacuumed, or inert gas protection is provided to retain accidental spills.

The heat generated during machining, grinding, sawing, and drilling of titanium may be sufficient to ignite the small pieces formed by these operations or to ignite mineral

oil base cutting lubricants. Consequently, water-based coolants should be used in ample quantity to remove heat, and cutting tools should be kept sharp. Fines should be removed regularly from work areas and stored in covered metal containers. To prevent titanium dust explosions, any operation which produces dust should be equipped with a dust collecting system discharging into a water-type dust collector.

Descaling baths of mineral acids and molten alkali salts may cause violent reactions with titanium at abnormally high temperatures. Titanium sheets have ignited upon removal from descaling baths. This hazard can be controlled by careful regulation of bath temperatures.

There have been several very severe explosions in titanium melting furnaces. These utilize an electric arc to melt a consumable electrode inside a water-cooled crucible maintained under a high vacuum. Stray arcing between the consumable electrode and crucible, resulting in penetration of the crucible, permits water to enter and react explosively with the molten titanium. Indications are that such explosions approach extreme velocities. The design and operation of these furnaces require special attention in order to prevent explosions and to minimize damage when explosions do occur.

Extinguishing Titanium Fires

Tests conducted by Industrial Risk Insurers (IRI) on titanium machinings in piles and in open drums showed that water in coarse spray was a safe and effective means of extinguishing fires in relatively small quantities of chips.

Carbon dioxide, foam, and dry chemical extinguishers are not effective on titanium fires, but good results have been obtained with extinguishing agents developed for use on magnesium fires.

The safest procedure to follow with a fire involving small quantities of titanium powder is to ring the fire with a Class D extinguishing agent and to allow the fire to burn itself out. Care should be taken to prevent formation of a titanium dust cloud.

Alkali Metals Sodium, Potassium, NaK, and Lithium

Properties

Sodium

At room temperature sodium oxidizes rapidly in moist air, but spontaneous ignitions have not been reported except when the sodium is in a finely divided form. When heated in dry air, sodium ignites in the vicinity of its boiling point (880°C or 1,616°F). Sodium in normal room air and at a temperature

only slightly above its melting point (98°C or 208°F) has been ignited by placing sodium oxide particles on its surface. This indicates the possibility of ignition at temperatures below the boiling point. Once ignited, hot sodium burns vigorously and forms dense white clouds of caustic sodium oxide fumes. During combustion, sodium generates about the same amount of heat as an equivalent weight of wood.

The principal fire hazard associated with sodium is the rapid reaction with water. It floats on water (specific gravity 0.97), reacting vigorously and melting. The hydrogen liberated by this reaction may be ignited and explode from the heat of the reaction. Sodium (like other burning, reactive metals) reacts violently with most chemicals that can oxidize, halogenated hydrocarbons, with halogens such as iodine, and with sulfuric acid.

Potassium

The fire hazard properties of potassium (K) are very similar to those of sodium with the difference that potassium is usually more reactive. For example, the reaction between potassium and the halogens is more violent, and, in the case of bromine, a deflagration/detonation can occur. There is an explosive reaction with sulfuric acid. Unlike sodium, potassium forms some peroxides and superoxides during combustion. These peroxides may react violently with organic contaminants (oils, etc.). Peroxides and superoxides may also react explosively with metallic potassium (see NaK below).

NaK (Sodium-Potassium Alloys)

NaK is the term used when referring to any of several sodium-potassium alloys. The various NaK alloys differ from each other in melting point, but all are liquids or melt near room temperature. NaK alloys possess the same fire hazard properties as those of the component metals except that the reactions are more vigorous. Under pressure, NaK leaks have ignited spontaneously.

The potassium in NaK will react with atmospheric oxygen to form three different oxides, potassium oxide (K_2O), potassium peroxide (K_2O_2), and potassium superoxide (KO_2). These oxides form a crust over the NaK surface. If this crust is permeated and the superoxide (KO_2) is allowed to mix with the potassium in the NaK, a very high temperature thermite-type reaction can occur. This reaction may take several minutes to develop if the NaK is stored under an inert atmosphere or it may occur instantly if stored under atmospheric oxygen.

Lithium

Lithium, like sodium and potassium, cesium, and rubidium is one of the alkali metals. Lithium undergoes many of the same reactions as sodium. For example, both sodium and lithium react with water to form hydrogen; but whereas the sodium-water reaction can generate sufficient heat to ignite the hydrogen, the far less violent lithium-water reaction does not. Lithium ignites and burns vigorously at a temperature of 180°C (356°F), which is near its melting point. Unlike sodium and potassium, it will burn in nitrogen. The caustic (oxide and nitride) fumes accompanying lithium combustion are more profuse and dense than those of other alkali metals burning under similar conditions. Lithium is the lightest of all metals. During combustion, it tends to melt and flow.

Storage and Handling

Because of their reactivity with water, alkali metals require special precautions to prevent contact with moisture. Drums and cases containing alkali metals should be stored in a dry, fire-resistive room or building used exclusively for alkali metal storage. Since sprinkler protection would be undesirable, no combustible materials should be stored in the same area. It is good practice to store empty as well as filled alkali metal containers in the same area, and all containers should be on skids. There should be no water or steam pipes, but sufficient heat should be maintained to prevent moisture condensation caused by atmospheric changes. Natural ventilation at a high spot in the room is desirable to vent any hydrogen that may be released by accidental contact of alkali metal with moisture.

Large quantities of alkali metal are often stored outdoors in aboveground tanks. In such installations weatherproof enclosures should cover tank manholes, and the free space within the tank should contain a nitrogen atmosphere. Argon or helium atmospheres should be substituted for nitrogen in the case of lithium.

For small-scale transfer of solid alkali metal from a storeroom to the use area, a metal container with a tight cover is recommended. Alkali metal should be removed from storage in as small quantities as practicable. When stored on work benches, it should be kept under kerosene or oil in a closed container. Alkali metal, with its great affinity for moisture, may react at the time it is sealed in a container with any atmospheric moisture. Because of the possible presence of hydrogen, containers should not be opened by hammering on the lid.

Process Hazards

Liquid alkali metal is valuable as a high temperature heat transfer medium. For example, it is used in hollow exhaust valve stems in some internal combustion engines and in the transfer of heat from one type of nuclear reactor to a steam generator. In the latter process or other large-scale use of molten alkali metal, any equipment leak may result in a fire. Where molten alkali metal is used in process equipment, steel pans should be located underneath to prevent contact with concrete floors. Contact of molten alkali metal with concrete will cause spalling of the concrete and spattering of the metal.

Processing of alkali metal is essentially remelting it to form sticks or bricks or to add as a liquid to closed transfer systems. During this handling, contact with moist air, water, halogens, halogenated hydrocarbons, and sulfuric acid must be avoided.

Extinguishing Fires in Sodium, Lithium, NaK, and Potassium

The common extinguishing agents, such as water, foam, and vaporizing liquids, should never be used because of the violent reactions upon application to alkali metals. Class D dry powders developed for metal fires, dry sand, dry sodium chloride, and dry soda ash are effective. These finely divided materials blanket the fire while the metal cools to below its ignition temperature. Alkali metal burning in an apparatus can usually be extinguished by closing all openings. Blanketing with nitrogen is also effective. In the case of lithium, argon or helium atmospheres should be used.

Zirconium and Hafnium

Properties

Zirconium

The combustibility of zirconium increases as the average particle size decreases, but other variables, such as moisture content, also affect its ease of ignition. In massive form, zirconium can withstand extremely high temperatures without igniting, whereas clouds of dust in which the average particle size is 3 microns have ignited at room temperature. Dust clouds of larger particle size can be readily ignited if an ignition source is present, and such explosions can occur in atmospheres of carbon dioxide or nitrogen as well as in air. Zirconium dust will ignite in carbon dioxide at approximately 621°C (1,150°F) and nitrogen at approximately 788°C (1,450°F). Tests have also indicated that layers of 3-micron-diameter dust are susceptible to spontaneous ignition. The depth of the dust layer and its moisture content are important variables for ignition. Spontaneous heating and ignition are also possibilities with scrap chips, borings, and turnings if fine dust is present.

Layers of 6-micron-diameter dust have ignited when heated to 190°C (374°F). Combustion of zirconium dust in air is stimulated by the presence of limited amounts of water (5 to 10%). When very finely divided zirconium powder is completely immersed in water, it is difficult to ignite, but once ignited it burns more violently than in air.

Massive pieces of zirconium do not ignite spontaneously under ordinary conditions, but ignition will occur when an oxide-free surface is exposed to sufficiently high oxygen concentrations and pressure. The explanation for this reaction is the same as that cited for a similar titanium reaction. Zirconium fires (like fires involving titanium and hafnium) attain very high temperatures, but generate very little smoke.

Explosions have occurred while zirconium was being dissolved in a mixture of sulfuric acid and potassium acid sulfate. Zirconium has exploded during and following pickling in nitric acid, and also during treatment with carbon tetrachloride or other halogen-containing materials. Spontaneous explosions have occurred during handling of moist, very finely divided, contaminated zirconium scrap.

Hafnium

Hafnium has similar fire properties to zirconium. Hafnium burns with very little flame, but it releases large quantities of heat. Hafnium in sponge form may ignite spontaneously.

Hafnium is generally considered to be somewhat more reactive than titanium or zirconium of similar form. Damp hafnium powder reacts with water to form hydrogen gas, but at ordinary temperatures this reaction is not sufficiently vigorous to cause the hydrogen to ignite. At higher temperatures, however, ignition of the hydrogen may be expected to proceed explosively.

Storage and Handling

Special storage precautions are not required for zirconium castings because of the very high temperatures that massive pieces of the metal can withstand without igniting. Zirconium powder, on the other hand, is highly combustible; consequently, it is customarily stored and shipped in 3.78-L (1-gal) containers with at least 25% water by volume. For specific details, refer to NFPA 482, *Standard for the Production, Processing, Handling, and Storage of Zirconium*.

Zirconium powder storerooms should be of fire-resistive construction equipped with explosion vents. Cans should be separated from each other to minimize the possibility of a fire at one can involving others and to permit checking of the cans

periodically for corrosion. One plant handling zirconium has established the procedure of disposing of cans containing powder that have been on the shelf for 6 months.

Process Hazards

In general, processing recommendations for zirconium and hafnium are the same. Handling of zirconium powder, whenever possible, should be under an inert liquid or in an inert atmosphere. If zirconium or hafnium powder is handled in air, extreme care must be used because the small static charges generated may cause ignition.

To prevent dangerous heating during machining operations, a large flow of mineral oil or water-base coolant is required. In some machining operations, the cutting surface is completely immersed. Turnings should be collected frequently and stored under water in cans. Where zirconium dust is a byproduct, dust collecting equipment which discharges into a water precipitation type of collector is a necessity.

Extinguishing Fires in Zirconium and Hafnium

Zirconium and hafnium fires can be extinguished in the same way. Fires exposing massive pieces of zirconium, for example, can be extinguished with water. Limited tests conducted by Industrial Risk Insurers have indicated that the discharge of water in spray form would have no adverse effect on burning zirconium turnings. When a sprinkler opened directly above an open drum of burning zirconium scrap, there was a brief flareup after which the fire continued to burn quietly in the drum. When a straight stream of water at a high rate of flow was discharged into the drum, water overflowed and the fire went out.

Where small quantities of zirconium powder or fines are burning, the fire can be ringed with a Class D extinguishing powder to prevent its spread, after which the fire can be allowed to burn out. Special powders developed for metal fires have been effective in extinguishing zirconium fires. When zirconium dust is present, the extinguishing agent should be applied so that a zirconium dust cloud will not form. If the fire is in an enclosed space, it can be smothered by introducing argon or helium.

Calcium and Zinc

Properties

Calcium

The flammability of calcium depends considerably on the amount of moisture in the air. If ignited in moist air, it burns without flowing at a somewhat lower rate than sodium. It decomposes in water to yield calcium hydroxide and hydrogen, which may burn. Finely divided calcium will ignite

spontaneously in air. It should be noted that barium and strontium are very similar to calcium in their fire properties.

Zinc

Zinc does not introduce a serious fire hazard in sheets, castings, or other massive forms because of the difficulty of ignition. Once ignited, however, large pieces burn vigorously. Moist zinc dust reacts slowly with the water to form hydrogen, and, if sufficient heat is released, ignition of the dust can occur. Zinc dust clouds in air ignite at 599°C (1,110°F). Burning zinc generates appreciable smoke.

Storage, Processing, and Extinguishing Fires in Calcium and Zinc

The storage, handling, and processing recommendations for magnesium are generally applicable to calcium and zinc.

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).

Plutonium

Plutonium is one of the most widely used pyrophoric materials in the DOE Complex. Some of the most serious fires occurring within the Complex are caused by the ignition of finely divided plutonium particles. Several plutonium compounds are pyrophoric. The radioactive decay of plutonium creates additional concerns such as dispersal of particles in a fire, pressurization of storage containers, and the production of hydrogen gas during decomposition of absorbed water.

Properties

Metal, Oxides, and Oxidation

Large pieces of plutonium metal react slowly with the oxygen in air at room temperature to form plutonium oxides. The rate of oxidation is dependent on a number of factors. These include (a) temperature, (b) surface area of the reacting metal, (c) oxygen concentration, (d) concentration of moisture and other vapors in the air, (e) the type and extent of alloying, and (f) the presence of a protective oxide layer on the metal surface. The rate of oxidation increases with increases in the first four factors and decreases with the last. Alloying can either increase or decrease the oxidation rate, depending on the alloying metal. Of all these factors, moisture has a large effect on the oxidation rate and is especially significant in evaluating conditions for storing plutonium metal and oxide.

Several plutonium oxides can be formed from oxidation of metal or decomposition of plutonium compounds. Oxide phases corresponding to sesquioxide (Pu_2O_3) and dioxide (PuO_2) compositions have been identified and are well characterized. Pu_2O_3 is pyrophoric in air and rapidly forms plutonium dioxide while releasing heat. The dioxide is unreactive in air, but reportedly heats slowly with water vapor at elevated temperatures.

Hydride

Plutonium hydride (PuH_x , $2 < x < 3$) forms during corrosion of plutonium metal by hydrogen from water, organic materials, and other sources. Hydride is rapidly oxidized by dry air at room temperature to produce PuO_2 and H_2 and reacts with nitrogen at 250°C to form plutonium nitride (PuN). The quality of hydride produced depends on the rate of hydrogen formation and on the magnitude of the hydrogen-containing source. The reactivity of plutonium hydride in air depends on factors such as particle size, presence/absence of protective oxide layer, and the hydrogen:plutonium ratio, x . Finely divided hydride is pyrophoric in air at room temperature. Thus, the only safe practice is to handle and store hydride in a dry, oxygen-free atmosphere.

Carbides and Nitride

Plutonium carbides, oxycarbides, and nitride are reactive and potentially pyrophoric materials that could pose handling problems if exposed to air or oxygen-containing atmospheres. These compounds react readily with moisture to form gaseous products such as methane, acetylene, and ammonia. Because plutonium compounds of this type have been prepared at several sites and may have been "temporarily" stored under special conditions (hermetically sealed within an inert atmosphere) without first oxidizing them, caution should be exercised in opening cans that might contain such materials.

Reactions Involving Water

Water vapor accelerates the oxidation of plutonium by oxygen and reacts directly with the metal. Oxidation is about ten times higher in humid air than in dry air at room temperature. For this reason, plutonium metal has routinely been handled in a very dry atmosphere such as one with a -40°C dew point. Inerting of glove boxes and enclosures for handling plutonium with nitrogen or argon is effective in reducing metal oxidation only if it also excludes water vapor. Rapid oxidation does not occur if oxygen is present at a level of 5% in nitrogen or argon. However, if 1.3% moisture (50% relative humidity) accompanies the oxygen, then rapid metal oxidation can be anticipated.

Plutonium dioxide can adsorb up to 8% of its weight as water on the surface. The quantity absorbed is a direct function of the surface area of the oxide. The principal hazard associated with absorbed water is pressurization of a sealed oxide container through any of several separate processes including evaporation of water, radiolysis to form oxygen and hydrogen, or direct reaction with the oxide to form a higher oxide and hydrogen gas.

Pressurization of oxide containers can be prevented by use of sealed containers fitted with durable, high-efficiency metal filters. Although gases can escape without release of plutonium-containing particles, air (possibly moist) is able to enter the container.

Pyrophoricity

When heated to its ignition temperature, plutonium reacts at an accelerated oxidation rate, which sustains continued oxidation. The burning temperature depends on the rate of heat dissipation to the surroundings and the rate of heat generation, which is dependent on the surface area of oxidizing metal. Temperatures of plutonium fires usually exceed the melting temperature of plutonium metal (640°C) which causes the material to consolidate into a molten configuration. As such, finely divided metal, turnings, and casting

skulls tend to ignite readily and achieve a high initial temperature which lasts until melting occurs and the surface area is reduced.

The oxide layer that forms during burning limits the oxidation rate of plutonium. The burning process is similar to that of a charcoal briquette. The ignition temperature of plutonium metal depends on the factors that increase the oxidation rate. Finely divided plutonium metal, such as metal powder or fine machine turnings, ignites near 150°C. This temperature is easily reached if a coexisting pyrophoric material such as a hydride spontaneously ignites at room temperature. Bulk or massive plutonium characterized as having a specific surface area less than 10 cm²/g requires temperatures in excess of 400°C to ignite. Many plutonium fires have occurred because samples containing finely divided metal have spontaneously ignited. Fires have not occurred with well-characterized metal existing in large pieces that have higher ignition temperatures. Thus, massive plutonium is not considered pyrophoric or capable of self-ignition.

An investigation of two instances in which kilogram-sized plutonium pieces were observed to "spontaneously ignite" in air at room temperature showed that they had been exposed to unlimited sources of hydrogen for extended periods, and that the samples were thermally insulated when ignition occurred. The amount of hydride present on these massive pieces apparently generated sufficient heat to cause ignition. These observations emphasize the need for well-characterized materials.

Storage and Handling

Plutonium should be stored as pure metal (Pu) or in its dioxide (PuO₂) form in a dry, inert or slightly oxidizing atmosphere. The formation of oxide from metal is accompanied by a large volume expansion (up to 70%) which may bulge or breach the primary container. Case studies show that mechanical wedging resulting from this expansion can even breach a second metal container, resulting in localized contamination release and possible exposure of personnel. Oxidation of the metal and rupture of the container by mechanical wedging are prevented if the storage container is hermetically sealed. Plutonium radioactively decays producing alpha particles and helium molecules. Over long-term storage, helium buildup can contribute to the pressurization of containers.

Plutonium sesquioxide and hydride should be converted to plutonium dioxide before storage. Primary and secondary containers should be hermetically sealed and contain no plastics or other materials that decompose as a result of radiation exposure.

For a more complete discussion of plutonium storage issues, refer to DOE/DP-123T, *Assessment of Plutonium Storage Issues at Department of Energy Facilities*, January 1994.

Extinguishing Plutonium Fires

Plutonium fires should not be approached without protective clothing and respirators unless the fire is enclosed in a glove box. The most effective agent for extinguishing plutonium fires has been found to be magnesium oxide sand. Glove boxes which contain pyrophoric forms of plutonium should also contain an amount of magnesium oxide adequate for extinguishment. The burning plutonium should be completely covered with the sand to as great a depth as possible. The magnesium oxide extinguishes the fire by providing a heat sink which cools the plutonium and by providing a barrier which limits the availability of oxygen.

Argon is a very effective extinguishing agent, providing the oxygen content in the atmosphere is maintained at 4% or less. Above 4% oxygen, flooding with argon will not extinguish a plutonium fire. This is an important point, since it is nearly impossible to reduce the oxygen content to 4% or less during argon flooding in most fume hoods. Argon may be used effectively to cool the burning plutonium prior to application of the magnesium oxide sand.

Other agents have been tested for use on plutonium fires; however, none have proven to be as effective as magnesium oxide. Typical foam or dry chemical agents are not effective extinguishing agents. Fusible salt agents have been shown to be effective on small-scale plutonium fires. However, the expansion which accompanies the oxidation of plutonium has caused the fusible salt coating to crack, allowing the plutonium to re-ignite.

Water is generally acceptable for use as an extinguishing agent for fires involving plutonium. In rare cases where criticality safety considerations preclude the introduction of moderators such as water, suitable alternative fire protection measures need to be incorporated into the facility design. Proper housekeeping which includes removal of combustibles from pyrophoric forms of plutonium is the most important aspect of fire loss minimization.

Uranium

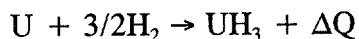
Properties

Nonenriched uranium is a radioactive metal that is also combustible. Its radioactivity does not affect its combustibility, but can have a bearing on the amount of fire loss. Most metallic uranium is handled in massive forms that do not present a significant fire risk unless exposed to a severe and prolonged external fire. Once ignited, massive metal burns very slowly. In the absence of strong drafts, uranium oxide smoke tends to deposit in the immediate area of the burning metal. Unless covered with oil, massive uranium burns with virtually no visible flame. Burning uranium reacts violently with carbon tetrachloride, 1,1,1-trichloroethane, and the Halons. For power

reactor purposes, uranium fuel elements are always encased in a metal jacket (usually zirconium or stainless steel).

Uranium in finely divided form is readily ignitable, and uranium scrap from machining operations is subject to spontaneous ignition. This reaction can usually be avoided by storage under dry (without moisture) oil. Grinding dust has been known to ignite even under water, and fires have occurred spontaneously in drums of coarser scrap after prolonged exposure to moist air. Because of uranium's thermal conductivity, larger pieces generally have to be heated entirely to their ignition temperature before igniting. Moist dust, turnings, and chips react slowly with water to form hydrogen. Uranium surfaces treated with concentrated nitric acid are subject to explosion or spontaneous ignition in air.

The pyrophoric characteristics of uranium are similar to those of plutonium except that uranium forms do not ignite as easily as those of plutonium. Both form pyrophoric oxides and hydrides. Both react violently with water and are best stored in their oxide form (UO_2 , PuO_2) in dry, inert atmospheres. Uranium metal (U) releases hydrogen gas (H_2) when allowed to react with water. The hydrogen may then react with the metal to form uranium hydride (UH_3) which may in turn react with oxygen in the air to form stable uranium oxide (UO_2) and hydrogen gas (H_2). This sequence of events is given by the equations



Note, in all instances, heat (ΔQ) is liberated, which increases the rates of reaction.

Under a dry, slightly oxidizing atmosphere, however, uranium corrodes quiescently according to the equation



The heat generated from slow corrosion is not sufficient to ignite the uranium.

Storage and Handling

The storage of the many forms of uranium is beyond the scope of this primer. For a complete discussion of uranium storage, the reader should refer to the draft *Assessment of Uranium Storage Safety Issues at Department of Energy Facilities* (referenced).

Extinguishing Uranium Fires

Uranium fires should be extinguished with the same techniques and precautions as plutonium fires (see corresponding paragraph on plutonium).

Combustible Metal Agents and Application Techniques

A variety of metals burn, particularly those in finely divided form. Some metals burn when heated to high temperatures by friction or exposure to external heat; others burn from contact with moisture or in reaction with other materials. Because accidental fires may occur during the transportation of these materials, it is important to understand the nature of the various fires and the hazards involved.

The hazards involved in the control or complete extinguishing of metal fires include extremely high temperatures, steam explosions, hydrogen explosions, toxic products of combustion, explosive reaction with some common extinguishing agents, breakdowns of some extinguishing agents with the liberation of combustible gases or toxic products of combustion, and, in the case of certain nuclear materials, dangerous radiation. Some agents displace oxygen, especially in confined spaces. Therefore, extinguishing agents and methods for their specific application must be selected with care. Metal fires should not be approached without suitable self-contained breathing apparatus and protective clothing, unless the fire is enclosed in a glove box.

Numerous agents have been developed to extinguish combustible metal (Class D) fires, but a given agent does not necessarily control or extinguish all metal fires. Although some agents are valuable in working with several metals, other agents are useful in combating only one type of metal fire. Despite their use in industry, some of these agents provide only partial control and cannot be considered actual extinguishing agents. Certain agents that are suitable for other classes of fires should be avoided for metal fires, because violent reactions may result (e.g., water on sodium; vaporizing liquids on magnesium fires).

Certain combustible metal extinguishing agents have been used for years, and their success in handling metal fires has led to the designations "approved extinguishing powder" and "dry powder." These designations have appeared in codes and other publications where it was not possible to employ the proprietary names of the powders. These terms have been accepted in describing extinguishing agents for metal fires and should not be confused with the name "dry chemical," which normally applies to an agent suitable for use on flammable liquid (Class B) and live electrical equipment (Class C) fires. Class B extinguishing agents may not be safely applied to combustible metal (Class D) fires. Other extinguishing agents discussed herein have been used only experimentally in limited areas or at specific installations, and require much judgment in application.

The successful control or extinguishment of metal fires depends heavily upon the method of application, training, and experience. Practice drills should be held on the particular

combustible metals on which the agent is expected to be used. Prior knowledge of the capabilities and limitations of agents and associated equipment is always useful in emergency situations. Fire control or extinguishment will be difficult if the burning metal is in a place or position where the extinguishing agent cannot be applied in the most effective manner. In industrial plant locations where work is performed with combustible metals, public fire departments and industrial fire brigades have the advantage of fire control drills conducted under the guidance of knowledgeable individuals.

Approved Combustible Metal Fire Extinguishing Agents

A number of proprietary combustible metal extinguishing agents have been submitted to testing agencies for approval or listing. Others have not, particularly those agents developed for special metals in rather limited commercial use. Those extinguishing agents described as follows have been approved or listed for use on fires involving magnesium, aluminum, sodium, potassium, and sodium-potassium alloy. Information on extinguishing agents was obtained from the 17th Edition of the NFPA Handbook.

G-1 Powder

"Pyrene" G-1 powder is composed of screened graphitized foundry coke to which an organic phosphate has been added. A combination of particle sizes is used to provide good packing characteristics when applied to a metal fire. The graphite acts as a heat conductor and absorbs heat from the fire to lower the metal temperature below the ignition point, which results in extinguishment. The closely packed graphite also smothers the fire, and the organic material in the agent breaks down with heat to yield a slightly smoky gas that penetrates the spaces between the graphite particles, excluding air. The powder is nontoxic and noncombustible.

G-1 powder is stored in cardboard tubes or metal pails, and can be stored for long periods of time without deterioration or caking. It is applied to the metal fire with a hand scoop or a shovel. The packing characteristics of the powder prevent its discharge from a fire extinguisher.

The powder is applied by spreading it evenly over the surface of the fire to a depth sufficient to smother the fire. A layer at least 12.5 mm (1/2 in.) deep is recommended for fires involving fines of magnesium and magnesium alloys. Larger chunks of metal require additional powder to cover the burning areas.

Where burning metal is on a combustible surface, the fire should be extinguished by (a) first covering it with powder, (b) shoveling the burning metal onto another 25 or 50 mm (1 or 2 in.) layer of powder that has been spread out on a nearby noncombustible surface, and (c) adding more powder as needed.

G-1 powder is effective for fires in magnesium, sodium, potassium, titanium, lithium, calcium, zirconium, and hafnium, and has been recommended for special applications on powder fires in aluminum, zinc, and iron. It is listed by Underwriters Laboratories Inc. (UL) for use only on magnesium and magnesium alloys (dry fines and moist fines that are not moistened or wetted with water or water soluble cutting oils) and is approved by the Factory Mutual System (FM) for use on fires in magnesium, aluminum, sodium, potassium, and sodium-potassium alloy. When plans call for use of G-1 powder on those metals mentioned, practice fire drills should be held in advance. For fires of thorium, uranium, beryllium, or plutonium, G-1 powder can be effective in covering the fire to prevent its spread, but will not extinguish these fires. The products of combustion of thorium, uranium, beryllium, and plutonium can be a health hazard, and precautions should be observed consistent with the usual procedures in combating fires in radioactive material.

MetalGuard Powder

MetalGuard powder is identical to G-1 powder in composition, and is simply a trade name variation.

Met-L-X Powder

This dry powder, with its particle size controlled for optimum extinguishing effectiveness, is composed of a sodium chloride base with additives. The additives include tricalcium phosphate to improve flow characteristics and metal stearates for water repellency. A thermoplastic material is added to bind the sodium chloride particles into a solid mass under fire conditions.

Met-L-X powder is noncombustible, and secondary fires do not result from its application to burning metal. No known health hazard results from the use of this agent. It is nonabrasive and nonconductive.

Stored in sealed containers or extinguishers, Met-L-X powder is not subject to decomposition or a change in properties. Periodic replacement of extinguisher charges is unnecessary. Extinguishers range from 14-kg (30-lb) portable hand units (carbon dioxide cartridge propellant), through 68- and 160-kg (150- and 350-lb) wheeled units, to 900 kg (2,000 lb) for stationary or piped systems. The wheeled units and piped systems employ nitrogen as the propellant.

The powder is suitable for fires in solid chunks (such as castings) because of its ability to cling to hot vertical surfaces. To control and then extinguish a metal fire, the nozzle of the extinguisher is fully opened and, from a safe distance (in order to prevent blowing the burning metal into other areas), a

thin layer of agent is cautiously applied over the burning mass. Once control is established, the nozzle valve is used to throttle the stream to produce a soft, heavy flow. The metal can then be completely and safely covered from close range with a heavy layer. The heat of the fire causes the powder to cake, forming a crust which excludes air and results in extinguishment.

Met-L-X extinguishers are available for fires involving magnesium, sodium (spills or in depth), potassium, and sodium-potassium alloy (NaK). In addition, Met-L-X has been successfully used where zirconium, uranium, titanium, and powdered aluminum present serious hazards.

Comparison of G-1 and Met-L-X Powder

Based upon their past usage and known value as extinguishing agents for metal fires, the two agents previously discussed (G-1 and Met-L-X powders) are the most notable. Continuous experience with these agents has provided sufficient information to list, in Table 3, the capabilities and limitations of each when applied to certain metal fires.

Na-X Powder

This powder was developed to satisfy the need for a low chloride content agent that could be used on sodium metal fires. Na-X has a sodium carbonate base with various additives incorporated to render the agent nonhygroscopic (does not absorb moisture) and easily fluidized for use in pressurized extinguishers. It also incorporates an additive which softens and crusts over an exposed surface of burning sodium metal. Na-X is noncombustible, and does not cause secondary fires when applied to burning sodium metal above temperatures ranging from 649 to 816°C (1,200 to 1,500°F). No known health hazard results from the use of this agent on sodium fires, and it is nonabrasive and nonconductive.

Stored in 23-kg (50-lb) pails, 14-kg (30-lb) hand portables, and 68- and 160-kg (150- and 350-lb) wheeled and stationary extinguishers, Na-X is listed by UL for fires involving sodium metal up to a temperature of 649°C (1,200°F). Na-X has been tested on sodium metal (spills and in depth) at fuel temperatures as high as 816°C (1,500°F). Stored in the supplier's metal pails and extinguishers, Na-X is not subject to decomposition, so periodic replacement of the agent is unnecessary.

Table 3. Comparison of G-1 and Met-L-X powders.

Type of fire	G-1 powder			Met-L-X		
	Capable of complete extinguishment	Capable of control only	Unsatisfactory	Capable of complete extinguishment	Capable of control only	Unsatisfactory
Dry or oily magnesium chips or turnings	X	—	—	X	—	—
Magnesium castings and wrought forms	X ¹	—	—	X ²	—	—
Dry or oily titanium turnings	X ³	—	—	X	—	—
Uranium turnings and solids	X	—	—	X	—	—
Zirconium chips and turnings coated with water soluble oil	X	—	—	X	—	—
Moist zirconium chips and turnings	—	X	—	—	X	—
Sodium spills or in-depth	X	—	—	X	—	—
Sodium sprayed or spilled on vertical surfaces	—	—	X	X ⁴	—	—
Potassium or sodium-potassium alloy spill	X	—	—	X	—	—
Potassium or sodium-potassium alloy fire in-depth	—	—	X ³	—	—	X ⁵
Lithium spill	X	—	—	X	—	—
Lithium fire in-depth	X	—	—	—	—	X ⁶
Aluminum powder	X	—	—	X	—	—

1. Requires sufficient powder to cover the burning pieces. More agent required than with Met-L-X.

2. Powder clings to vertical surfaces. Unnecessary to bury burning parts.

3. More effective pound for pound than Met-L-X.

4. Adheres to molten sodium on vertical surfaces.

5. Extinguished with difficulty.

6. Powder sinks into molten metal, the sodium chloride reacting with lithium to form lithium chloride and sodium. If continued until sodium is in excess, the fire can then be extinguished.

Other Combustible Metal Extinguishing Agents

Foundry Flux

In magnesium foundry operations, molten magnesium is protected from contact with air by layers of either molten- or crust-type fluxes. These fluxes, which are also used as molten metal cleaning agents, consist of various amounts of potassium chloride, barium chloride, magnesium chloride, sodium chloride, and calcium fluoride. The fluxes are stored in covered steel drums. When applied to burning magnesium, these fluxes melt on the surface of the solid or molten metal, excluding air. The thin layer of protection can be provided by properly applying relatively small amounts of flux.

Fluxes are valuable in extinguishing magnesium spill fires from broken molds or leaking pots and in controlling and extinguishing fires in heat treating furnaces. In open fires, the flux is applied with a hand scoop or a shovel. Areas of furnaces that are difficult to reach can be coated by means of a flux throwing device similar to those used to throw concrete onto building forms.

While fluxes would rapidly extinguish chip fires in machine shops, such use is not recommended. The fluxes are hygroscopic and the water picked up from the air, combined with the salt, causes severe rusting of equipment.

Copper Powder

Advances in the science of alternative propulsion systems have led to the development of copper powder as a viable extinguishing agent for combustible metals. Work sponsored by the Naval Sea Systems Command was conducted to evaluate the adequacy of existing lithium fire suppression agents and to develop new agents should deficiencies exist.

Copper powder was found to be superior to known lithium fire extinguishing agents in extinguishing capacity. The dry powder is of uniform particle size and extinguishes a lithium fire more quickly and efficiently than existing agents. The process of extinction is by formation of a copper-lithium alloy, which is nonreactive and forms preferentially on the surface of the molten lithium. The alloy becomes an exclusion boundary between air and the molten metal, preventing reignition and promoting cooling of the unreacted lithium.

Copper powder can be applied from hand-portable extinguishers. The nominal charge for each extinguisher is 14 kg (30 lb); it is 68 and 160 kg (150 and 350 lbs) for wheeled units, as well as fixed systems. Argon is used as the propellant. The method of application is similar to that of other metal fire powders, in that the fuel surface is coated with the copper powder in an initial

pass, with a throttled application following once control is achieved. Typical application densities are 3.6 kg (8 lbs) of copper powder per pound of lithium for complete extinguishment of the lithium. An 18-kg (40-lb) lithium fire can be fully controlled in 30 seconds and completely extinguished in 9 minutes. Copper powder also has been used to extinguish magnesium and aluminum fires.

Lith-X Powder

This dry powder is composed of a special graphite base with additives. The additives render it free flowing so it can be discharged from an extinguisher. The technique used to extinguish a metal fire with this agent is the same as that used with Met-L-X. Lith-X does not cake or crust over when applied to burning metal. It excludes air and conducts heat away from the burning mass to effect extinguishment. It does not cling to hot metal surfaces, so it is necessary to completely cover the burning metal.

Lith-X will successfully extinguish lithium fires and is suitable for the control and extinguishment of magnesium and zirconium chip fires. It will extinguish sodium spill and sodium fires in-depth. Sodium-potassium alloy spill fires are extinguished, and fires in-depth are controlled.

TMB Liquid

TMB is the chemical abbreviation for trimethoxyboroxine. The agent contains methanol to render it free flowing. It is classed as a flammable liquid for shipping purposes. The liquid is colorless and hydrolyzes readily to form boric acid and methanol. Contact with moist air or other sources of water must be avoided to prevent hydrolysis.

This agent is applied with a specially adapted 9.5 L (2-1/2 gal) stored-pressure extinguisher which delivers either spray or a straight stream. Typical application of TMB to a metal fire yields a heat flash because of the breakdown of the chemical compound and ignition of the methanol. A molten boric oxide coating on the hot metal prevents contact with air. A stream of water may be used to cool the mass as soon as metal flames are no longer visible; this should be done cautiously to avoid rupture of the coating. Indoor application (such as in machine shops) is not recommended because of the large volume of boric oxide smoke produced. Boric oxide is only slightly toxic.

While TMB has been used primarily on magnesium fires, it has shown value in application to fires in zirconium and titanium. Although TMB applied as a spray has been used to control small sodium and sodium-potassium alloy fires,

it is not recommended for fires in sodium, sodium-potassium alloy, and lithium. TMB reacts violently with lithium and sodium-potassium alloy. It will extinguish sodium in-depth, but the protective coating formed by the TMB absorbs moisture very rapidly and in time may penetrate through to the sodium, resulting in a violent reaction. Field experience has been limited to aircraft fires.

Pyromet Powder

Pyromet powder is composed of specially processed sodium chloride, diammonium phosphate, protein, and a waterproofing and flow promoting agent. The powder is discharged under pressure provided by a carbon dioxide gas cartridge. The unit contains 11 kg (25 lb) of powder. The applicator consists of a tubular extension from the control valve, terminating in a cone-shaped nozzle. A mechanism in the nozzle absorbs the discharge pressure by swirling the powder as it is expelled. This enables the operator to let the powder fall gently on the burning metal rather than to scatter burning material under the blast of a jet of powder.

Pyromet has proven effective in handling fires involving sodium, calcium, zirconium, and titanium, as well as magnesium and aluminum in the form of powder or chips.

TEC Powder

TEC (ternary eutectic chloride) powder is a mixture of potassium chloride, sodium chloride, and barium chloride that is effective in extinguishing fires in certain combustible metals. The powder tends to seal the metal, excluding air. On a hot magnesium chip fire its action is similar to that of foundry flux. In tests reported in *Fire Technology*, TEC powder was the most effective salt for control of sodium, potassium, and sodium-potassium alloy fires. TEC should not be used on plutonium, uranium, and alkali metal fires because it is hygroscopic.

Nonproprietary Combustible Metal Extinguishing Agents

Talc (Powder)

Talc, which has been used industrially on magnesium fires, acts to control rather than extinguish fire. Talc acts as an insulator to retain the heat of the fire, rather than as a coolant. It does, however, react with burning magnesium to provide a source of oxygen. The addition of organic matter (such as protein) to talc assists in the controlling action, but does not prevent the reaction which releases oxygen to the fire.

Carbon Microspheres

Specially formulated extinguishing powders are generally used to suppress fires involving metals. Because of the reaction many metals have with water, sprinklers and the use of other water-based agents are not appropriate and, in some cases, quite dangerous. However, many of the special agents for metal fires are at times unsatisfactory because they are corrosive, applied manually rather than by an extinguishing system, capable of clogging extinguishing nozzles, and expensive.

Studies have been undertaken to examine the effectiveness of carbon microspheres or microspheroids to extinguish fires involving alkali metals, such as sodium, sodium-potassium, and lithium. These microspheres are petroleum-coke-based particles with a diameter of approximately 100 to 500 microns. The particles possess high thermal conductivity, chemical inertness, and excellent flow characteristics and are capable of being directed onto fires from dry-chemical-type extinguishers and conventional nozzles.

Tests have shown that carbon microspheres compare favorably in performance to other metal extinguishing agents. In particular, experiments with carbon microspheroids incorporating neutron absorbers have been effective in extinguishing fires involving nuclear fissionable materials, such as uranium metal powder. The excellent flow characteristics and noncoking properties of these microspheres suggest an effective way to extinguish radioactive metal fires within the inert atmosphere glovebox enclosures used in the nuclear industry.

Graphite Powder

Graphite powder (plumbago) has been used as an extinguishing agent for metal fires. Its action is similar to that of G-1 powder in that the graphite acts as a coolant. Unless the powder is finely divided and closely packed over the burning metal, some air does get through to the metal and extinguishment is not as rapid as with G-1 powder.

Sand

Dry sand has often been recommended as an agent for controlling and extinguishing metal fires. At times it seems to be satisfactory, but usually hot metal (such as magnesium) obtains oxygen from the silicone dioxide in the sand and continues to burn under the pile. Sand is seldom completely dry. Burning metal reacting with the moisture in the sand produces steam and, under certain conditions, may produce an explosive metal-water reaction. By

laying the sand around the perimeter of the fire, fine dry sand can be used to isolate incipient fires of aluminum dust.

Cast Iron Borings

Cast iron borings or turnings are frequently available in the same machine shop as the various combustible metals. Clean iron borings applied over a magnesium chip fire cool the hot metal and help extinguish the fire. This agent is used by some shops for handling small fires where, with normal good housekeeping, only a few combustible metal chips are involved. Contamination of the metal chips with iron may be an economic problem. Oxidized iron chips must be avoided to prevent possible thermite reaction with the hot metal, and the iron chips must be free from moisture.

Sodium Chloride

Alkali metal fires can be extinguished by sodium chloride, which forms a protective blanket that excludes air over the metal so that the metal cools below its burning temperature. Sodium chloride is an agent that is used for extinguishing sodium and potassium fires. It can also be used to extinguish magnesium fires.

Soda Ash

Sodium carbonate or soda ash (not dry chemical) is recommended for extinguishing sodium and potassium fires. Its action is similar to that of sodium chloride.

Lithium Chloride

Lithium chloride is an effective extinguishing agent for lithium metal fires. However, its use should be limited to specialized applications because the chemical is hygroscopic to a degree and may present problems because of the reaction between the moisture and the lithium.

Zirconium Silicate

This agent has been used successfully to extinguish lithium fires.

Dolomite

If zirconium or titanium in the form of dry powder becomes ignited, neither can be extinguished easily. Control can be effected by spreading dolomite (a carbonate of calcium and magnesium) around the burning area and then adding more powder until the burning pile is completely covered.

Boron Trifluoride and Boron Trichloride

Boron trifluoride and boron trichloride have both been used to control fires in heat treating furnaces containing magnesium. The fluoride is considerably more effective. In the case of small fires, the gases provide complete extinguishment. In the case of large fires, the gases effect control over the flames and rapid burning, but reignition of the hot metal takes place on exposure to air. A combined attack of boron trifluoride gas followed by application of foundry flux completely extinguishes the fire. For details of gas application, see NFPA 480, *Standard for the Storage, Handling, and Processing of Magnesium*.

Inert Gases

In some cases, inert gases (such as argon and helium) will control zirconium fires if they can be used under conditions that will exclude air. Gas blanketing with argon has been effective in controlling lithium, sodium, and potassium fires. Caution should be exercised when using the agent in confined spaces because of the danger of suffocation of personnel.

Water

When burning metals are spattered with limited amounts of water, the hot metal extracts oxygen from the water and promotes combustion. At the same time, hydrogen is released in a free state and ignites readily. Since small amounts of water do accelerate combustible metal fires (particularly where chips or other fines are involved), use of common portable extinguishers containing water is not recommended except to control fires in adjacent Class A materials.

Water, however, is a good coolant and can be used on some combustible metals under proper conditions and applications to reduce the temperature of the burning metals below the ignition point. The following paragraphs discuss the advantages and limitations of using water on fires involving various combustible metals.

Water on Sodium, Potassium, Lithium, NaK, Barium, Calcium, and Strontium Fires

Water must not be used on fires involving these metals. Water applied to sodium, potassium, lithium, sodium-potassium alloys (NaK), barium, calcium, and strontium will induce chemical reactions that can lead to fire or explosion even at room temperatures.

Water on Zirconium Fires

Powdered zirconium wet with water is more difficult to ignite than the dry powder. However, once ignition takes place, wet powder burns more violently than dry powder. Powder containing about 5 to 10% water is considered to be the most dangerous. Small volumes of water should not be applied to burning zirconium, but large volumes of water can be successfully used to completely cover solid chunks or large chips of burning zirconium (e.g., by drowning the metal in a tank or barrel of water). Hose streams applied directly to burning zirconium chips may yield violent reactions.

Water on Plutonium, Uranium, and Thorium Fires

Water is generally acceptable for use as an extinguishing agent for fires involving enriched uranium, plutonium, and thorium fires (fissionable materials). In rare cases where criticality safety considerations preclude the introduction of moderators such as water, suitable alternative fire protection measures need to be incorporated into the facility design. Limited amounts of water add to the intensity of a fire in natural uranium or thorium, and greatly increase the contamination cleanup required after the fire. A natural uranium scrap fire can be fought with water by personnel (wearing face shields and gloves and using long-handled shovels) shoveling the burning scrap into a drum of water in the open. The hydrogen formed may ignite and burn off above the top of the drum. The radioactivity hazard of nonenriched uranium is extremely low (in reality, uranium is a heavy metal poison, although considerably less toxic than lead). If ingested, plutonium is considerably more hazardous to humans than uranium.

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.

Water on Titanium Fires

Water must not be used on fires in titanium fines and should be used with caution on other titanium fires. Small amounts of burning titanium (other than fines) can be extinguished and considerable salvage realized by quickly dumping the burning material into a large volume of water to completely submerge it. Hose streams have been used effectively on fires in outside piles of scrap, but violent reactions have been reported in other cases where water was applied to hot or burning titanium, resulting in serious injury to personnel. Additional information on the use of water on titanium fires can be found in NFPA 481, *Standard for the Production, Processing, Handling, and Storage of Titanium*.

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.

Recent Coal Fire at a DOE Site

In 1992, a DOE site experienced a coal fire initiated by spontaneous combustion. Because of the nature of the fire and initial ineffectiveness of the means used to fight it, the fire required more than 28 hours to completely extinguish from the time a hot spot was first detected in a coal bunker. The initial strategy involved trying to remove coal from the bunker by feeding it more rapidly to the boiler and by using a drag chain to move more of it to the field. The drag chain failed in 30 minutes, however. Subsequent efforts to control the fire with carbon dioxide applied through inspection ports at the bottom of the bunker and from the tripper (switchgear) room high above the bunker were ineffective, and may have worsened the situation. The drag chain emptying coal from the bunker worked intermittently after being repaired, and finally stopped. Boiler plant personnel then began to remove burning coal by hand shovel.

Twenty-one hours after the fire was discovered, it had involved a large amount of the bunker. At one point, flames appeared at the tripper room windows, which were approximately 75 feet above the seat of the hot spots. A strong concern for a steam explosion delayed the application of water, but the decision was finally made to use water, which was applied without incident and eventually ended the fire.

Zirconium Incidents (Smith, 1956)

Up to May 1955, no serious fires had been encountered during storage of scrap Zr turnings, chips, plates, rods, etc. Such scrap had been stored (pending contemplated future recovery)

in segregated open-top bins. Several days after a heavy rain, a fire of unknown origin took place in one of the bins with flames extending 100 feet into the air. Shortly afterwards, contents of other (but not necessarily adjoining) bins suddenly and intermittently flared up. Material in all bins soon became involved and 159,000 pounds of Zr were consumed. The heat was sufficiently intense to crack windows and ignite wood located over 150 feet away. Particles of burning Zr were carried over one-quarter mile through the air.

In 1951, some water-wet scrap Zr powder in wooden barrels was placed in outside storage pending development of scrap-recovery processes. During the next several years, a few minor spontaneous fires broke out in this material. In January 1956, the material in several deteriorated wooden barrels was wet with water and repackaged in steel drums. In May 1956, employees working in the area noted that one of the steel drums lying on its side contained a black material "similar to carbon dust." What happened is uncertain, but a spontaneous explosion occurred accompanied by streaks of red fire with black smoke extending 100 feet into the air. A pronounced concussion wave was noted and the sound of the blast was heard several miles away. Two employees were killed, one having been blown 80 feet through the air, and a the third lost an arm. The drum contained Zr, probably in the form of a fine powder. Using extensive precautions, the remaining drums of scrap Zr were subsequently burned. During this operation, one of the drums exploded.

Two men died and two others were seriously injured in 1954 in a spontaneous explosion initiated during removal of the friction-top lid from a polythene-bag-lined, 1-gallon metal can containing Zr powder 16 percent wet with water. A ball of flame enveloped the entire area, accompanied by a concussion wave.

A 2-pound sample of carbon-tetrachloride-moistened powdered Zr was placed in a glass flask, vacuum applied, and the flask very gently heated with a Bunsen burner. The Zr suddenly began to heat up and detonated with a blinding flash. The explosion was attributed to a small amount of water.

Uranium Incidents (Smith, 1956)

In January 1955, an attempt was made to roll two 1,000-lb U slabs into 0.01-inch thick strips. After initial heating to 1,150°F in a lithium-carbonate-potassium/carbonate bath, several 30 percent reductions were made by rolling. It was observed that heavy work passes had caused overheating. The strip, then 3/4 inch thick, was cooled to 1,200°F. The strip again excessively heated during the next three reductions and became so ductile on entering the fourth that it pulled into two parts. The strip at this stage was cherry red, but by the time it had been removed to the mill floor it was observed to increase in temperature to a white heat followed by melting and burning.

In February 1956, a technician was attempting to roll a plate consisting of Zr-clad U, which, in turn, was clad in a low-carbon-steel jacket. During preheating, the furnace temperature control (which had been set to 1,450°F) failed, allowing the temperature to rise to 1,800°F.

During subsequent rolling, molten Fe-Zr eutectic alloy within the steel jacket was forced to one end of the strip where it burst into flames as it sprayed out over an area approximately 10 feet wide, 10 feet high, and 25 feet long. One employee was seriously injured.

In the early program for the large-scale manufacture of metallic U, fine powder was allowed to collect under roughly 25 feet of water. At approximately 1-month intervals, and without prior warning, a geyser about 30 feet high would suddenly develop over the powder and then immediately subside.

A series of cases is known in which massive pieces of metallic U, Pu, and Th have displayed unusual pyrophoricity, e.g., spontaneously igniting at room temperature. Spontaneous fires in U chips are, however, much more common and in one case ignition occurred 6 months after the chips had been placed in storage. One investigator of spontaneous fires in briquette U chips opened a drum filled with briquettes that had been in outside storage for several weeks. After noting that the drum contents were normal and at approximately room temperature, he was warned by an operator to stand back. A few seconds later, a flame shot to a height of about 25 feet and then immediately subsided. Upon reinspecting the drum interior, he noted that all of the briquettes were at an incandescent temperature.

A series of incidents have been experienced in which U and Ti alloys have displayed explosive surface films following acid treatment. Studies at Argonne National Laboratory showed that such explosions could be averted through use of adequate fluoride ion concentrations in nitric acid etching baths. Witnesses have described metal-surface explosions of this type as involving a brilliant flash of white light, accompanied by a sound similar to that of a 22-caliber rifle shot.

Thorium Incidents (Smith, 1956)

For several years scrap thorium (Th) powder had been disposed of by burning in successive small amounts. In July 1956, employees were engaged in burning scrap Th powder that had previously been washed with several aqueous solutions and vacuum-dried 3 days earlier. Some of the Th was placed in a special hood and ignited without incident. An employee took a "golf-ball-size" piece of Th from a metal pail containing 30/40 pounds, replaced the pail lid, and placed the piece on a small Th fire. An immediate sharp explosion blew the employee 20 feet across the room. Almost immediately, a second blast involving the Th in the pail was accompanied by a jet of orange fire and big cloud of dust. A third explosion occurred in a nearby vacuum dryer containing about 7 pounds of moist Th powder. One employee suffered fatal burns, while three others suffered serious injuries.

In preparing an experimental charge for making metallic Th in a reduction bomb, a mixer was being used to blend metallic calcium, dry zinc chloride, and dry thorium fluoride. After several revolutions of the mixer, the operator opened the mixer vent and, noting the dust and gas were escaping, decided to call his foreman. A second operator closed the vent, started the mixer, and soon heard a rumbling noise, followed by a sudden burst of flame covering a 45° angle and extending parallel to the floor for 40 feet. Of the eight persons injured by

the blaze, two subsequently died. Reason for initiation of the reduction reaction in the blender is uncertain and unprecedented. It was subsequently found that the calcium used was particularly reactive.

Miscellaneous Incidents (Smith, 1956)

On June 16, 1954, employees of a high-energy-fuel laboratory were sampling 15 drums of "bag fines" Mg powder, which were opened in a special room that had been purged with nitrogen until the oxygen content had dropped below 1 percent. During sampling of the fifth drum, the powder ignited suddenly. The flame shot out from the drum, immediately subsided, and the operators left the room after replacing the drum cover. From an external observation window, the employees noticed a gradual darkening of the drum's exterior, moving down to within 2 to 4 inches of the drum bottom. The following day the drum was opened and contained a definite yellow coloration, which was presumed due to formation of magnesium nitride.

A massive block of metallic barium was cut into 3/4-inch square pieces while submerged in kerosene. During attempts to remove residual kerosene with carbon tetrachloride (an operation that had been performed many times before without incident), a violent reaction dispersed glass fragments and burning barium over the immediate area. Similar explosions have also occurred when Na, U, and Zr were treated with carbon tetrachloride.

Trouble had been experienced in getting a Kroll process reduction of ZrCl₄ with Mg to go to completion. When the furnace was opened up, a slate grey material was noted on the surface, which was thought to consist of Zr, Mg, and MgCl₂. A sample of this material, roughly 1/4 inch thick and 8 inches square, was removed for test and was totally inert when scratched with a file or hit with a hammer. A piece of the sample melted under an oxyacetylene flame but showed no pyrophoric properties. Samples were then placed in water and a slight evolution of gas was noted. The following day an attempt was made to further wash the samples in several changes of water. While under 5 inches of water and without any prior evidence of reaction, an explosion occurred that shattered the laboratory bench, threw the technician against the wall, and blew out a window 25 feet away. Portions of the water-washed sample blown to the floor ignited and "spit" when stepped upon. Small samples were subsequently tested and found to contain Mg, Zr, and 1 percent C.

Rocky Flats Plant Fire, 1969

On May 11, 1969, Rocky Flats Plant experienced the worst accident in plant history, a major fire in the 776-777 building, initially caused by pyrophoric plutonium scrap. One of the costliest industrial fires of all time—damages were estimated at between \$26 to \$50 million dollars—this accident was intensified and confounded by a number of operational errors.

The fire at 2:27 p.m. Sunday was reportedly caused by spontaneous ignition of a 1.5-kg briquette of plutonium alloy scrap contained in a metal can. This scrap was believed to have

been oily and coated with residual CCl_4 (carbon tetrachloride). Once ignited, the fire spread through several hundred interconnected gloveboxes in the two connected buildings.

The fire started in the west end of the north line, progressed eastward, crossed over to the south line through the interconnecting boxes, and spread through the south line. The fire spread through the machining boxes at the east end of 776 and into the inspection boxes in 777. Damage was extensive. Both Benelex, a combustible neutron shielding material added to the gloveboxes, and the combustible Plexiglas glove box windows contributed to rapid spread of the fire.

The main fire lasted about 4 hours, with minor flareups occurring through the next night. After futile attempts to control the fire with conventional procedures, the firemen finally resorted to the unorthodox procedure of applying water to bring the fire under control. This was the first time in history that water had been used to fight a plutonium fire. Despite attendant criticality dangers, the use of water was successful in controlling the fire.

The interiors of the two extremely large, high-bay buildings were grossly contaminated. An extensive, long-term cleanup effort was necessary for decontamination. Limited production was restarted about 6 months later in a temporary production line constructed in an adjacent building.

As damaging as the fire was, the water use prevented breaching of the outer walls and ceiling of 776 and 777, thus preventing a major release of plutonium to the environment. The small amount of plutonium released—almost entirely contained on plantsite—was about 0.0002 curies. Slightly contaminated external areas were subsequently cleaned up.

Fortunately, the fire caused no direct deaths. However, one fireman received significant plutonium lung burdens, and other firemen and personnel incurred smaller radiation inhalations and exposures while fighting the fire and later cleaning up heavily contaminated areas.

Immediately prior to the fire, personnel levels were significantly cut with no real decrease in work load or production demands. Strict attention to plutonium chip handling no longer seemed to have been a top priority.

The many lessons learned from this 1969 fire include the following:

- Plutonium pyrophoricity is unpredictable as to when it may occur.
- Combustible materials such as Benelex and Plexiglas must be kept to a minimum in process buildings.
- Uncleaned and uncanned briquettes cannot be left unprotected and unattended on off-shifts.

- Buildings 776-777 were essentially one large room with interconnected glovebox trains with basically no fire breaks or fire walls. This setup allowed for rapid, large-area spread of fire and radioactive contamination.

These lessons learned from the 1969 fire have led to a number of current-day, continuing safety improvements including the following equipment modifications and procedural revisions:

- A central, computerized alarm system has been installed.
- A sprinkler/water system has been put in place.
- Gloveboxes with inert atmospheres, heat detectors, and minimal Benelex and Plexiglas shielding are used.
- Water-filled double walls have been constructed.
- Firewater dams on doors are in place.
- Removal of flammable material from gloveboxes is done regularly.
- Briquettes are stored in metal containers with tight lids.
- Containers are placed on metal racks with heat detectors.
- Canning of briquettes is done in an inert atmosphere or vacuum for unattended (overnight or longer) storage.

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Appendix A

Materials Subject to Spontaneous Heating

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APPENDIX A

Materials Subject to Spontaneous Heating

Materials subject to spontaneous heating.¹ (From NFPA Handbook, 17th Edition).

Name	Tendency of spontaneous heating	Usual shipping container or storage method	Precautions against spontaneous heating	Remarks
Alfalfa meal	High	Bags, bulk	Avoid moisture extremes; tight cars for transportation are essential.	Many fires attributed to spontaneous heating probably caused by sparks, burning embers, or particles of hot metal picked up by the meal during processing. Test fires caused in this manner have smoldered for 72 hours before becoming noticeable.
Burlap bags "used"	Possible	Bales	Keep cool and dry.	Tendency to heat is dependent on previous use of bags. If oily would be dangerous.
Castor oil	Very slight	Metal barrels, metal cans in wooden boxes	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Possible heating of saturated fabrics in badly ventilated piles.
Charcoal	High	Bulk, bags	Keep dry; supply ventilation.	Hardwood charcoal must be carefully prepared and aged. Avoid wetting and subsequent drying.
Coal, bituminous	Moderate	Bulk	Store in small piles; avoid high temperatures.	Tendency to heat depends upon origin and nature of coals. Highly volatile coals are particularly liable to heat.
Cocoa bean shell tankage	Moderate	Burlap bags, bulk	Extreme caution must be observed to maintain safe moisture limits.	This material is very hygroscopic and is liable to heating if moisture content is excessive. Precaution should be observed to maintain dry storage, etc.
Coconut oil	Very slight	Drums, cans, glass	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Only dangerous if fabrics, etc., are impregnated.
Cod liver oil	High	Drums, cans, glass	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Impregnated organic materials are extremely dangerous.

1. Originally prepared by the NFPA Committee on Spontaneous Heating and Ignition which has been discontinued. Omission of any material does not necessarily indicate that it is not subject to spontaneous heating.

Materials subject to spontaneous heating (continued).

Name	Tendency of spontaneous heating	Usual shipping container or storage method	Precautions against spontaneous heating	Remarks
Colors in oil	High	Drums, cans, glass	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	May be very dangerous if fabrics, etc., are impregnated.
Copra	Slight	Bulk	Keep cool and dry.	Heating possible if wet and hot.
Corn-meal feeds	High	Burlap bags, paper bags, bulk	Material should be processed carefully to maintain safe moisture content and to cure before storage.	Usually contains an appreciable quantity of oil which has rather severe tendency to heat.
Corn oil	Moderate	Barrels, tank cars	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Dangerous heating of meals, etc., unlikely unless stored in large piles while hot.
Cottonseed	Low	Bags, bulk	Keep cool and dry.	Heating possible if piled wet and hot.
Cottonseed oil	Moderate	Barrels, tank cars	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	May cause heating of saturated material in badly ventilated piles.
Distillers' dried grains with oil content	Moderate	Bulk	Maintain moisture 7 to 10%; cool below 100°F (38°C) before storage.	Very dangerous if moisture content is 5% or lower.
(Brewers' grains) -no oil content	Moderate	Bulk	Maintain moisture 7 to 10%; cool below 100°F (38°C) before storage.	Very dangerous if moisture content is 5% or lower.
Feeds, various	Moderate	Bulk, bags	Avoid extremely low or high moisture content.	Ground feeds must be carefully processed. Avoid loading or storing unless cooled.
Fertilizers organic, inorganic, combination of both mixed	Moderate	Bulk, bags	Avoid extremely low or high moisture content.	Organic fertilizers containing nitrates must be carefully prepared to avoid combinations that might initiate heating.
Fertilizers synthetic, containing nitrates and organic matter	Moderate	Bulk, bags	Avoid free acid in preparation.	Ensure ventilation in curing process by small piles or artificial drafts. If stored or loaded in bags, provide ventilation space between bags.
Fish meal	High	Bags, bulk	Keep moisture 6 to 12% Avoid exposure to heat.	Dangerous if overdried or packaged over 100°F (38°C).
Fish oil	High	Barrels, drums, tank cars	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Impregnated porous or fibrous materials are extremely dangerous. Tendency of various fish oils to heat varies with origin.

Materials subject to spontaneous heating (continued).

Name	Tendency of spontaneous heating	Usual shipping container or storage method	Precautions against spontaneous heating	Remarks
Fish scrap	High	Bulk, bags	Avoid moisture extremes.	Scrap loaded or stored before cooling is extremely liable to heat.
Foam rubber in consumer products	Moderate		Where possible remove foam rubber pads, etc., from garments to be dried in dryers or over heaters. If garments containing foam rubber parts have been artificially dried, they should be thoroughly cooled before being piled, bundled, or put away. Keep heating pads, hair dryers, other heat sources from contact with foam rubber pillows, etc.	Foam rubber may continue to heat spontaneously after being subjected to forced drying as in home or commercial dryers and after contact with heating pads and other heat sources. Natural drying does not cause spontaneous heating.
Grain (various kinds)	Very slight	Bulk, bags	Avoid moisture extremes.	Ground grains may heat if wet and warm.
Hay	Moderate	Bulk, bales	Keep dry and cool.	Wet or improperly cured hay is almost certain to heat in hot weather. Baled hay seldom heats dangerously.
Hides	Very slight	Bales	Keep dry and cool.	Bacteria in untreated hides may initiate heating.
Iron pyrites	Moderate	Bulk	Avoid large piles; keep dry and cool.	Moisture accelerates oxidation of finely divided pyrites.
Istle	Very slight	Bulk, bales	Keep cool and dry.	Heating possible in wet material; unlikely under ordinary conditions. Partially burned or charred fiber is dangerous.
Jute	Very slight	Bulk	Keep cool and dry.	Avoid storing or loading in hot wet piles. Partially burned or charred material is dangerous.
Lamp black	Very slight	Wooden cases	Keep cool and dry.	Fires most likely to result from sparks or included embers, etc., rather than spontaneous heating.
Lanolin	Negligible	Glass, cans, metal drums, barrels	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Heating possible on contaminated fibrous matter.
Lard oil	Slight	Wooden barrels	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Dangerous on fibrous combustible substances.

Materials subject to spontaneous heating (continued).

Name	Tendency of spontaneous heating	Usual shipping container or storage method	Precautions against spontaneous heating	Remarks
Lime, unslaked (calcium oxide, pebble lime, Quicklime)	Moderate	Paper bags, wooden barrels, bulk	Keep dry; avoid hot loading.	Wetted lime may heat sufficiently to ignite wood containers, etc.
Linseed	Very slight	Bulk	Keep cool and dry.	Tendency to heat dependent on moisture and oil content.
Linseed oil	High	Tank cars, drums, cans, glass	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Rags or fabrics impregnated with this oil are extremely dangerous. Avoid piles, etc. Store in closed containers, preferably metal.
Manure	Moderate	Bulk	Avoid extremes of low or high moisture contents; ventilate the piles.	Avoid storing or loading uncooled manures.
Menhaden oil	Moderate to high	Barrels, drums, tank cars	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Dangerous on fibrous product.
Metal powders ²	Moderate	Drums, etc.	Keep in closed containers.	Moisture accelerates oxidation of most metal powders.
Metal turnings ²	Practically none	Bulk	Not likely to heat spontaneously.	Avoid exposure to sparks.
Mineral wool	None	Pasteboard boxes, paper bags	Noncombustible; if loaded hot may ignite containers and other combustible surroundings.	This material is mentioned in this table only because of general impression that it heats spontaneously.
Mustard oil, black	Low	Barrels	Avoid contact of leakage with rags, cotton, or other fibrous combustible materials.	Avoid contamination of fibrous combustible materials.
Oiled clothing	High	Fiber boxes	Dry thoroughly before packaging.	Dangerous if wet material is stored in piles without ventilation.
Oiled fabrics	High	Rolls	Keep ventilated; dry thoroughly before packing.	Improperly dried fabrics extremely dangerous. Comparatively tight rolls are safe.
Oiled rags	High	Bales	Avoid storing in bulk in open.	Dangerous if wet with drying oil.
Oiled silk	High	Fiber boxes, rolls	Supply sufficient ventilation.	Improperly dried material is dangerous in form of piece goods. Rolls relatively safe.

2. Refers to iron, steel, brass, aluminum, and other common metals. Metals known to heat spontaneously are covered in a later section.

Materials subject to spontaneous heating (continued).

Name	Tendency of spontaneous heating	Usual shipping container or storage method	Precautions against spontaneous heating	Remarks
Oleic acid	Very slight	Glass bottles, wooden barrels	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Impregnated fibrous materials may heat unless ventilated.
Oleo oil	Very slight	Wooden barrels	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	May heat on impregnated fibrous combustible matter.
Olive oil	Moderate to low	Tank, drums, cans, glass	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Impregnated fibrous materials may heat unless ventilated. Tendency varies with origin of oil.
Paint containing drying oil	Moderate	Drums, cans, glass	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Fabrics, rags, etc., impregnated with paints that contain drying oils and driers are extremely dangerous. Store in closed containers, preferably metal.
Paint scrapings	Moderate	Barrels, drums	Avoid large unventilated piles.	Tendency to heat depends on state of dryness of the scrapings.
Palm oil	Low	Wooden barrels	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Impregnated fibrous materials may heat unless ventilated. Tendency varies with origin of oil.
Peanut oil	Low	Wooden barrels, tin cans	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Impregnated fibrous materials may heat unless ventilated. Tendency varies with origin of oil.
Peanuts, "Red Skin"	High	Paper bags, cans, fiber board boxes, burlap bags	Avoid badly ventilated storage.	This is the part of peanut between outer shell and peanut itself. Provide well ventilated storage.
Peanuts, shelled	Very slight or Negligible	Paper bags, cans, fiber board boxes, burlap bags	Keep cool and dry.	Avoid contamination of rags, etc., with oil.
Perilla oil	Moderate to high	Tin cans, barrels	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Impregnated fibrous materials may heat unless ventilated. Tendency varies with origin of oil.
Pine oil	Moderate	Galls, drums	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Impregnated fibrous materials may heat unless ventilated. Tendency varies with origin of oil.
Powdered eggs	Very slight	Wooden barrels	Avoid conditions that promote bacterial growth; inhibit against decay; keep cool.	Possible heating of decaying powder in storage.

Materials subject to spontaneous heating (continued).

Name	Tendency of spontaneous heating	Usual shipping container or storage method	Precautions against spontaneous heating	Remarks
Powdered milk	Very slight	Wooden and fiber boxes, metal cans	Avoid conditions that promote bacterial growth; inhibit against decay; keep cool.	Possible heating by decay or fermentation.
Rags	Variable	Bales	Avoid contamination with drying oils; avoid charring; keep cool and dry.	Tendency depends on previous use of rags. Partially burned or charred rags are dangerous.
Red oil	Moderate	Glass bottles, wooden barrels	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Impregnated porous or fibrous materials are extremely dangerous. Tendency varies with origin of oil.
Roofing felts and papers	Moderate	Rolls, bales, crates	Avoid overdrying the material; supply ventilation.	Felts, etc., should have controlled moisture content. Packaging or rolling uncooled felts is dangerous.
Sawdust	Possible	Bulk	Avoid contact with drying oils; avoid hot, humid storage.	Partially burned or charred sawdust may be dangerous.
Scrap film (nitrate)	Very slight	Drums and lined boxes	Film must be properly stabilized against decomposition.	Nitrocellulose film ignites at low temperature. External ignition more likely than spontaneous heating. Avoid exposure to sparks, etc.
Scrap leather	Very slight	Bales, bulk	Avoid contamination with drying oils.	Oil-treated leather scraps may heat.
Scrap rubber or buffings	Moderate	Bulk, drums	Buffings of high rubber content should be shipped and stored in tight containers.	Sheets, slabs, etc., are comparatively safe unless loaded or stored before cooling thoroughly.
Sisal	Very slight	Bulk bales	Keep cool and dry.	Partially burned or charred material is particularly liable to ignite spontaneously.
Soybean oil	Moderate	Tin cans, barrels, tank cars	Avoid contact with rags, cotton, or fibrous materials.	Impregnated fibrous materials may heat unless well ventilated.
Sperm oil—see whale oil				
Tankage	Variable	Bulk	Avoid extremes of moisture contents; avoid loading or storing while hot.	Very dry or moist tankages often heat. Tendency more pronounced if loaded or stored before cooling.
Tung nut meals	High	Paper bags, bulk	Material must be very carefully processed and cooled thoroughly before storage.	These meals contain residual oil which has high tendency to heat. Material also susceptible to heating if over-dried.

Materials subject to spontaneous heating (continued).

Name	Tendency of spontaneous heating	Usual shipping container or storage method	Precautions against spontaneous heating	Remarks
Tung oil	Moderate	Tin cans, barrels, tank cars	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Impregnated fibrous materials may heat unless ventilated. Tendency varies with origin of oil.
Turpentine	Low	Tin, glass, barrels	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Has some tendency to heat but less so than the drying oils. Chemically active with chlorine compounds and may cause fire.
Varnished fabrics	High	Boxes	Process carefully; keep cool and ventilated.	Thoroughly dried varnished fabrics are comparatively safe.
Wallboard	Slight	Wrapped bundles, pasteboard boxes	Maintain safe moisture content; cool thoroughly before storage.	This material is entirely safe from spontaneous heating if properly processed.
Waste paper	Moderate	Bales	Keep dry and ventilated.	Wet paper occasionally heats in storage in warm locations.
Whale oil	Moderate	Barrels and tank cars	Avoid contact of leakage from containers with rags, cotton, or other fibrous combustible materials.	Impregnated fibrous materials may heat unless ventilated. Tendency varies with origin of oil.
Wool wastes	Moderate	Bulk, bales, etc.	Keep cool and ventilated or store in closed containers; avoid high moisture.	Most wool wastes contain oil, etc., from the weaving and spinning and are liable to heat in storage. Wet wool wastes are very liable to spontaneous heating and possible ignition.

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Appendix B

Oxidizing Agents by NFPA Classification

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APPENDIX B

Oxidizing Agents by NFPA Classification

The degree of hazard of oxidizing agents may be evaluated by consideration of the National Fire Protection Association (NFPA) classification for oxidizers. NFPA identifies four classes of oxidizers with Class 1 nominally the least hazardous and Class 4 the most hazardous. The four classes of oxidizers are as follows:

Class 1 oxidizer: An oxidizing material whose primary hazard is that it may increase the burning rate of combustible material with which it comes in contact.

Class 2 oxidizer: An oxidizing material that will moderately increase the burning rate or that may cause spontaneous ignition of combustible material with which it comes in contact.

Class 3 oxidizer: An oxidizing material that will cause a severe increase in the burning rate of combustible material with which it comes in contact or that will undergo vigorous self-sustained decomposition when catalyzed or exposed to heat.

Class 4 oxidizer: An oxidizing material that can undergo an explosive reaction when catalyzed or exposed to heat, shock, or friction.

Thus, the relative degree of hazard decreases in the following order for oxidizers:
 $4 > 3 > 2 > 1$. The following table illustrates examples of oxidizers in each NFPA class.

Some typical oxidizers by NFPA classification.^a

Class 1

All Inorganic nitrates (unless otherwise classified)
All Inorganic nitrites (unless otherwise classified)
Ammonium persulfate
Barium peroxide
Calcium peroxide
Hydrogen peroxide solutions (greater than 8 percent up to 27.5 percent)
Lead dioxide
Lithium Hypochlorite (39 percent or less available chlorine)
Lithium peroxide
Magnesium peroxide
Manganese dioxide
Nitric acid (40 percent concentration or less)
Perchloric acid solutions (less than 50 percent by weight)

Class 2

Barium bromate
Barium chlorate
Barium hypochlorite
Barium perchlorate
Barium permanganate
1-Bromo-3-chloro-5,5-dimethylhydantoin
Calcium chlorate
Calcium chlorite
Calcium hypochlorite (50 percent or less by weight)
Calcium perchlorate
Calcium permanganate
Chromium trioxide (Chromic acid)
Copper chlorate
Halane (1,3-Dichloro-5,5-dimethylhydantoin)
Hydrogen peroxide (greater than 27.5 percent up to 52 percent)
Lead perchlorate
Lithium chlorate
Lithium hypochlorite (more than 39 percent available chlorine)
Lithium perchlorate
Magnesium bromate
Magnesium chlorate
Magnesium perchlorate

Class 1 (continued)

Potassium dichromate
Potassium percarbonate
Potassium persulfate
Sodium carbonate peroxide
Sodium dichloro-s-triazinetriene dihydrate
Sodium dichromate
Sodium perborate (anhydrous)
Sodium perborate monohydrate
Sodium perborate tetrahydrate
Sodium percarbonate
Sodium persulfate
Strontium peroxide
Zinc peroxide

Class 2 (continued)

Mercurous chlorate
Nitric acid (more than 40 percent but less than 86 percent)
Perchloric acid solutions (more than 50 percent but less than 60 percent)
Potassium perchlorate
Potassium permanganate
Potassium peroxide
Potassium superoxide
Silver peroxide
Sodium chlorite (40 percent or less by weight)
Sodium perchlorate
Sodium perchlorate monohydrate
Sodium permanganate
Sodium peroxide
Strontium chlorate
Strontium perchlorate
Strontium peroxide
Thallium chlorate
Trichloro-s-triazinetriene (Trichloroisocyanuric acid)
Urea hydrogen peroxide
Zinc bromate
Zinc chlorate
Zinc permanganate

a. NFPA 43A-1980, Code for the Storage of Liquid and Solid Oxidizing Materials.

Some typical oxidizers by NFPA classification. (continued)

Class 3

Ammonium dichromate
Calcium hypochlorite (over 50 percent by weight)
Chloric acid (10 percent maximum concentration)
Hydrogen peroxide solutions (greater than 52 percent up to 91 percent)
Mono-(trichloro)-tetra-(monopotassium dichloro)-penta-s-triazinetriene
Nitric Acid, fuming (more than 86 percent concentration)
Sodium chlorite (over 40 percent by weight)

Class 4

Ammonium perchlorate (particle size greater than 15 microns)
Ammonium permanganate

Class 3 (continued)

Perchloric acid solutions (60 percent to 72 percent by weight)
Potassium bromate
Potassium chlorate
Potassium dichloro-s-triazinetriene (Potassium dichloroisocyanurate)
Sodium bromate
Sodium chlorate
Sodium dichloro-s-triazinetriene (sodium dichloroisocyanurate)

Class 4 (continued)

Guanidine nitrate
Hydrogen peroxide solutions (greater than 91 percent)
Tetranitromethane

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CONCLUDING MATERIAL

Reviewing activities:

DOE Facilities

ANL-W, BNL, EG&G Idaho,
EG&G Mound, EG&G Rocky Flats,
LLNL, LANL, MMES, ORAU, REEC_o,
WHC, WINCO, and WSRC.

DOE Program Offices

AD, DP, EH, EM, ER, NP, NS, RW.

DOE Field Offices

AL, CH, ID, NV, OR, RL, SR, OAK, RF.

Preparing activities:

DOE-EH-63

Project Number 6910-0040



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