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# NFPA 53
# Guide on Fire Hazards in Oxygen-Enriched Atmospheres
## 1994 Edition

NFPA

National Fire Protection Association, 1 Batterymarch Park, PO Box 9101, Quincy, MA 02269-9101

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## Policy Adopted by NFPA Board of Directors on December 3, 1982

The Board of Directors reaffirms that the National Fire Protection Association recognizes that the toxicity of the products of combustion is an important factor in the loss of life from fire. NFPA has dealt with that subject in its technical committee documents for many years.

There is a concern that the growing use of synthetic materials may produce more or additional toxic products of combustion in a fire environment. The Board has, therefore, asked all NFPA technical committees to review the documents for which they are responsible to be sure that the documents respond to this current concern. To assist the committees in meeting this request, the Board has appointed an advisory committee to provide specific guidance to the technical committees on questions relating to assessing the hazards of the products of combustion.

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# NFPA 53

## Guide on

# Fire Hazards in Oxygen-Enriched Atmospheres

## 1994 Edition

This edition of NFPA 53, *Guide on Fire Hazards in Oxygen-Enriched Atmospheres,* was prepared by the Technical Committee on Oxygen-Enriched Atmospheres and acted on by the National Fire Protection Association, Inc. at its Fall Meeting held November 15-18, 1993, in Phoenix, AZ. It was issued by the Standards Council on January 14, 1994, with an effective date of February 11, 1994, and supersedes all previous editions.

The 1994 edition of this document has been approved by the American National Standards Institute.

Changes other than editorial are indicated by a vertical rule in the margin of the pages on which they appear. These lines are included as an aid to the user in identifying changes from the previous edition.

## Origin and Development of NFPA 53

Development of NFPA 53 was initiated in 1965 largely as a result of interest in the area of oxygen-enriched atmospheres by the aerospace industry and medical personnel/researchers who expressed a need for a single source of general data on the hazards of oxygen-enriched atmospheres.

The first edition was published in 1969 under NFPA procedures that did not require Association meeting action for manuals at that time. A second edition was formally adopted under NFPA procedures at the NFPA Annual Meeting in 1974. Subsequent editions were adopted in 1979, 1985, and 1990.

This 1993 edition reflects a complete review of the contents of the document and incorporates much new information gained by research at the National Aeronautic and Space Administration during the last 10 years.

## Technical Committee on Oxygen-Enriched Atmospheres

**Bryan J. Coleman,** *Chair*
NASA/Kennedy Space Center, FL

**James H. Chappee,** System Safety Assoc., TX
**Albert L. de Richemond,** Emergency Care Research Inst., PA
**George J. Frankel,** Highland Park, NJ
**James G. Hansel,** Air Products and Chemicals, Inc., PA
**Walter G. Holland,** University of Southern California Medical Center, CA
(Rep. American Hospital Assn.)
**Paul W. Ledoux,** McDonnell Douglas, TX
**Douglas F. Nelson,** Industrial Risk Insurers, CA
(Rep. Industrial Risk Insurers)
**Joel Stoltzfus,** NASA White Sands Test Facility, NM
**Frederick Williams,** U.S. Naval Research Laboratory, DC
**Gerald L. Wolf,** SUNY/HCSB, NY
(Rep. Brooklyn Anesthesiology Research Corp.)
**Robert Zawierucha,** Praxair, Inc., NY

### Alternate

**Douglas S. Erickson,**
American Hospital Assn., IL
(Alt. to W. G. Holland)

**Burton R. Klein, PE,** NFPA Staff Liaison

*This list represents the membership at the time the Committee was balloted on the text of this edition. Since that time, changes in the membership may have occurred.*

NOTE: Membership on a Committee shall not in and of itself constitute an endorsement of the Association or any document developed by the Committee on which the member serves.

**Committee Scope:** This Committee shall have primary responsibility for documents on the fire and explosion hazards that may exist in oxygen-enriched atmospheres. The Committee will correlate its work with the Committee on Health Care Facilities and other related NFPA committees as required.

# Contents

# NFPA 53

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# Fire Hazards in Oxygen-Enriched Atmospheres

## 1994 Edition

Note: Footnotes within each chapter appear at the end of each chapter.

## Chapter 1 Introduction and Definitions

**1-1 Introduction.** The phenomenon known as "fire" is a chemical reaction between a fuel and oxygen. The initiation and rate of the reaction is subject to the laws of chemical reaction kinetics. In particular, the reaction is affected by the concentrations of the reactants.

In most fire hazard environments, the concentration of oxygen is controlled at a reasonably constant value due to its availability only from air at atmospheric pressure. Therefore, fire researchers and fire protection engineers have concerned themselves primarily with those reaction parameters that are related to the nature of the fuel.

The earliest experience with oxygen-enriched atmospheres and the resulting need to consider the effect of an increased oxygen availability for the reaction was possibly in tunnel and caisson work. The available oxygen was increased because the air environment was compressed. Even though the available nitrogen was also increased and the proportions of oxygen and nitrogen remained unchanged, an overall increase in hazard (expressed in terms of an increase in ease of ignition and rate of combustion) was reportedly evidenced. However, the problem was apparently of minor consequence, as NFPA 243, *Construction and Tunnel Operations* (adopted in 1937 and subsequently withdrawn from publication) made no mention of it.

With the appearance of compressed oxygen cylinders and piping systems in the late 1800s, the fire behavior of both organic and inorganic materials in 100 percent oxygen at high pressures was studied at length in configurations inherent in such equipment. Because of the presence of oxygen-enriched atmospheres in diving chambers and submarines, the U.S. Navy has studied the problem in detail for many years.

One of the earliest treatments of the fire hazards in oxygen-enriched atmospheres (aside from the internals of oxygen systems) was the NFPA recommended practice titled, NFPA 565, *Anesthetic Gases and Oxygen in Hospitals*, which was adopted in 1934. This covered oxygen tents and included a section titled "Oxygen Chambers." The document was superseded by NFPA 56F, *Nonflammable Medical Gas Systems*, which, however, did not cover oxygen chambers. The so-called oxygen chamber (which contained an oxygen-enriched atmosphere at atmospheric pressure) apparently either was used for inhalation therapy or was the ancestor of the modern hyperbaric chamber.

Current coverage of the fire hazards of oxygen-enriched atmospheres is contained in the following chapters of NFPA 99, *Standard for Health Care Facilities*:

Chapter 2 — "Definitions"
Chapter 4 — "Gas and Vacuum Systems"
Chapter 8 — "Gas Equipment"
Chapter 12 — "Hospital Requirements"
Chapter 13 — "Ambulatory Health Care Center Requirements"
Chapter 19 — "Hyperbaric Facilities."

Requirements also are included in NFPA 99B, *Standard for Hypobaric Facilities*.

In 1965, the NFPA was approached by groups engaged in the design, manufacture, and operation of space cabins as possible sources of data or other assistance.

The NFPA Board of Directors recognized a similarity in the problems associated with various applications and believed that all involved would benefit by a coordinated study. Accordingly, the Committee on Fire Hazards in Oxygen-Enriched Atmospheres, as it was first called, was organized.

The authorized Scope of this committee at that time was "to prepare a manual and such other material as may be necessary for guidance relating to the fire and explosion hazards that may exist in oxygen-enriched atmospheres." The committee has coordinated its work with the Committee on Health Care Facilities and other related NFPA committees and has been of material assistance to other NFPA committees.

This guide is intended to provide a source of broad, general information on hazards in oxygen-enriched atmospheres to aid in the recognition of the problem and its solution. It does not contain specific recommendations, as these are more properly the subject of study by groups concerned with specific applications of oxygen-enriched atmospheres.

Starting with a discussion of where and how oxygen-enriched atmospheres may be encountered (intentionally or unintentionally), a number of examples of fire and explosion incidents are then described to illustrate the number and variety of problems that have been experienced. The fundamentals of ignition and combustion, as influenced by their occurrence in oxygen-enriched atmospheres, are discussed in Chapter 4. These are followed by a detailed discussion of the basic behavior of many materials that have been considered for use in these atmospheres. Chapter 6 attempts to relate the basic behavior of materials to their end-use configuration as components of mechanical and electrical systems. Finally, problems of fire detection and control in oxygen-enriched atmospheres are discussed.

### 1-2 Definitions.

**Activation Energy.** The minimum energy that colliding fuel and oxygen molecules must possess to permit chemical interaction.

**Auto or Autogenous Ignition Temperature.** See Ignition Temperature.

**Combustible Material.** The fuel involved in combustion.

**Combustion.** A complex sequence of chemical reactions between a fuel and an oxidant accompanied by the evolution of heat and, usually, by the emission of light.

**Concentration.** The ratio of the amount of one constituent of a homogeneous mixture to the total amount of all constituents in the mixture.

**Deflagration.** Rapid combustion without the generation of a shock wave.

**Detonation.** Extremely rapid combustion resulting in the generation of a shock wave in the combustible mixture.

**Flame Propagation Rate.** (1) The velocity with which the combustion front travels through a body of gas, measured as the highest gas velocity at which stable combustion can be maintained; (2) the velocity at which combustion travels over the surface of a solid or liquid.

**Flammable.** Capable, when ignited, of maintaining combustion under the specified environmental conditions.

**Flammable Limits.** The minimum and maximum concentration of fuel vapor or gas in a fuel vapor or gas/gaseous oxidant mixture (usually expressed as percent by volume) defining the concentration range (flammable or explosive range) over which propagation of flame will occur on contact with an ignition source. The minimum concentration is known as the lower flammable limit (LFL) or the lower explosive limit (LEL). The maximum concentration is known as the upper flammable limit (UFL) or the upper explosive limit (UEL).

**Flash Point.** The minimum temperature of a liquid or solid at which it gives off vapor sufficient to form an ignitible mixture with a gaseous oxidant (i.e., oxygen) near the surface of the liquid or solid under specified environmental conditions.

**Fuel.** Any material that will maintain combustion under specified environmental conditions.

**Gas Anesthesia Apparatus.** An item of equipment used to administer inhalation anesthesia, and including a source of oxygen and anesthetic gas(es), flow meters and flow control valves, vaporizers, ventilators, rebreathing bag, carbon dioxide absorber, and appropriate tubing, mask, and connectors.

**Hyperbaric.** Pressure greater than ambient.

**Hyperbaric Oxygenation.** The administration of oxygen by inhalation to a patient who is enclosed in a pressure chamber and is exposed during the oxygen therapy to pressures greater than ambient atmosphere.

NOTE: This technique is employed to treat certain severe infections and carbon monoxide poisoning and as an adjunct to certain types of surgical procedures and radiation therapy.

**Hypobaric.** Pressure less than ambient.

**Ignition Energy, Minimum.** The minimum energy required to ignite a flammable mixture; usually the minimum energy of an electric spark or arc expressed in joules.

NOTE: The minimum ignition energy is different for different flammable mixtures and varies with the concentration, temperature, and pressure, as well as the geometry and material, of the sparking or arcing electrodes.

**Ignition Temperature.** The minimum temperature required to initiate or cause self-sustaining combustion independently of the heating or heated element. Ignition temperatures are commonly reported as the autogenous ignition temperature (AIT), autoignition temperature (AIT), or spontaneous ignition temperature (SIT).

NOTE: Spontaneous ignition temperature (SIT) should not be confused with temperatures associated with the spontaneous heating or combustion phenomenon that certain highly oxidizer-receptive materials undergo.

**Lean Mixture.** A fuel and oxidizer mixture having less than the stoichiometric concentration of fuel.

**Lower Flammable Limit or Lower Explosive Limit.** See Flammable Limits.

**Oxidant.** A chemical compound that supports combustion.

NOTE: Examples of oxidants include nitrous oxide, nitric oxide, chlorates, and chlorine.

**Oxidation.** For purposes of this guide, reaction with oxygen either in the form of the element or in the form of one of its compounds.

**Oxygen.** A chemical element that, at normal atmospheric temperatures and pressures, exists as a colorless, odorless, and tasteless gas.

NOTE: Oxygen comprises about 21 percent by volume of the earth's atmosphere.

**Oxygen-Enriched Atmosphere (OEA).** An atmosphere in which the concentration of oxygen exceeds 21 percent by volume or the partial pressure of oxygen exceeds 160 torr (millimeters of mercury), or both.

**Pressure.** The force per unit of area. Values in this guide are based on the unit of pressure derived from the International System of units (SI), which is the pascal or newton per square meter ($N/m^2$).

NOTE 1: A newton is that force that causes a mass of 1 kilogram to accelerate 1 meter per second per second.

NOTE 2: 1 atmosphere = 33 feet of water (39.2°F) = 14.7 pounds per square inch (psi) = 760 millimeters of mercury (0°C) (mm Hg) = 760 torr = 101,325 newtons per square meter ($N/m^2$) = 101,325 pascals.

**Pressure, Absolute.** The total pressure being measured.

NOTE: Absolute pressure equals gauge pressure plus atmospheric pressure.

**Pressure, Gauge.** Pressure measured with reference to atmospheric pressure.

NOTE: Gauge pressure equals absolute pressure minus atmospheric pressure.

**Respiratory Therapy.** The treatment of respiratory, circulatory, and allied disorders with oxygen and other gases and various medicaments.

**Resuscitation, Pulmonary, Oxygen.** The ventilation of a nonbreathing patient with oxygen, automatically or manually, to reestablish voluntary breathing.

**Rich Mixture.** A fuel and oxidizer mixture having more than the stoichiometric concentration of fuel.

**Spontaneous Ignition Temperature.** See Ignition Temperature.

**Stoichiometric Mixture.** A balanced mixture of fuel and oxidizer such that no excess of either remains after combustion.

**Upper Flammable Limit or Upper Explosive Limit.** See Flammable Limits.

**Ventilator.** An item of equipment used to assist or control the breathing of a patient.

NOTE: Ventilators are often used with an oxygen-enriched atmosphere and nitrous oxide.

## Chapter 2 Utilization of Oxygen-Enriched Atmospheres

(*Footnote to Chapter 2 can be found at the end of the chapter.*)

### 2-1 General.

**2-1.1** Oxygen is a clear, colorless, odorless, and tasteless gas comprising about 21 percent of the atmosphere of the earth. It supports combustion and is necessary for plant and animal life. The concentration of oxygen available in the atmosphere generally is sufficient for human needs during normal conditions of health and for most combustion applications. However, in the treatment of disease, in special types of fuel combustion, and in some chemical processes, an oxygen-enriched atmosphere is necessary. In addition, oxygen-enriched atmospheres are employed for life support in closed environmental systems. This chapter describes some of these applications as a basis for considering the extent of application of oxygen-enriched atmospheres, the fire hazards associated with their use, and the methods for eliminating or controlling those hazards.

**2-1.2** The degree of fire hazard of an oxygen-enriched atmosphere varies with the concentration of oxygen present, the diluent gas, and the total pressure. An oxygen-enriched atmosphere is defined as any atmosphere in which the concentration of oxygen exceeds 21 percent by volume or the partial pressure of oxygen exceeds 160 torr (millimeters of mercury), or both. In most commonly encountered oxygen-enriched atmospheres, an increased fire hazard is produced by the increased partial pressure of oxygen (as, for example, in an atmosphere of compressed air) or by the absence of the diluting effect of an inert gas (as, for example, in pure oxygen at a pressure of one-fifth atmosphere). An oxygen-enriched atmosphere does not, however, by definition produce an increased fire hazard. Certain oxygen-enriched atmospheres can exhibit combustion-supporting properties similar to ambient air, while others are incapable of supporting the combustion of normally flammable materials (a decreased fire hazard). The latter case can frequently arise under hyperbaric conditions when the volumetric percentage of oxygen is significantly reduced in a nitrogen or helium mixture, even though the partial pressure of oxygen is equal to or greater than 160 torr (for example, a 4 percent oxygen mixture in nitrogen or helium at a total pressure of 12 atmospheres will not support the combustion of paper even though the partial pressure of oxygen is 365 torr). A similar condition (i.e., a reduced fire hazard) can exist at very low hypobaric pressure, even though the volumetric percentage of oxygen is significantly high.

**2-1.2.1** Table 2-1.2.1 compares units of pressure to altitude above, or depth below, sea level. It also shows the partial pressure of oxygen in a rarefied or compressed air atmosphere.

**Table 2-1.2.1 Partial Pressure of Oxygen in a Rarified or Compressed-Air Atmosphere**

| Total Absolute Pressure | | | Altitude Above or Depth Below Sea Level | Partial Pressure of Oxygen if Atmosphere Is Air | Concentration of Oxygen if Partial Pressure of Oxygen Is 160 mm Hg or torr |
|---|---|---|---|---|---|
| Atmospheres | mm Hg or torr | psia (kPa) | Meters (Feet) Air or Sea Water | mm HG or torr* | % by Volume |
| ⅕ | 152 | 2.9 (20) | 11,735 (38,500) | 32 | 100.0† |
| ⅓ | 253 | 4.9 (33.8) | 8,832 (27,500) | 53 | 62.7† |
| ½ | 380 | 7.3 (50.3) | 5,486 (18,000) | 80 | 42.8† |
| ⅔ | 506 | 9.8 (67.6) | 3,353 (11,000) | 106 | 31.3† |
| 1 | 760 | 14.7 (101.4) | Sea Level | 160 | 20.9 |
| 2 | 1,520 | 29.4 (202.7) | -10 (-33) | 320† | 10.5 |
| 3 | 2,280 | 44.1 (304.1) | -20 (-66) | 480† | 6.9 |
| 4 | 3,040 | 58.8 (405.4) | -30 (-99) | 640† | 5.2 |
| 5 | 3,800 | 73.5 (506.8) | -40 (-132) | 800† | 4.2 |

* This column shows the increased available oxygen in compressed air atmospheres.

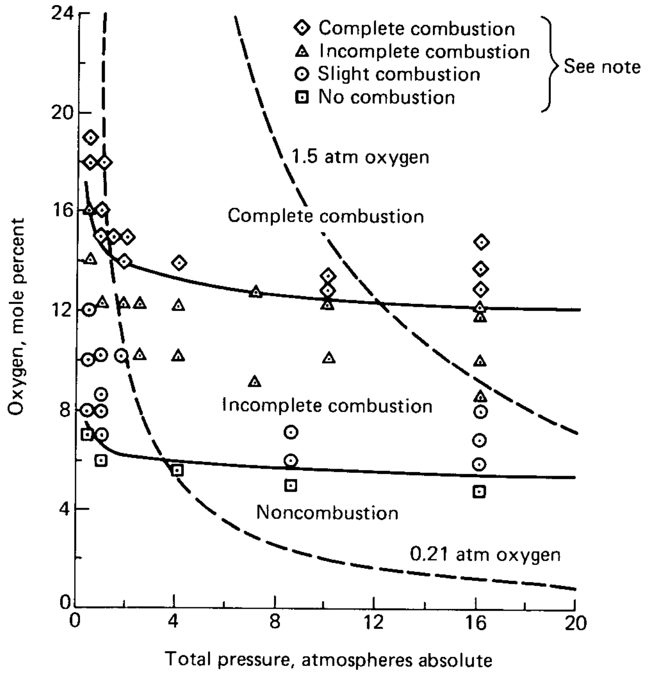
† Oxygen-enriched atmosphere.

**2-1.2.2** Figures 2-1.2.2(a) and (b) depict three combustion zones for vertical filter paper strips in hyperbaric mixtures of oxygen-nitrogen and oxygen-helium, respectively. Those combinations of oxygen concentrations and total pressure lying above the 0.21 atm oxygen partial pressure isobar (lower dashed line) are, by definition, oxygen-enriched atmospheres, but they could be located in any of three zones: noncombustion, incomplete combustion, or complete combustion.

**2-1.3** Oxygen-enriched atmospheres routinely exist or are utilized intentionally in medical practice, industry, underwater tunneling and caisson work, space and deep sea exploration, and in commercial and military aviation. Such atmospheres are inherent to oxygen processing, transport, and storage facilities. Oxygen-enriched atmospheres may develop inadvertently at any time when oxygen or compressed air is transported, stored, or utilized.

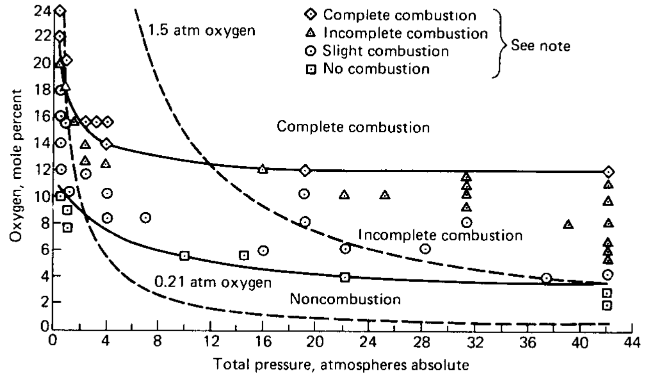
**2-1.4** Oxygen is stored either in its liquid state or as a compressed gas. Compressed gas storage pressures are variable and may be as high as 51,712 kPa (7500 psig). The density of oxygen in such conditions is high, and the fire hazard within pressure-containing components is greatly increased.

**2-1.4.1** Liquid oxygen is the most concentrated common source of oxygen. Contamination of liquid oxygen with most organic substances often renders the mixture subject to violent explosion.



NOTE: *Complete Combustion:* The filter paper strip burns completely. *Incomplete Combustion*: The filter paper strip burns for a length greater than 1 cm (2.54 in.) from a resistance wire igniter, but the flame extinguishes itself before the strip is completely consumed. *Slight Combustion*: The filter paper strip flames or smolders but does not burn more than 1 cm (2.54 in.) from the resistance wire igniter. *No Combustion*: No ignition.

**Figure 2-1.2.2(a) Illustration of varying degrees of combustion in an oxygen-nitrogen OEA (*see 2-1.2.2*).**[1]



**NOTE:** *Complete Combustion:* The filter paper strip burns completely. *Incomplete Combustion*: The filter paper strip burns for a length greater than 1 cm (2.54 in.) from a resistance wire igniter, but the flame extinguishes itself before the strip is completely consumed. *Slight Combustion*: The filter paper strip flames or smolders but does not burn more than 1 cm (2.54 in.) from the resistance wire igniter. *No Combustion*: No ignition.

**Figure 2-1.2.2(b) Illustration of varying degrees of combustion in an oxygen-helium OEA (*see 2-2.3*).**[1]

**2-1.4.2** Most common textile materials, including clothing, that become contaminated with oxygen are susceptible to rapid combustion. Certain specialized materials, such as glass fabric, are not susceptible to combustion in oxygen-enriched atmospheres. Other special materials burn less rapidly than common textiles in oxygen-enriched atmospheres. (*See Chapter 5.*)

**2-1.4.3** Whenever liquid oxygen is exposed to materials at ambient temperatures, rapid warming and evaporation of the liquid take place. Oxygen-enriched atmospheres are created around and within the materials upon which the liquid is spilled.

**2-1.5** Nitrous oxide, a stable, nontoxic oxide of nitrogen, is employed widely for medical and industrial uses. As a gas, nitrous oxide is useful as a mild anesthetic agent. It also is used as a combustion-enhancing agent in racing vehicles. In industry, nitrous oxide is used as a propellant for a variety of aerosol products. It is used as a liquid refrigerant for the rapid freezing of certain food products.

NOTE: An oxygen-enriched atmosphere may develop in situations in which nitrous oxide is employed.

**2-1.6** The use of other oxidants, such as chlorine, chlorates, nitric oxide, and ozone, may result in enhanced combustion. Appropriate safety literature, such as material safety data sheets, should be reviewed.

## 2-2 Processing, Transport, Storage, and Dispensing of Oxygen.

**2-2.1** Preparation of oxygen conventionally involves the compression of air, followed by cooling and reexpansion, that is repeated until the temperature of the air falls below the oxygen's critical temperature, causing it to liquefy. Fractional distillation of the liquid air then separates its various gaseous components. The oxygen is collected and may be stored as a compressed gas or as a liquid. Oxygen is also separated from air by adsorption and membrane-based systems.

**2-2.2** Oxygen is transported to the consuming facility as a compressed gas or as a liquid, or it is transmitted by pipeline. NFPA 50, *Standard for Bulk Oxygen Systems at Consumer Sites*, covers these applications.

**2-2.2.1** Transport of liquid oxygen to the site of the consuming facility is usually in cryogenic tank trucks. Spillage of liquid oxygen during transport, or transfer from the tank, can create oxygen-enriched atmospheres.

**2-2.3** When gaseous oxygen is dispensed at the consuming facility, it is drawn from the storage container(s) through pressure-reducing regulators and interconnecting piping.

**2-2.3.1** Leakage or venting of oxygen from any storage or dispensing equipment can create an oxygen-enriched atmosphere. (*See 2-8.1.*)

**2-2.4** Contamination of any pressure-containing component of an oxygen storage or dispensing system with any flammable or combustible substance, such as oil, grease, flammable solvents, dust, lint, or any organic substance, may produce a serious fire or explosion hazard.

**2-2.5** Consult NFPA 50, *Standard for Bulk Oxygen Systems at Consumer Sites*, for the installation of storage systems.

## 2-3 Medical Applications.

**2-3.1** Oxygen-enriched atmospheres have been associated with inhalation anesthesia since the development, in 1887, of a gas anesthesia apparatus incorporating means of administering oxygen and nitrous oxide. The use of such a machine allows for both the anesthetization of patients and the often necessary administration of high oxygen concentrations. The use of a flammable volatile liquid or gaseous inhalation anesthetic agent in such an atmosphere, however, creates severe fire and explosion hazards. Prior to the formation of the NFPA Committee on Health Care Facilities, a significant number of fatalities and injuries resulted from operating room fires and explosions. Such incidents have been drastically reduced through widespread adherence to the provisions of 12-4.1 of NFPA 99, *Standard for Health Care Facilities.*

The reduction in use of flammable anesthetics in operating rooms has allowed for increased use of potential ignition sources (electrosurgical units, lasers, etc.). Advances in materials-science have also introduced polymers (endotracheal tube) and fabrics (drapes and gowns) that are flammable in the oxygen-enriched atmosphere of operating rooms. Therefore, the operating room environment continues to present fire hazards.

**2-3.2** Since the turn of the century, the therapeutic value of oxygen in the treatment of respiratory and allied disorders has been recognized by the medical profession. In consequence, inhalation therapy, including ventilator-support of patients, currently is practiced widely. Most hospitals of larger size are equipped with central piping systems for oxygen for use in patient care facilities throughout the hospital. The NFPA, recognizing the potential hazards of oxygen-enriched atmospheres created by such use, published NFPA 56F, *Nonflammable Medical Gas Systems,* and NFPA 56B, *Respiratory Therapy,* both of which are now part of NFPA 99, *Standard for Health Care Facilities.*

**2-3.2.1** Since ambulatory as well as hospital patients may require respiratory therapy, some patients purchase or rent therapy equipment, oxygen cylinders, oxygen concentrators, and liquid oxygen containers for use in their homes. Thus, the medical applications of oxygen-enriched atmospheres are not limited to locations within hospitals. Chapter 13, "Ambulatory Health Care Center Requirements," of NFPA 99, *Standard for Health Care Facilities,* covers nonhospital use.

**2-3.3** Ambulances, rescue squads, fire and police vehicles, and swimming pools are often equipped with oxygen for resuscitation and life-support purposes. Use of oxygen in such an enclosed space may create a hazardous oxygen-enriched atmosphere.

**2-3.4** The medical profession uses pressure chambers to allow hypersaturation of patients with oxygen. The patient, with or without attendants, is placed in a chamber that then is sealed and pressurized, sometimes to 4 atmospheres absolute or greater. Generally, pressurization is accomplished with compressed air, and the patient breathes pure oxygen from a mask. However, in some single-occupant (patient only) chambers, the atmosphere is pure oxygen. Although there might be some flammability-inhibiting effect of the increased nitrogen present in compressed air, this effect is more than offset by the increased partial pressure of the oxygen present (up to 5 atmospheres). (*See Chapter 19, "Hyperbaric Facilities," of NFPA 99, Standard for Health Care Facilities.*)

**2-3.4.1** A particularly hazardous oxygen-enriched atmosphere exists in a chamber pressurized with oxygen or in a compressed air chamber with inadequate ventilation when pure oxygen is spilled from the therapy apparatus.

## 2-4 Industrial Applications.

**2-4.1** Oxygen, as an industrial gas, is in widespread use in a variety of industries. Furthermore, its use continues to increase in new applications where additional environmental or service conditions may place severe demands on equipment, materials, and systems. Elevated temperatures, high corrosivity, and reduced contamination levels are examples of factors, in addition to flammability, that need to be considered, because they could limit materials selection options for oxygen services in advanced applications.

**2-4.2** In the petrochemical industry, large quantities of oxygen are utilized for partial oxidation of gaseous and liquid organics and coal to prepare other products. These include alcohols, aldehydes, and syngases. Elevated temperature stability and corrosion resistance, in addition to oxygen compatibility, which need to be considered, also could limit the use of certain alloys that are resistant to ignition and combustion in oxygen.

**2-4.3** In the steel industry, oxygen is used to refine steel in the basic oxygen furnace as well as to lance molten steel in several operations. Oxy-fuel burners are used to reheat ingots and slabs and to preheat ladles. Oxy-fuel burners are also used in glass furnaces. Generally, materials selection issues and operating practices have been well-defined in the steel industry.

**2-4.4** In the metal fabrication industry, oxy-fuel burners are used to weld, cut, braze, silver-solder, and harden various metals. This work is done in large and small factories, automobile repair shops, and in home workshops. NFPA 51, *Standard for the Design and Installation of Oxygen-Fuel Gas Systems for Welding, Cutting, and Allied Processes;* NFPA 51B, *Standard for Fire Prevention in Use of Cutting and Welding Processes;* and ANSI Z49.1, *Safety in Welding and Cutting,* cover such applications.

**2-4.5** In the mining industry, oxygen is used to refine copper, gold, and other metals by means of pressure oxidation processes where sulphurous "refractory ores" are mined. Elevated temperatures and severe corrosivity place severe limitations on materials selection options.

**2-4.6** Oxygen, as an alternative to air, is widely used for secondary treatment of both municipal and industrial wastewaters. Ozone from oxygen is sometimes used as an intermediate or for tertiary water treatment. Increased corrosivity may be experienced in certain wastewaters that contain both oxygen and ozone. Ozone will aggressively attack certain nonmetallics.

**2-4.7** Further developments in hazardous waste disposal include incineration involving oxygen-enriched atmospheres and wet oxidation where supercritical water is used to dissolve and oxidize hazardous species. Supercritical wet oxidation is a particularly challenging environment for structural materials since it involves high temperatures, high pressures, and corrosive species.

**2-4.8** Ultra-high purity (UHP) oxygen is used to manufacture microchips in the semiconductor industry. The necessity to eliminate contaminants to reduce chip defects results in ultraclean systems that reduce the tendency towards promoted ignition-combustion scenarios. However, the presence of UHP oxygen may increase the flammability hazard with certain metals and nonmetallics. Aluminum alloys are a prime example of materials that show a dramatic increase in flammability when exposed to UHP oxygen (99.999+%). (*See 5-3.4.4.*)

**2-4.9** The paper and pulp industry uses extensive amounts of oxygen in the bleaching and delignification processes as an alternative to chlorine. The use of ozone in this industry may also increase. Materials selection issues are similar to those encountered in various other processes where oxygen and aqueous environments are involved.

**2-4.10** As a result of new technologies, the oxygen concentration of systems originally designed for air may be increased by a few percent to increase efficiency. Such systems, which might not have been cleaned initially for oxygen service or designed with oxygen-compatible or combustion-resistant materials, may be unique. They should be treated on an individual basis with respect to issues such as cleaning, filtration, degree to which the oxygen levels are increased, etc.

**2-4.11** Oxygen fireflooding is an example of a tertiary enhanced oil recovery process that has been pilot-tested. Oxygen is injected at high pressures into heavy oil deposits that cannot be recovered by primary or secondary oil recovery techniques. Downhole combustion of heavy oil results in high temperatures, high corrosivity when water is present, but also increased oil mobility, allowing recovery at collection wells. Oxygen fireflooding requires careful system design and special operating procedures for the safe production of heavy oils.

**2-4.12** In many applications, the motivation to use oxygen is driven by at least one of many factors, including:

(a) Higher combustion temperatures;

(b) Higher purity gaseous product (no nitrogen from air);

(c) Higher output from a given size reactor (often in conjunction with debottlenecking a process);

(d) Higher conversion efficiency;

(e) Reduced combustion emissions ($NO_X$ emissions may be reduced without the nitrogen from air); and

(f) Previously unobtainable production from mineral or oil deposits.

Service environments may limit or eliminate the use of many materials that can be selected on the basis of combustion resistance in oxygen-enriched atmospheres. Experimental programs might be needed to optimize materials selection and systems design problems in advanced oxygen applications for safe operation.

**2-4.13** Large users of oxygen are generally supplied by a pipeline from a nearby oxygen plant that uses cryogenic distillation. Smaller user requirements may be met by liquid oxygen that is transported by truck to a storage tank at the site, from a membrane or adsorption oxygen generator at the site, or from high pressure cylinders. Requirements for system design, materials selection, cleaning, safe operation, etc., are well-established for oxygen supply systems.

**2-5 Caisson Work and Underwater Tunneling.** Where driving a tunnel under or setting a foundation on a river bed, it may be necessary to seal off the work area with an airtight compartment and elevate the air pressure therein to prevent the pressure of the overlying water from inundating the compartment with mud or water. For every 10 m (33 ft) of depth of water outside the compartment, the pressure therein needs to be raised one atmosphere to compensate (*see Table 2-1.2.1*). An oxygen-enriched atmosphere exists within the compartment while it is pressurized.

## 2-6 Space and Deep Sea Exploration.

**2-6.1** Liquid oxygen is employed as the oxidizer in liquid propellant rockets, and gaseous oxygen is used in the breathing atmospheres of spacecraft and spacecraft simulators. Oxygen-enriched atmospheres also exist in certain deep sea diving equipment.

**2-6.2** Liquid-fueled rockets employ liquid oxygen as the oxidizing agent. Oxygen-enriched atmospheres can, and generally do, develop from blow-off and leakage whenever the rocket is tanked or while it is standing in readiness.

**2-6.2.1** Oxygen-enriched atmospheres may develop inside underground missile silos.

**2-6.3** The practice of using aviator breathing oxygen (ABO) for spacecraft life-support systems has been the norm in the past and may be required in the future for long-duration missions. Previous space programs, such as Gemini, Mercury, and Apollo, used an ABO atmosphere in life-support systems. An oxygen-enriched atmosphere is currently used in the space shuttle program. During normal operations, the orbiter oxygen concentration can reach as high as 25.9 percent oxygen due to calibration margins in the control and caution/warning systems. Prior to each extra vehicular activity (EVA), the orbiter atmosphere is changed to a 30 percent oxygen atmosphere at 10.2 psia (70.3 kPa). This 30 percent oxygen atmosphere is used for 6 to 10 hours prior to the actual EVA to precondition the crew for the space suit environment of 34.5 kPa (5 psia) 100 percent ABO atmosphere.

**2-6.3.1** The space station is designed to operate at 70.3 kPa (10.2 psia) with a 30 percent oxygen atmosphere until it is permanently manned. The current schedule is for the space station to be manned tended (manned only when a shuttle is docked) for the first 5 to 6 years of operations. Once the space station is permanently manned, it is expected to operate at one atmosphere with up to 25 percent oxygen concentration. The space station will have a hyperbaric chamber to treat the bends if necessary. This chamber will be operated at 4 atmospheres at 21 percent oxygen concentration and used only in an emergency.

**2-6.3.2** The oxygen concentration on the spacecraft can be increased by leakage in the primary oxygen supply system or the emergency oxygen system. This has occurred in the orbiter cabin several times over the years. A leak in one of the systems caused the cabin oxygen concentration to reach 35 percent for a few hours. Once the leaks were found and corrected, the oxygen concentration was reduced to normal limits within a short time.

**2-6.4** Experimental and conventional deep sea diving equipment, including pressure chambers, will contain an oxygen-enriched atmosphere if the partial pressure of oxygen exceeds 160 torr.

### 2-7 Commercial and Military Aviation.

**2-7.1** All high altitude commercial aircraft of moderate and large size are equipped with emergency oxygen breathing systems for use in case of failure of equipment to maintain normal cabin pressure during flight. All military high performance aircraft are equipped with similar systems for routine use. Pressure within the components of such a system range from 12,411 kPa to 15,169 kPa (1800 psig to 2200 psig) in storage cylinders and from 103 kPa to 483 kPa (15 psig to 70 psig) in the dispensing system.

**2-7.1.1** Use of such a system during flight may result in the development of an oxygen-enriched atmosphere at the site or sites of such use. Where use is routine, as in military applications, proper personnel indoctrination and the exercise of proper precautions tend to mitigate the frequency of incidents. However, in commercial aircraft, safety demands that the "no smoking" provisions be rigidly enforced during system use.

**2-7.2** Oxygen-enriched atmospheres can develop in or around aircraft during servicing of oxygen systems. Chapter 3, "Aircraft Breathing Oxygen Systems," of NFPA 410, *Standard on Aircraft Maintenance*, covers this application. In general, proper personnel indoctrination and the exercise of proper precautions tend to mitigate the frequency of incidents.

**2-7.2.1** Contamination of an aircraft oxygen system with oil, grease, or any flammable or combustible substance will create a hazardous situation.

**2-7.3** Oxygen is more soluble in aircraft fuel than nitrogen. If such fuel is exposed to air for a significant interval, enough oxygen may dissolve in the fuel and come out of the solution (as gaseous oxygen) during flight because of the decreased atmospheric pressure, creating a hazardous oxygen-enriched atmosphere.

### 2-8 Inadvertent Utilization.

**2-8.1** An inadvertent oxygen-enriched atmosphere may be created because of improper design, malfunction, or improper use of oxygen storage or dispensing equipment. Leakage of oxygen from, or improper use of, such equipment can create an oxygen-enriched atmosphere, especially if the equipment is stored or used in a confined or poorly ventilated space. Such an atmosphere is especially dangerous because personnel might not be aware that oxygen-enrichment exists.

**2-8.1.1** An oxygen-enriched atmosphere may be created inadvertently by the use of oxygen to ventilate closed compartments, either intentionally or because of a mistaken belief that the terms "oxygen" and "air" are synonymous.

**2-8.1.2** An oxygen-enriched atmosphere could develop inadvertently if an oxygen stream were employed in lieu of compressed air to clear sawdust or metallic chips from wood or metalworking equipment.

**2-8.1.3** An oxygen-enriched atmosphere may be created inadvertently within insulation on piping and equipment containing materials at temperatures below the condensation temperature of oxygen (e.g., liquid hydrogen or nitrogen) if the oxygen in atmospheric air is condensed within the insulation.

**2-8.1.4** An oxygen-enriched atmosphere may be created inadvertently within a vented storage vessel containing liquid air due to the preferential evaporation of nitrogen.

Footnote to Chapter 2

[1]Dorr, V. A. "Fire Studies in Oxygen-enriched Atmospheres." *J. Fire and Flammability*, Vol. 1, 1970, pp. 91-106.

## Chapter 3 Fire Experience

*(Footnotes to Chapter 3 can be found at the end of the chapter.)*

### 3-1 Introduction.

**3-1.1** This chapter is a compilation of reports of fires and explosions involving both intentional and inadvertent oxygen-enriched atmospheres that have been reported to the NFPA.

**3-1.2** This compilation is by no means a record of all such incidents that have occurred. Many incidents are not reported to the NFPA or even to local authorities.

**3-1.3** The purpose of this chapter is to present examples that illustrate the common manner in which ostensibly diverse circumstances result in similar accidents. Because the sources of data vary, the NFPA cannot guarantee the accuracy of the reports. However, each report has been subjected to expert review by the Committee on Fire Hazards in Oxygen-Enriched Atmospheres and is believed to be consistent with present theory.

### 3-2 Utilization of OEA.

#### 3-2.1 Oxygen Production, Transportation, and Transfer.

**3-2.1.1** A reciprocating oxygen transfer pump, operating at 6,895 kPa (1000 psi), had nitrogen seals in the crosshead section to prevent contamination of oxygen with lube oil from crankcase or crosshead areas. A seal(s) failed and there was an explosion within the pump, projecting parts as far as 91 m (300 ft). Loss estimate — $20,000.

**3-2.1.2** Explosion and fire occurred in the filter of high pressure oxygen pump equipment. The equipment was used for charging inhalation and self-contained breathing equipment oxygen cylinders. It was concluded that the explosion was due to the presence and burning of an oxidizable material in the bottom of the filter. The oxidizable material might have been glycerine that was used for lubricating the pump.

**3-2.1.3** An explosion, believed to have been initiated in a hydrocarbon buildup in the reboiler of an oxygen column, destroyed the column. The column, 30 m (99 ft) high and varying in diameter from 11 m to 6.7 m (36 ft to 22 ft), was insulated in a fine granular and noncombustible material. The adjacent insulation silo was also destroyed. Loss estimate — $830,000.

**3-2.1.4** Due, probably, to excess wear on Teflon® rider rings on a compressor piston rod, lubricating oil escaped into an oxygen cylinder, where ignition occurred. Steel and brass parts were consumed or damaged in the fire, while a sudden release of high pressure oxygen out of the suction manifold and into the building caused steel walls to buckle or blow out. A deluge system protected a 373-kW (500-hp) synchronous motor. Loss estimate — $125,000.

**3-2.1.5** There have been several incidents involving vacuum-insulated liquid oxygen (LOX) tanks and pipelines in which palladium oxide getter packets used for vacuum maintenance have been implicated as an ignition source. The function of palladium oxide, as it is used in vacuum maintenance, is to react with off-gassed hydrogen to form water. Over a period of time, the palladium oxide may be reduced to finely divided palladium metal or palladium hydride.

If LOX is suddenly introduced into a vacuum by failure of a structural joint, the reduced palladium oxide might undergo an exotherm, which could ignite the superinsulation. A recommended solution is to make certain that palladium oxide is suitably encapsulated within a heat sink to ensure that the exotherm does not accelerate if LOX is inadvertently introduced into the vacuum space.

**3-2.1.6** A seismic survey vessel with an estimated cost of $1,250,000 was destroyed and three individuals were killed as a consequence of an incident involving a 7,570.8 L (2000 gal) LOX tank carried on board the ship for seismic experiments. Investigation concluded that excessive force applied to a valve stem sheared the stem collar. The internal tank pressure was approximately 413.7 kPa (60 psig.)

An oxygen cloud spread over the ship. There was no shortage of combustibles. Steel deck plates were embrittled and cracked. Several flashes preceded an explosion. The precise ignition source is unknown. During the post-accident investigation, questions were raised about the system maintenance, personnel awareness of the oxygen hazards, and the absence of fail-safe back-up shutoff valves.

**3-2.1.7** A 4,921-L (1300-gal) aluminum LOX tank truck exploded shortly after a delivery at a customer's tank. Two individuals were killed. The explosion occurred shortly after one of the individuals reported that a submerged transfer pump was not working properly. Improper bearing lubrication and pump reversal due to improper maintenance procedures were possible causes of the pump failure. Approximately eight pounds of aluminum from the pump were consumed. All submerged pumps were removed from service and replaced with external pumps.

**3-2.1.8** A LOX tank truck exploded after making a delivery to a hospital. Two individuals were killed. Approximately 73.5kg (162 lb) of aluminum were consumed and contributed to the intensity of the explosion. The definitive cause of the accident was not firmly established. It is believed that various factors contributed to contaminant buildup; this provided a kindling chain, causing a further participation of aluminum in the scenario.

### 3-2.2 Medical.

**3-2.2.1** Improper maintenance of a device used with oxygen led to this fire. A humidifier was used alongside a two-year-old child's crib fitted with an oxygen tent. There were indications of low water in the humidifier, failure of its thermal safety feature, and of fire originating in its blower, feeding on accumulated dust and lint. The flames were blown into the oxygen tent, where the little girl was burned to death.

**3-2.2.2** A patient in a semiprivate room awoke and saw the oxygen tent on the other bed afire. He set off the alarm, but the patient in the tent could not be rescued before he died. Extensive investigation failed to reveal positively the source of ignition, but a cigarette butt was found on the bed table as well as the remains of a book of matches in the victim's bed.

**3-2.2.3** A pressure regulator, which had been in service for some time, had just been disconnected from a cylinder and connected to another cylinder to maintain oxygen to an infant's incubator oxygen tent. When the cylinder valve was turned on, the regulator components ignited and rapid burn-through occurred. The infant was killed and five persons were injured in the resulting flash fire. Adiabatic compression ignition in the regulator was the probable cause of this fatal fire.

NOTE: Other well-documented cases suggest that shock, friction, or compression heating from the sudden opening of a high pressure oxygen valve can cause ignition of valve or regulator components without intervention of foreign combustibles. Regulators should always be in the closed position (fully backed-off) when opening valves on oxygen cylinders.

**3-2.2.4** A tracheotomy was being performed on a 33-year-old ventilator-dependent woman with multiple medical problems, anesthetized with intravenous agents, and ventilated with 100 percent oxygen via a polyvinylchloride endotracheal tube passed through her mouth into her trachea. Fifteen minutes after the anterior neck incision, and during the use of electrocautery, a loud "pop" was heard followed by a fire in the surgical field. Moist towels were used to extinguish the fire, and the charred endotracheal tube that had ignited was replaced with a tracheotomy tube. Examination revealed a burn of the trachea. The patient tolerated the remainder of the procedure well but died one month later from underlying multiple medical problems.[1]

**3-2.2.5** During a tonsillectomy on a four-year-old boy under approximately 50 percent oxygen, 50 percent nitrous oxide, and 1 percent halothane general anesthesia, fire "blow-torched" from the mouth. The fire was extinguished by a combination of deluge with saline solution and cessation of the flow of oxygen-enriched atmosphere caused by occlusion of the charred polyvinylchloride (PVC) endotracheal tube, which was immediately replaced. The patient's burns of the tongue, pharynx, and trachea were managed in an intensive care unit, and he was discharged five days later. Ignition of the PVC tube occurred during electrocauterization of bleeding vessels adjacent to the tube in the oxygen- and nitrous oxide-enriched anesthetic atmosphere.[2]

**3-2.2.6** A fifty-six-year old man with a vocal cord polyp was anesthetized with 66 percent nitrous oxide, 33 percent oxygen, and up to 1.5 percent isoflurane for surgical resection of the polyp using a $CO_2$ laser. The anesthetic gases were administered via an endotracheal tube, specifically manufactured for $CO_2$ laser surgery, consisting of a silicone rubber shaft externally coated with a silicone rubber layer containing metal particles. After excision of the polyp and during control of vocal cord bleeding using the laser, smoke emerged from the mouth, flames emerged from the endotracheal tube, and flames were noted within the tubing of the anesthesia breathing circuit. The flames were extinguished with saline solution, and the burned endotracheal tube was replaced. The patient suffered extensive burns of the trachea and bronchi, from which he eventually recovered.

Examination of the burned endotracheal tube revealed combustion of the cuff, which had been filled with saline solution to isolate the anesthetic gases within the breathing circuit and lung, and combustion of the distal shaft. The $CO_2$ laser had most likely perforated the cuff and then ignited the silicone rubber in the oxygen and nitrous oxide-enriched atmosphere.[3]

**3-2.2.7** The use of a dry gauze pad in an oxygen-enriched atmosphere led to a fire in the incision site. A gauze pad was placed in the incision site during a lung resection. The dry pad was being used to blot blood from the tissues. At the time when the fire occurred, an electrosurgical unit (ESU) was being used to cauterize a bleeder immediately next to the gauze. The lung lobe had already been resected, and oxygen was flowing out of the resected area, enriching the operative site. The oxygen enriched the gauze and allowed it to be easily ignited by the ESU. The burning gauze pad was thrown to the floor and extinguished without any apparent injury to the patient.[4]

**3-2.2.8** The creation of an oxygen-enriched atmosphere, caused by an open oxygen source, allowed this fire to occur. A patient was having several skin lesions removed from her right breast. She had been given a tranquilizer and was being given oxygen with a face mask at a flow rate of approximately 4 L/min (1.06 gal/min). The surgeon had initially removed a lesion from her neck without incident. The window in the surgical drape was then moved down toward her right breast. This area was prepped in the usual fashion with an iodine solution, and the incision site was anesthetized with a local anesthetic. During use of the ESU, the surgeon stated that a spark flew from the operative site toward the edge of the surgical drape.

The method of flame propagation in this case is not absolutely clear, but surface-fiber flame propagation was involved. Two possibilities are likely:

(a) The nap fibers on the reusable drape burned, or

(b) The patient's fine body hair burned and rapidly spread the fire under the surface of the drape toward the patient's face.

The fire then ignited the oxygen mask and resulted in some minor burns to the patient's face and neck.[5]

**3-2.2.9** An oxygen-enriched atmosphere, created by the presence of oxygen and nitrous oxide, allowed easy ignition of facial hair. A patient was undergoing oral surgery with general anesthesia maintained through a nose mask with a concentration of 25 percent oxygen, 75 percent nitrous oxide, and a small percentage of halogenated anesthetic. The patient had a moustache. As the surgeon was grinding a filling with a tungsten-carbide bur, an incandescent spark flew from the bur and arced out of the patient's mouth, over his upper lip, and landed in his moustache. Because of the oxygen- and nitrous oxide-enriched atmosphere, the moustache immediately burst into flame and ignited the nasal mask. The fire then flashed back toward the anesthesia machine along the gas delivery hoses. As soon as the fire was noticed, the nasal mask was removed from the patient's face, but not before significant burning of his nose and upper lip had occurred.[6]

**3-2.2.10** Improper use of an oxygen concentrator caused this face fire. A patient requiring oxygen therapy was at home using an oxygen concentrator with a nasal cannulae. While grinding metal in his shop, grinding sparks ignited the nasal cannulae. He pulled the tubing from his face and was slightly burned in the incident.[7]

### 3-2.3 Cutting and Welding.

**3-2.3.1** A gunsmith in a sporting goods store was loosening the connections on a used oxygen cylinder, part of a welding outfit, with greasy hands and a wrench. A mechanical spark ignited the grease in the oxygen-enriched atmosphere, burning the gunsmith on the hands and arms and starting a fire in the store. Loss estimate — $100,000.

**3-2.3.2** A pressure gauge, previously used to test the pressure in a hydraulic system, was subsequently installed on an oxygen system and exploded when the system was turned on. The chief mechanic received facial cuts when the gauge exploded in his face.

**3-2.3.3** A construction pipe fitter/welder received severe second- and third-degree burns of the face and neck when a welding spark ignited his clothing and the oxygen-fed sandblaster's hood that he was wearing. The employee was working in a small tunnel where there was little air circulation. On his own initiative, he obtained a sandblaster's hood, fabricated of heavy plastic, and connected that air line directly to a tank of oxygen.

The employee was working in a prone position when a spark ignited his clothing and, following the stream of oxygen, the flame flared up inside the hood, igniting the hood and his clothing. His presence of mind in holding his breath until the hood was removed may have saved his life, and, without question, his eyes were saved by the goggles he was wearing.

**3-2.3.4** A workman was welding in an open ditch where the nature of the work required that he wear an air-line respirator. Because no respirable compressed air was readily available, an oxygen tank with a pressure reducing and regulating valve was attached to the inlet end of his air-supply hose. A spark from the welding came in contact with the facepiece, which, of course, was surrounded with oxygen-enriched air from the exhalation valve. The facepiece virtually exploded on the workman's face, killing him immediately.

**3-2.3.5** A welder and his helper entered a 0.91-m (36-in.) diameter conduit that ran horizontally for 3 m (10 ft), then angled downward 6.1 m (20 ft), terminating in a 3-m (10-ft) horizontal section against a closed bulkhead. A standpipe from this last 3-m (10-ft) section to the surface was used to admit compressed air for ventilation. Unknown to the welders, when the compressed air supply was exhausted, a cylinder of oxygen was connected to the standpipe, and the conduit was ventilated with pure oxygen. The welder's clothing was ignited and began to burn furiously. The helper managed to escape. The welder was found cremated in his protective suit.

**3-2.3.6** An employee was performing cutting operations with an oxyacetylene torch in a sewer while wearing demand-type breathing equipment connected by a hose line to a supply cylinder of compressed air on the surface. While he was using the torch, his facepiece (of the full-face type) began to burn at the top edge. He immediately pulled the facepiece off, but the mask was burning so intensely that it burned his hands.

Although the supply cylinder was painted gray and labeled "Breathing Air," investigation disclosed that the cylinder was filled with oxygen, not air.

Apparently, there was leakage of oxygen around the periphery of the mask, and a spark ignited the upper edge of the mask, which, under the influence of escaping oxygen, began to burn intensely. When the mask was removed, the high flow of oxygen (the employee had opened the bypass valve on his regulator to provide a constant flow to the mask) caused the entire mask to burst into intense flames.

### 3-2.4 Industrial Processing.

**3-2.4.1** Fluctuations in oxygen concentration in an ethylene-oxygen reactor feed stream were noticed. After determining that there were no obvious abnormalities in the oxygen plant operation, two successive adjustments were made by the plant operators. An explosion or detonation followed immediately, simultaneously involving the oxygen gas holder, the second stage oxygen compressor, the oxygen-ethylene mixing nozzle, and connected piping. Ensuing fire in discharged ethylene was controlled by plant personnel with hose streams. Automatic deluge sprinkler protection was effective in controlling damage to equipment not in the immediate fire area. Production interruption of five weeks cost $300,000, and damage was estimated at $350,000.

**3-2.4.2** An electrical failure caused a reducing valve to open in an oxygen plant, permitting oxygen to enter a nitrogen stream to an ammonia plant. While the valve was being repaired, compressors were allowed to idle, maintaining pressure against a closed valve in the contaminated nitrogen stream. After 3½ hours, the piping ruptured when oxygen reacted with hot lubricating oil. The explosion caused damage to condensers, coolers, and piping, while fire damage to the refrigeration equipment, nitrogen scrubbing unit, pipe trestle, and other equipment was extensive. Loss estimate — $485,000.

**3-2.4.3** A small explosion and fire occurred in a 152-mm (6-in.) liquid nitrogen fill and bypass line that was insulated with 127 mm (5 in.) of polyurethane foam. The reaction originated at an elbow and ran lengthwise in the insulation along the piping on either side. The fire extinguished itself. This particular section of piping had been in a cool-down condition followed by a warm-up.

The subsequent investigation concluded that a breakdown of the vapor barrier permitted air to penetrate the insulation, and the oxygen in the air was liquefied inside at cryogenic temperatures. A localized oxygen-enriched atmosphere was created within the insulation when this liquid oxygen evaporated. The actual cause of ignition was not established.

### 3-2.5 Laboratories.

**3-2.5.1** A high pressure oxygen valve ruptured, discharging oxygen gas and metal debris on 300-volt DC power cables. The debris broke the insulation, causing arcing, and insulation then ignited in the oxygen-enriched atmosphere. Another account states that the cable short-circuited to the oxygen pipe, burning a hole in the pipe. In either event, the wood roof ignited, and it was necessary to summon the fire department. Steelwork and copper in the cables also burned, and the laboratory was heavily damaged. Loss estimate — $160,000.

**3-2.5.2** During a routine test on a heat exchanger in a rocket engine testing laboratory, a break occurred in a liquid oxygen line. Oxygen intermingled with fuel that had previously been wasted into a floor drain. The resulting mixture was ignited by hot surfaces, damaging equipment and metal partitions. Loss estimate — $65,000.

**3-2.5.3** A fire occurred in a liquid-to-gaseous oxygen recharger assembly that converted low-pressure liquid oxygen to high-pressure, ambient temperature gaseous oxygen. During operation of the assembly, a stainless steel rupture disk in a recharger assembly burst, and an oxygen fire ensued that destroyed large portions of the assembly. Analysis of the fire revealed that the rupture disk failed at nearly 21 MPa (3000 psia) below the design burst pressure, probably due to mechanical fatigue. It is postulated that the fire was caused by particle impact downstream of the rupture disk or by frictional heat generated from the disk fragments being extruded through the outlet fitting of the rupture disk housing.

**3-2.5.4** A fire occurred in a stainless steel body regulator containing a fluoroelastomer diaphragm. The 28 MPa (4000 psia) oxygen in the dome and body was not flowing at the time of ignition. It was postulated that the ignition occurred due to a leak beyond the seal between the diaphragm and the body. The fire propagated from the diaphragm to the body, destroying the regulator and other parts of the system.

**3-2.5.5** A fire occurred during the first use of a newly installed mechanical impact test system that had been cleaned for oxygen service. After a test sample had been installed in the test chamber, it was purged with oxygen at less than 0.3 MPa (50 psia). The remotely operated test chamber pressurization valve was opened, initiating the flow of 41 MPa (6000 psia) oxygen into the chamber. Immediately, the technician reported that there was a "slight explosion and sparks flying all over the test cell," and a "huge brown cloud" was observed coming from the test cell. The investigation revealed that a manually operated metering valve located between the high pressure oxygen pressurization valve and the test chamber had ignited and burned. The metering valve was heavily eroded internally, and the valve port nearest to the chamber was burned out. The fluid piping line from the metering valve to the test chamber was burned. It appeared that the fire originated in the seat area of the metering valve. It was surmised that lubricant or a particle had ignited during passage through the metering valve. As a result of this fire, the practice of performing a vigorous inert gas purge was implemented to remove assembly-generated contaminants prior to pressurization of a system with oxygen.

### 3-2.6 Space.

**3-2.6.1** A Titan missile in a silo was being defueled when a leak in the liquid oxygen line was detected. The liquid oxygen infiltrated the adjacent equipment silo through a utility tunnel. It is thought that a spark from some of the equipment ignited combustibles in the oxygen-enriched atmosphere, causing a fire in the equipment silo and a subsequent explosion of fuel in the missile silo. Fortunately, all workers were safely evacuated before the explosion, although some were injured by smoke inhalation. Loss estimate — $7,186,000.

**3-2.6.2** A fire in the two-man space environment simulator at Brooks Air Force Base, Texas, occurred on January 31, 1967. An animal experiment underway in the chamber involved investigation of the hematopoietic effects of exposure to 100 percent oxygen. Environmental conditions in the chamber at the time of the fire were approximately 100 percent oxygen at 380 mm Hg [50.7 kPa (7.35 psia)]. The simulator was built and equipped with materials of low combustibility, but large quantities of paper, inorganic litter, and other highly combustible materials were brought into the chamber for use in animal experiments. The chamber occupants were wearing combustible clothing. A portable electric light with an ordinary two-wire cord had been brought into the chamber. Shorting of this cord on the metal floor of the chamber is believed to have been the ignition source. The animals' fur caught fire, and their movement helped to spread the fire. The two airmen occupants of the chamber at the time of the fire were fatally burned, even though the chamber was repressurized with air and opened within approximately 30 seconds subsequent to initiation of the fire. The fire extinguishing equipment in the chamber at the time of the fire consisted of two, small, portable, manually operated carbon dioxide extinguishers, neither of which were used, although one overheated and discharged through the pressure relief valve.

**3-2.6.3** On January 27, 1967, three astronauts died as a result of a fire in an Apollo spacecraft command module on the launch pad at Kennedy Space Center, Florida. The atmosphere in the spacecraft was 100 percent oxygen at approximately 110 kPa (16 psia).

The origin or ignition source of the fire was not definitely determined in spite of an extremely intensive investigation. The most probable source of ignition was thought to be an anomaly associated with the spacecraft wiring. The extent of damage to the vehicle prevented final determination. The fire was propagated through the spacecraft by materials that were not considered significantly flammable in a normal air atmosphere but that were very flammable in the 100 percent oxygen, 110 kPa (16 psia) atmosphere.

The propagation rate of the fire, while quite rapid in its initial stages, was even greater after the pressure in the spacecraft built up and ruptured the vehicle wall.

Large amounts of heavy smoke seriously hindered and slowed rescue attempts; however, it was believed that the fatalities occurred during the first 30 seconds of the conflagration.

The investigative board concluded that the conditions that led to the disaster included:

(a) A sealed cabin, pressurized with an oxygen atmosphere.

(b) An extensive distribution of combustible materials in the cabin.

(c) Vulnerable wiring carrying spacecraft power.

(d) Vulnerable plumbing carrying a combustible and corrosive coolant.

(e) Inadequate provisions for the crew to escape.

(f) Inadequate provisions for rescue or medical assistance.

**3-2.6.4** During a space cabin experiment performed at an altitude of 10,058 m (33,000 ft) [26.2 kPa (3.8 psia)] with 96 percent oxygen, a power tube in the cabin TV monitor overheated. The "resin" base of the tube ignited and hot plastic dripped out of the chassis onto the coolant lines passing beneath. These coolant lines were covered with insulation of as yet undetermined composition. The lines did not catch on fire. Fumes from the hot resin affected the cabin crew. The mission was aborted without further damage to cabin or crew. Instead of focusing attention on the hazards of fire, the accident provided a false sense of security. The fact that neither the molten resins nor the Ruberoid insulation flamed violently in 100 percent oxygen gave the investigators more confidence in the safety of this potentially hazardous environment than they had prior to the incident.

**3-2.6.5** The same chamber under the same atmosphere conditions described in 3-2.6.4 was being used to study temperature control factors in pressure suits and cabins. Two subjects were dressed in pressure suits with closed helmet visors. One subject had both the inlet and outlet of his suit connected to the heat exchanger. The other subject had only the inlet side of the suit connected to the heat exchanger and was actually asleep when the fire broke out. The fire was not detected by the sight or smell of smoke. The crewman saw a glow behind the instrument panel. Within several seconds, the rear of the panel was ablaze. The crewman who was asleep awoke when the fire alarm went off and, for some reason, opened the visor of his helmet. He inhaled the fumes issuing from the blazing panel. The other crewman, who had his visor closed and both inlet and outlet air hoses attached to the heat exchanger, inhaled none of the cabin fumes directly. Both subjects reportedly lost consciousness. The crewman wearing the open visor suffered respiratory tract damage, probably from the direct inhalation of fumes. His pulmonary function later returned to normal. The crewman wearing the closed visor suffered no apparent respiratory tract damage, even though he remained in the chamber longer (2 to 3 minutes after he noticed the glow) than the crewman wearing the open visor. Neither subject experienced clothing or body burns. The fire was extinguished with difficulty by means of a carbon dioxide device.

The exact cause of the fire was not determined. The glow appeared at the back of the instrument panel where the wiring passed behind an access panel. The panel was not hinged (as first reported by rumor) but was opened by a "Dzus fastener." The flexion of wires "at a hinged edge of the panel" was evidently not, as previously reported, responsible for the fire. The wires were in a 24- to 26-volt circuit. The circuit breaker or fuse system was operative when checked after the fire. There were apparently no obvious sites of defective circuitry. Damage by the fire, however, probably obscured any subtle defect that might have been responsible. The wire insulation was of polyvinyl plastic and was probably the major source of fuel. The Ruberoid insulation covering the coolant pipes also caught fire. The electrical insulation behind the instrument panel was totally burned.

During the experiment, the vapors in the cabin were being sampled in a cryogenic trap. The vapors and fumes generated during the fire were thus studied by both gas chromatography and infrared spectroscopy. The following compounds were new or had levels above those ordinarily present in the cabin: benzene, diazomethane, ethyl ether, formaldehyde, inorganic isocyanates, acetylene, methyl chloride, and ethyl chloride. The isocyanates were thought to come from the Ruberoid insulation on the coolant pipes. No polyurethane diisocyanate foams were reported to have been on fire, though the Ruberoid might well have contained this plastic as a component. It is of interest that no burning of hydrogen chloride or phosgene was reported, since pyrolysis of polyvinyl chloride has been shown to produce these materials. It is possible, of course, that the screening tests were not able to detect these materials. It is not known how sophisticated a fire safety analysis was performed on the materials that were used in the cabin.

**3-2.6.6** During the launch preparation of an Apollo spacecraft, liquid oxygen was flowed through portions of the pumping system and discharged into a drainage ditch approximately 12 m (40 ft) wide and 1.5 m (5 ft) deep. The purpose of this operation was to precool the pumps and piping in the LOX storage area preparatory to vehicle LOX loading.

Shortly after precooling was completed, two security cars arrived in the area, the drivers having completed their final security check of the area. The driver of the first car drove his vehicle about 3 m (10 ft) past the gate, turned the engine off, got out, and walked back to stand beside the second car, which the driver had moved forward to the middle of the gate. The driver of the second car noted that his engine went dead when he came to a stop; he therefore turned off the ignition and remained in his seat. A third security car driver arrived about 6 minutes later and parked about 3 m (10 ft) behind the second car. His engine also died as the vehicle came to a stop. He remained in the car. At that time, the driver of the second car turned his ignition on. A distinct "pop" was heard, smoke began issuing from the hood, followed by flames shortly thereafter. The driver of the first car ran to move his vehicle away from the flames; however, on reaching it, he noted a distinct glow under the front of the car and concluded that it was already on fire (it was not fully daylight at the time). The third car burst into flames at about the same time.

Statements by the drivers indicate that when they first arrived at the gate there was little fog visible. However, by the time the fires had started, the fog had increased to a dense layer approximately 0.9 m to 1.2 m (3 ft to 4 ft) deep.

Several measurements of oxygen concentration in the area were made by safety personnel 30 minutes to an hour after the fire, using a portable oxygen analyzer. The results indicated a concentration of approximately 75 percent to 100 percent just inside the cloud; however, the concentration dropped to normal (21 percent) just outside the visible edge of the cloud.

The fog persisted for over 2 hours. Weather conditions were calm, with winds ranging from 0 to 0.1 km/s (0 to 4 mph) at ground level. A marked temperature inversion was recorded, and some natural ground fog was noted.

The mechanisms whereby the fires were ignited were probably complex, and at least two different mechanisms appear to have been involved. Discussions with automotive engineers indicate that small quantities of gasoline vapor from the carburetors and fuel pumps are vented under the hoods of most cars. Other combustibles present included oil and grease on the external surfaces of the engines and small quantities of hydrogen from the batteries. Vapors are continuously swept from the engine compartment and, therefore, probably do not reach hazardous concentrations while the vehicle is moving and the fan is in operation. After engine shutoff, however, vapors tend to accumulate. The amount of gasoline required to provide a combustible mixture throughout the engine compartment is approximately 0.1 L (4 oz). However, since the vapors probably form largely at one or two points (the carburetor, the fuel pump, or both) and expand in all directions from those points, the amount required to provide a flammable mixture in the area of the exhaust manifold would be only a few grams.

Information from several sources indicates that outer surfaces of the exhaust manifold commonly reach temperatures in excess of 315°C (600°F) during operation. Sparking of relays and brushes is normal during start-up and operation. These considerations suggest that even in a normal environment there exists a definite potential for ignition to occur. (In fact, such instances are not rare. Seven vehicle fires per month have been reported in a city of approximately 45,000.) Any increase in the oxygen concentration in this environment results in an increased potential for ignition. Thus, the minimum spark energy required for the ignition, the flash point, and the autoignition temperatures is decreased substantially. The fuel concentration corresponding to the upper flammability limit is increased; however, this may not be significant. The lower flammability limit is not appreciably affected, but the flame propagation rate is increased.

In this incident, it appears that a flammable mixture of oxygen and hydrocarbons accumulated under the hoods of the three cars while they were parked with the engines off. In the case of the second car, this mixture was probably ignited by a spark that resulted from turning on the ignition key. In the case of the other two cars, ignition probably took place spontaneously when the concentration of the oxygen/hydrocarbon mixture in contact with the hot surface of the exhaust manifold reached some critical value. The fact that all three cars underwent similar phenomena rules out the possibility of a freak accident.

**3-2.6.7** A space shuttle extra-vehicular mobility unit (spacesuit and life-support backpack) was destroyed in a flash fire during a functional test in the Johnson Space Center's crew systems laboratory (*see Figure 3-2.6.7*). A technician, who was standing next to the suit, received second-degree burns over his upper body in the accident. It was determined that the fire originated in an aluminum-bodied regulator/valve assembly when 41 MPa (6000 psi) oxygen was released through the valve into the regulator. It was postulated that the fire was caused by:

(a) The rupture of a thin, internal section of the aluminum body;

(b) The ignition of a silicone O-ring by compression heating of the oxygen; or

(c) Particle impact.

As a result of the post-fire investigation, the regulator/valve assembly was redesigned and the aluminum in this assembly was replaced with Monel®. This change and several others were implemented in the version of the suit that is in use today.

### 3-2.7 Aircraft Oxygen Systems.

**3-2.7.1** It is thought that a short circuit in the battery of a Beech C-45 in a hangar ignited fuel leaking from the line supplying the heater in the nose of the plane. An aluminum fitting was melted off the oxygen control panel, allowing oxygen to be fed into the fire. The aluminum then burned, including the top of the gasoline tank. Fire spread to five other small planes after causing nylon draw curtains separating the planes to fail. The fire department was handicapped by a shortage of hydrants. Loss estimate — $177,000.

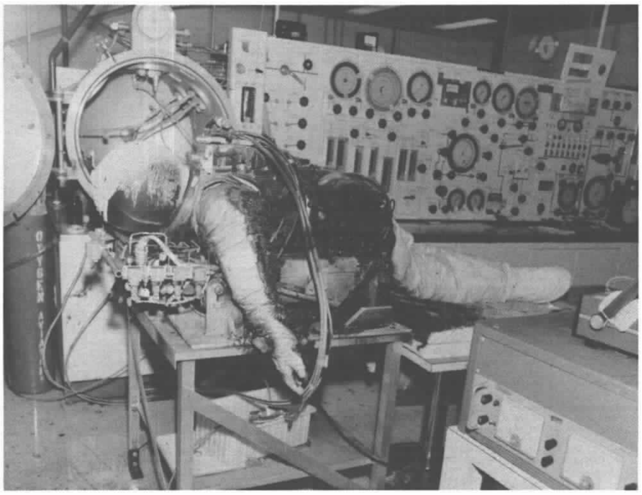


**Figure 3-2.6.7 A fire occurred in which this space suit was destroyed. No one was in the suit at the time of the fire.** ***(Photo courtesy of NASA/Johnson Space Center)***

**3-2.7.2** While an inspector was opening an oxygen valve in the cockpit of a jet transport parked in an aircraft maintenance dock, a fire of unknown cause occurred at the valve. Adiabatic compression downstream of the valve was possibly responsible for ignition of valve components, or the fire might have been caused by an impurity in the system. Escape of oxygen and burning particles resulted in a "cutting-torch-like" action that burned through the aircraft cabin soundproofing insulation and the fuselage skin directly above the valve, damaging surrounding crew compartment equipment. The hangar dock's deluge sprinkler system operated, and carbon dioxide hand extinguishers, followed by dry chemical from a 2.54-cm (1-in.) hose line, extinguished the interior fire.

**3-2.7.3** In January of 1984, the Royal Australian Air Force experienced a ground fire that destroyed a six million dollar P3B Orion aircraft. The incident occurred during removal of an onboard oxygen cylinder, one of three that supplied the flight crew. Examination of the aircraft's oxygen system revealed that the fire had initiated in an oxygen manifold check valve assembly. The primary cause of the incident was a leaking poppet valve, which allowed oxygen stored at 12 MPa (1800 psia) to escape to the atmosphere. Deterioration of the silicone rubber seal and galvanic corrosion are believed responsible for the valve failure. Contributory causes to the fire were system contamination and failure to bleed the oxygen system before cylinder disconnection. A thermite reaction involving the aluminum check valve housing, metal particles, and metal oxide was thought to be the most likely cause of ignition. Investigators' findings indicate the need to consider using materials other than silicone rubber in oxygen systems. It was also determined that further investigation into the ignition of aluminum and other materials by metal particle impingement in the presence of metal oxides in a high-pressure oxygen environment is required.[8]

**3-2.7.4** An aircraft burned while parked at a passenger loading gate. A preflight check was being made by the flight engineer. He turned on the aircraft oxygen system, and fire started immediately thereafter behind the coatroom. An oxygen valve in this area apparently sustained fatigue failure, and the escaping oxygen impinged directly on glass wool insulation, resulting in ignition of the resin of the insulation. Since it was not possible to shut off the oxygen supply, the fire was accelerated by the addition of gaseous oxygen to the fire area.

Several employees tried to fight the fire from the interior of the aircraft with portable fire extinguishers but were unsuccessful. Airport fire fighters responded to the fire using a foam nozzle and 6.35-cm (2½-in.) fog lines before extinguishment could be secured, but major damage had been caused, and the aircraft was written off as a total loss.

**3-2.7.5** A B-66 crew circled for more than 2 hours to reduce their fuel load. One of the crewmen removed his mask and lit a cigarette. Immediately after returning the lighter to his breast pocket, the mask and helmet ignited.

The mask and helmet were removed and flung to the deck where the fire was snuffed out using a hand extinguisher. The pilot suffered second- and third-degree burns on his face and hands. Evidence indicated that either a spark from the cigarette or momentary contact with the flame of the lighter ignited the helmet and mask, which still contained a high concentration of oxygen.

**3-2.7.6** The fuselage of a Boeing 707 was gutted by fire that started while the crew's oxygen system was being checked during a ground preflight inspection. The fire spread, intensified by the oxygen escaping from service piping in the passenger compartment, but the fire department used foam to good advantage through openings that the fire had made in the roof, and through a cabin window, until extinguishment was achieved 1½ hours after the fire started.

**3-2.7.7** An airman removed the oxygen regulator from the cockpit of an F2H-4 for a routine check. Instead of disconnecting the bottles, he removed the oxygen supply line from the regulator and capped it with a check valve and cap.

At the same time, an electrician was troubleshooting a voltage regulator discrepancy in the cockpit, and the battery was not disconnected.

Because of the small working area in the cockpit, the airman removed his bulky jacket and closed the canopy to keep warm. While the oxygen supply line was being disconnected and capped off, a quantity of oxygen apparently escaped into the closed cockpit. As the airman removed the regulator from the console structure, it contacted the terminals; the resulting arcing ignited combustible material in the cockpit and the flash fire was supported by the high concentration of oxygen.

The airman opened the canopy, dove out, and rolled on the ground to extinguish his burning clothes and hair. He suffered first- and second-degree burns of the upper body. The airplane was damaged extensively.

**3-2.7.8** At a military base, an order was issued for inerting fuel manifold lines with nitrogen. An experienced technician who had performed the same operation many times before was assigned to the job. Because he needed assistance, he selected a helper and ordered a nitrogen cart. The lines from the cart were connected to the aircraft, at which time another crew arrived to relieve the first crew for lunch.

Minutes later, a tremendous explosion rocked the aircraft; of the four men working on the task, the only one to survive was the man who was thrown from the cockpit by the explosion.

The cylinders on the cart were prominently stenciled "Oxygen." This, as well as the color of the bottles (green instead of gray), went unnoticed. The result was that oxygen under high pressure was injected into lines that had just previously been drained of combustible fuel.

**3-2.7.9** A commercial aircraft fire occurred during servicing of the passenger oxygen system. Three crew members, four flight attendants, and twelve passengers were onboard the plane when the fire erupted. All passengers and crew were evacuated safely. Shortly after the preboarding of passengers had begun, a sound, described as a muffled "bang" or "boom," came from an area near the forward galley. Within seconds, thick black smoke started to fill the cabin, and flames began to burn through the forward right side of the fuselage. Witnesses stated that they saw a three- to four-foot flame extending sideways from the fuselage on the forward right side of the airplane. A hole, several feet in diameter, burned through the fuselage, just behind the right, forward-galley service door.

The passenger oxygen system is located in the forward right side of the airplane. The system is composed of two oxygen cylinders, each charged initially to a pressure of 12.8 MPa (1,850 psia). The cylinders supply oxygen through steel tubing to the flow control unit, which reduces the pressure of the oxygen and then controls its flow to the passenger masks. During a preflight inspection of the airplane, a mechanic found that the quantity of oxygen in the cylinders was below the acceptable level and, therefore, changed the cylinders. He said that, as he was about to leave the area, he saw a flash of white light that enveloped the oxygen system flow control unit.

The inspection team from the National Transportation Safety Board concluded that the fire originated in the passenger oxygen system's flow control unit.[9]

### 3-2.8 Deep Sea.

**3-2.8.1** An accident occurred in a chamber with an internal atmosphere of 100 percent oxygen at 34 kPa (5 psia). There were four men in the chamber taking part in experiments.

A light bulb in the ceiling fixture burned out. One man climbed up to replace the bulb. After the bulb was replaced, he heard a "sound like the arcing of a short circuit." A small flame [about 12 mm (1/2 in.) long] was seen coming from an insulated wire in the fixture. The composition of this insulation is still unknown. The man who replaced the bulb requested water but was told to snuff the fire out with a towel. The towel caught on fire and blazed so vigorously that it set the man's clothing on fire. An "asbestos fire blanket" was used to snuff out the clothing fire, but it, too, burst into flames. The asbestos blanket reportedly had an organic filler or coating that "kept the asbestos from flaking off." The clothing of the other men who were using the blanket also caught on fire. The four men received second-degree burns. Carbon dioxide was used to extinguish the fire after evacuation of personnel from the chamber. It was believed that the blanket and towel had been "saturated with oxygen for 17 days and burned much more vigorously than would be expected at sea level conditions."

NOTE: Long-term storage in oxygen does not significantly enhance the combustibility of textile materials. (*See footnote 62, Chapter 5.*)

An interesting aspect of this case is the fact that burning insulation dripped from the light fixture onto a bunk. One crewman tried to snuff out the resulting fire, and "his skin caught on fire." The burns on his hands were "severe" and necessitated treatment for 11 or 12 days in the hospital. The cabin was being vented continuously, and no analysis of the vapors was being performed at the time of the accident.

NOTE: Laboratory experiments suggest that human skin is difficult to ignite in low pressure oxygen.[10] It will burn readily, however, in the presence of other more easily ignitible combustibles, such as grease or molten plastics, which can act as localized ignition sources.

**3-2.8.2** A fire occurred in the inner lock of a heavy steel decompression chamber, the interior surface of which was painted with a navy enamel. The electrical equipment was of ordinary types. The basic chamber wiring was in conduit. The fixed electrical equipment consisted of lights, two air conditioners, two fans, and an intercom. A portable outlet box containing four ordinary receptacles connected to an electrical supply with a heavy-duty rubber cord was provided. A portable motor-operated carbon dioxide scrubber was cord-connected to one of these receptacles.

The scrubber inlet was equipped with a filter containing paper elements that had been dipped in kerosene to remove dust particles from the "air."

In addition to the rubber insulation and the paint, other combustibles included a cotton mattress with plastic cover, at least two pillows, reading matter, toilet paper, and the filter paper (coated with kerosene?) in the scrubber. The two men in the chamber were wearing cotton trunks and cotton terry cloth robes.

At the time of the fire, the inner-lock atmosphere consisted of approximately 28 percent oxygen, 35 percent helium, and 37 percent nitrogen by volume at a pressure of 276 kPa (40 psig) and a temperature of about 26.7°C (80°F).

The chamber contained no fire extinguisher or other fire extinguishing equipment.

The two divers had completed a 2-hour test dive at a simulated depth of 76 m (282 ft), breathing a mixture of 15 percent oxygen and 85 percent helium. During this period, the decompression chamber was prepared with an atmosphere consisting of 30 percent oxygen, 35 percent helium, and 35 percent nitrogen at 296 kPa (43 psig). It was planned to decompress the divers for 8 hours and 42 minutes, with the final hour at 100 percent oxygen at near-normal pressures.

While the men were being transferred from the tunnel to the inner lock, the inner-lock oxygen concentration was decreased. After the door had been closed, the oxygen concentration was 27 percent. Additional oxygen was added in two slugs over a 2- or 3-minute period.

About 3 minutes after entry, a cry was heard over the intercom: "We have got a fire in here." A column of yellow-orange flame about 102 mm (4 in.) in diameter and 0.3 m to 0.6 m (1 ft to 2 ft) high was visible (through a viewing port) issuing from the carbon dioxide scrubber. Very shortly thereafter, a flash engulfed the compartment and smoke prevented further observation.

The pressure in the inner lock jumped to over 758 kPa (110 psig) [indicative of an atmosphere temperature of about 427°C (800°F)]. Rescue was attempted by entering the "igloo" and raising the pressure to equalize with that of the inner lock. The pressure in the inner lock was decreasing because of heat losses and the fact that the fire had consumed enough oxygen to be reduced to a smoldering stage. The two pressures equalized at about 400 kPa (58 psig).

When the two rescuers opened the door to the inner lock, they met a blast of heat, smoke, and gases. The act of opening the door slightly caused oxygen to enter the inner lock, producing further burning.

At 10:06 A.M., the fire department received a call reporting that there had been a fire and that its services were needed in case the fire rekindled. The fire department completed extinguishment with a booster line and about 76 L (20 gal) of water after access to the chamber was made.

The scrubber motor single-phased, the insulation on the electrical supply cord overheated and ignited, and flames spread to the filter. It is not known what the ignition temperature would have been under the existing atmospheric conditions.

The two divers perished, and the two rescuers were injured. Estimated physical damage to the chamber and its equipment amounted to $20,000.

**3-2.8.3** A fire in a decompression chamber, resulting in the death of a diver, was apparently caused by ignition of a cotton shirt hung around a light bulb to reduce the amount of light. The chamber pressure was at an equivalent depth of 9 m (30 ft) with 20 to 28 percent oxygen and the balance in nitrogen. Oxygen had been used during the decompression period by means of an open-loop mask system. The chamber had been ventilated during the use of oxygen, but the precise amount of oxygen enrichment was unknown.

Flammables in the chamber included cellulose, rubber, clothes, the bunk, and sneakers. All flammables were involved a few seconds after ignition.

**3-2.8.4** A dive shop that filled SCUBA tanks had a series of 14 MPa (2000 psia) oxygen bottles manifolded together. The manifold had quick-opening ball valves leading from each of the oxygen tanks. After the system was allowed to bleed down to ambient pressure, a new bottle was added to the system, and the manifold quick-opening ball valve was opened. The high pressure in the bottle caused compression ignition at the first T in the line. The resultant fire did considerable damage to the dive shop equipment and injured an employee.

### 3-2.9 Other.

**3-2.9.1** A diesel-engine shrimp boat had a compressed air starter. Through leakage, the compressed air was lost. The skipper asked a boat hand to bring a cylinder of "air" to start the engine. The boat hand went to a welding shop and secured a cylinder of "air" and a regulator; 68 kg (150 lb) of this "air" was put into the air reserve tank, and the valve was opened. The engine rotated and a blast took place that tore through the solid oak keel. The skipper, 13 m (42 ft) above in the control room, was fatally burned. The deck hand who turned on the "air" was not hurt. The cylinder actually contained oxygen.

**3-2.9.2** A workman, after disconnecting the air supply and exhaust lines from his air-supplied suit and leaving the "controlled atmosphere" room, removed his helmet and lit a cigarette. He then connected what he thought was an air supply line from another room to his suit to flush and cool the suit. His underclothing caught fire, and he received severe burns to the chest, shoulders, neck, stomach, and legs from the combustion of the cotton underwear.

Investigation disclosed that the respiratory air supply to the second room (the line that the workman connected to flush out and cool the suit) actually contained 68 percent to 76 percent oxygen as a result of failure of the air-oxygen mixture control valve.

**3-2.9.3** Five workers were asphyxiated in a fire that flashed through a compartment of a vessel in which they were working. Although the source of ignition is unknown, the inadvertent introduction of oxygen into the compartment obviously contributed to the fire's intensity. The air hose, which the men were using to blow out the ship's suction lines, was connected to an oxygen manifold rather than to an air compressor.

Footnotes to Chapter 3

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## Chapter 4 Fundamentals of Ignition and Combustion in Oxygen-Enriched Atmospheres

*(Footnotes to Chapter 4 can be found at the end of the chapter.)*

### 4-1 General.

**4-1.1** Although considerable technical knowledge of the ignition, flammability, and flame propagation characteristics of various combustible materials (solids, liquids, and gases) exists, this technical knowledge is inadequate in many instances. Thus, valid predictions of the probability of fire initiation or of the consequences of such initiation, even under normal atmospheric conditions, are difficult to make. Most of the specific knowledge relates to premixed gaseous fuel-oxidant combinations because of the obvious advantages of conducting controlled experiments. Unfortunately, most unwanted fires occur under non-premixed conditions. The investigation of the ignition and combustion properties of solid and liquid combustibles is more complex due to the heterogeneity of the reaction mechanisms involved. Thus, much of the available information on the fire properties of liquid combustible materials has evolved empirically, with the specific data reported exhibiting a high degree of test method dependency.

**4-1.2** The application of this knowledge to the assessment of the fire problem in oxygen-enriched atmospheres (OEA) currently is largely qualitative, but OEA generally can be considered more hazardous than normal atmospheric conditions. The general properties of oxygen-enriched atmospheres will be reviewed, and the fundamental aspects of the ignition and combustion properties of gaseous, liquid, and solid materials in such atmospheres will be discussed within these limitations.

### 4-2 Properties of Atmospheres.

**4-2.1** The chemical composition of oxygen-enriched atmospheres can be very different from that of air. Nitrogen makes up slightly more than 78 percent of dry air by volume. Oxygen contributes approximately 21 percent by volume. The other 1 percent is almost entirely argon with very small amounts of other gases, such as carbon dioxide, neon, helium, krypton, xenon, nitrous oxide, methane, ozone, and hydrogen. All or only certain of the constituents may be found in the various oxygen-enriched atmospheres under consideration. The specific properties of these constituents are indicated in Table 4-2.1.

**4-2.2** In addition to the specific chemical composition of a particular atmosphere, pressure, temperature, and volume have a significant bearing on an environment's fire hazard. For an atmosphere of given chemical composition, pressure defines the concentration of oxygen available for initiation of flame reaction. Pressure and volume together define the total quantity of oxygen available for the support of combustion and determine the associated maximum thermal energy yield possible in that particular environment. The heat capacity and thermal conductivity of the atmosphere will affect ignition, the combustion processes, and the temperature and pressure rise occurring during a fire.

### 4-3 Ignition Mechanisms.

#### 4-3.1 General.

**4-3.1.1** Flames involve strongly exothermic reactions between oxidants and fuels, producing combustion products at high temperatures. Temperature, pressure rise, and radiation are the criteria utilized to determine whether ignition has occurred. The initiation mechanisms involved in the flame reaction are complex.

**4-3.1.2** In general, if a fuel molecule and an oxygen molecule are to interact chemically, sufficient energy has to be imparted to these molecules to enable a collision between the two to result in a chemical transformation. The minimum energy that the molecules need to possess to permit chemical interaction is referred to as the activation energy. For most fuel-oxygen combinations, the activation energy is much greater than the average energy of the molecules at room temperature.

**4-3.1.3** An increase in temperature increases the number of molecules with energy equal to the activation energy and increases the reaction rate. As the temperature is further increased, enough fuel and oxygen molecules eventually react with enough additional thermal energy released to enable the combustion reaction to become self-sustaining until one or both of the reactants have essentially been consumed.

**4-3.1.4** The minimum ignition energy for combustion will vary with the type of ignition source, the specific chemical

**Table 4-2.1 Properties of Standard and Oxygen-Enriched Atmopshere Constituents**

| Constituent | Molecular Formula | Molecular Wt. (0 = 16.00) | Melting Pt. °C | Boiling Pt. °C | Density gm/L | Thermal Conductivity X* | $C_p$25°C cal/gm | $\frac{C_p}{C_v}$ |
|---|---|---|---|---|---|---|---|---|
| Nitrogen | $N_2$ | 28.016 | -209.9 | -195.8 | 1.2507 | 62.40 | 0.219 | 1.404 |
| Oxygen | $O_2$ | 32.0000 | -218.8 | -182.96 | 1.4289 | 63.64 | 0.219 | 1.401 |
| Argon | Ar | 39.944 | -189.2 | -185.9 | 1.7828 | 42.57 | 0.124 | 1.568 |
| Carbon Dioxide | $CO_2$ | 44.010 | -56.6<br>5.2ATM | -78.5<br>Subl. | 1.9768 | 39.67 | 0.202 | 1.303 |
| Sodium | Na | | | | | | | |
| or | | | | | | | | |
| Neon | Ne | 20.183 | -248.67 | -245.9 | 0.835 | 115.71 | 0.246 | 1.64 |
| Helium | He | 4.003 | -272.2<br>26ATM | -268.9 | 0.1785 | 360.36 | 1.24 | 1.660 |
| Krypton | Kr | 83.80 | -157.1 | -152.9 | 3.6431 | ≃23 | 0.059 | 1.68 |
| Xenon | Xe | 131.30 | -112 | -107.1 | 5.897 | — | 0.038 | 1.66 |
| Methane | $CH_4$ | 16.04 | -182.5 | -161.5 | 0.7167 | 81.83 | 0.533 | 1.307 |
| Nitrous Oxide | $N_2O$ | 44.016 | -102.4 | -89.49 | 1.997 | 41.45 | 0.2003 | 1.303 |
| Ozone | $O_3$ | 48.0000 | -192.5 | -111.9 | 2.144 | — | 0.1959 | — |
| Hydrogen | $H_2$ | 2.0160 | -257.14 | -252.8 | 0.0898 | 446.32 | 3.41 | 1.410 |

* X = cal/(sec) (cm$^2$) (°C/cm) × $10^{-6}$

nature and physical character of the combustible, and the composition and pressure of the atmosphere. Though most combustion is accompanied by a gas or vapor-phase combustion reaction, certain materials, such as metals, often burn in the liquid phase or solid phase; that is, a condensed phase reaction.[1-5] If the reaction is to continue in the vapor phase, in the case of solids or liquids, sufficient thermal energy first needs to be supplied to convert a part of the fuel to a vapor. In all cases, for the combustion to proceed, the ignition source has to impart energy to the fuel at a faster rate than the fuel loses the energy. The ignition sources of principal concern for oxygen-enriched atmosphere application can be categorized into six types:

(a) Electrical sources, such as electrostatic and break (arc) sparks;

(b) Hot surfaces, such as friction sparks and heated wires;

(c) Heated gases, independent of surfaces, generated by adiabatic compression or jets of hot gas (includes pilot flames);

(d) Exothermic chemical reactions;

(e) Mechanical sources, such as frictional heating and particle impact; and

(f) Laser sources.

### 4-3.2 Effects of Atmosphere Composition and Environmental Pressure and Temperature on Ignition Energy.

**4-3.2.1** Flame initiation energies cannot yet be calculated for various combustibles (solids, liquids, and gases) in environments of differing chemical composition, temperature, and pressure but need to be determined experimentally in each case. It is possible, however, to assess qualitatively the effects of these environmental parameters on the ignition energy requirements using typical electrical and thermal ignition sources.

**4-3.2.2** Figure 4-3.2.2 depicts, in an oversimplified manner, the effects of variations in oxygen concentration and environmental pressure. In general, at a given environmental pressure, the minimum ignition energy varies inversely with the concentration of oxygen. For a fixed volume percent oxygen, the minimum ignition energy varies inversely with the square of the pressure. There exists a minimum pressure below which ignition does not occur. As the temperature of a given system increases, less and less energy is required to ignite the mixture until it reaches a sufficiently high temperature to ignite spontaneously. This minimum temperature is referred to as the autoignition or spontaneous ignition temperature.

### 4-3.3 Effects of Inert Gas on Ignition, Energy, Flammability Limits, and Flame Propagation.

**4-3.3.1** The likelihood of ignition and the rate of flame propagation of a combustible are primarily influenced by the oxygen content of the environment. An inert gas, such as nitrogen or helium, if present in sufficient quantities, provides an obstacle to the effective interaction of fuel and oxygen molecules. Where inert gases are present in sufficient concentrations, ignition cannot be accomplished and a flame will not propagate. Minimum oxygen concentration is also a correlating parameter for another means of preventing combustion. Thus, a minimum amount of oxygen needs to be present for a flame to propagate, regardless of the ratio of fuels and inerts present. For a given fuel gas, triatomic inert gases allow a higher minimum oxygen concentration than diatomic inert gases.

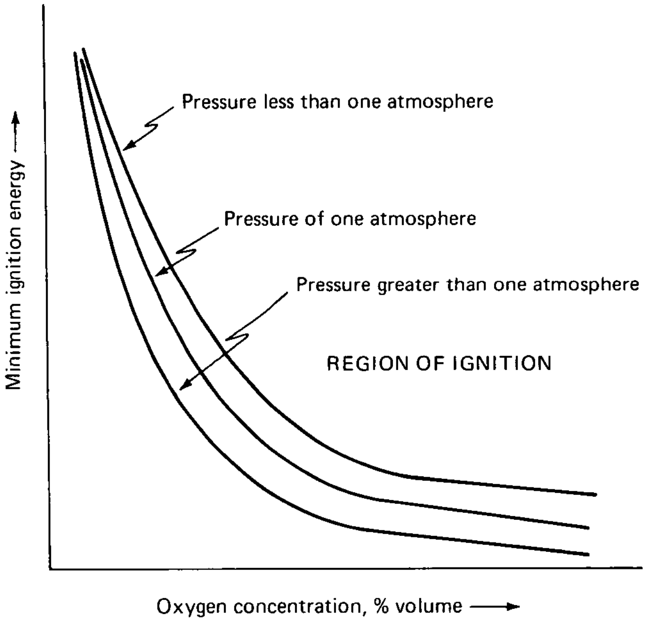

**Figure 4-3.2.2 Minimum ignition energy behavior of combustibles in oxygen-diluent atmospheres at different pressures.**

**4-3.3.2** The specific effect on ignition energy requirements by the typical ignition sources will vary with the particular inert gas selected. This also is true for the flame propagation rate. These effects in certain instances correlate with the heat capacity and thermal conductivity properties of the different inert diluents. For example, the flame propagation rate for a given material in a particular helium-oxygen atmosphere is greater than that in a corresponding nitrogen-oxygen atmosphere because of the higher thermal conductivity and lower heat capacity per equivalent volume of helium.[6]

**4-3.3.3** Once ignited, the likelihood of flame propagation and the rate of propagation of a combustible are primarily dependent on the stoichiometry of the fuel and oxygen, the concentrations of oxygen with the inert gas present, and the velocity of the gas mixture. In general, inert gases vary in their ability to render a mixture nonflammable, with triatomic gases (e.g., $CO_2$, $H_2O$) being more effective than diatomic gases (e.g., $N_2$), which are, in turn, more effective than monatomic gases (e.g., Ar). This trend has been correlated with the heat capacity of the gas, which increases with the structure of the inert gas molecue. Helium is an exception to this trend. Due to its very high thermal conductivity, the flame propagation rate in helium dilation is higher than would be expected by examining heat capacity ranking alone.

## 4-4 Combustion Mechanisms.

### 4-4.1 General.

**4-4.1.1** Combustion is a complex sequence of chemical reactions between a fuel and an oxidant accompanied by the evolution of heat and, usually, by the emission of light. The rate of the combustion process depends upon the chemical nature and physical character of the fuel and oxidant, their relative concentrations, environmental pressure and temperature, and other physical parameters, such as geometry and ventilation. A comprehensive discussion of the combustion process is beyond the scope of this guide.

**4-4.1.2** However, it is important to review the essential features of the combustion process to obtain a better appreciation of the fire hazard problem under various oxygen-enriched atmospheres. For this purpose, the various combustible materials can be divided into two categories, the first consisting of combustible liquids, vapors, and gases and the second consisting of combustible solids.

### 4-4.2 Combustible Gases, Vapors, and Liquids.

**4-4.2.1** In Section 4-3, it was indicated that, for ignition to be possible, an adequate fuel concentration needs to be available in the particular oxidizing atmosphere. Once ignition does occur, the sustainment of combustion requires a continued supply of fuel and oxidant. In the case of combustible gases, vapors, and liquids, two types of mixtures, homogeneous or heterogeneous, can exist within the atmosphere.

**4-4.2.2** A homogeneous mixture is one in which the components are intimately and uniformly mixed so that any small volume sample is truly representative of the whole mixture. If the mixture is not homogeneous, it is necessarily heterogeneous (i.e., nonuniformly mixed). A flammable homogeneous mixture is one whose composition lies between the limits of flammability of the combustible gas or vapor in the particular atmosphere at a specified temperature and pressure.

**4-4.2.3** The limits of flammability represent the extreme concentration limits of a combustible in an oxidant through which a flame, once initiated, will continue to propagate at the specified temperature and pressure. For example, hydrogen-air mixtures will propagate flame between 4.0 and 74 volume percent hydrogen at 21°C (70°F) and atmospheric pressure. The smaller value is the lower (lean) limit and the larger value is the upper (rich) limit of flammability. When the mixture temperature is increased, the flammability range widens. A decrease in temperature can result in a previously flammable mixture becoming nonflammable by placing it either above or below the limits of flammability for the specific environmental conditions.

**4-4.2.4** Note in Figure 4-4.2.4 that, for liquid fuels in equilibrium with their vapors in air (or in oxygen), a minimum temperature exists for each fuel above which sufficient vapor is released to form a flammable vapor-air (or vapor-oxygen) mixture. The experimentally determined value of this minimum temperature is commonly referred to as the flash point. The flash point temperature for a combustible liquid varies directly with environmental pressure. An increase in oxygen concentration also widens the flammability range, the upper limit being affected much more than the lower limit. For example, in an oxygen atmosphere at 21°C (70°F) and 1 atm, the upper limit for hydrogen increases to 95 volume percent compared to 74 percent in air, while the lean limit remains essentially the same. A reduction in oxygen concentration results in a narrowing of the flammability range until, at a certain oxygen concentration, the limits merge and flame propagation is no longer possible. Reduction of the oxygen content below this minimum value is one means of effecting fire control. In practice, carbon dioxide or nitrogen is often utilized for this purpose. Nitrogen pressurization[7] provides effective fire control, and as long as the oxygen partial pressure is about 0.14 atmosphere, the environment remains habitable.

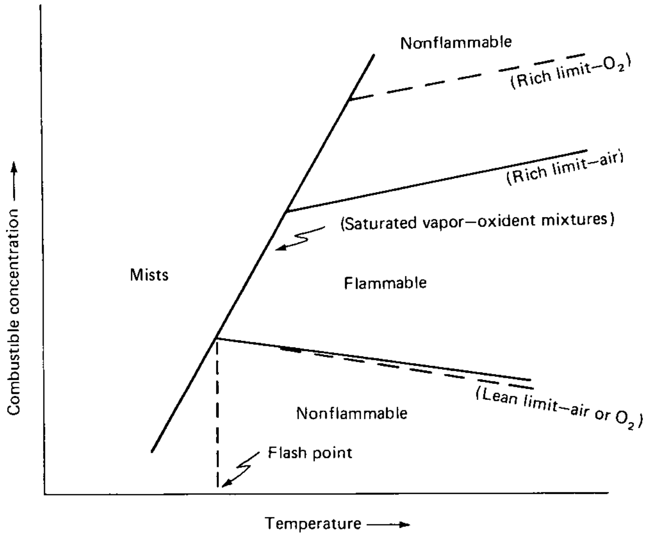

**Figure 4-4.2.4 Effects of temperature on the limits of flammability of a combustible vapor in air and oxygen.[8]**

**4-4.2.5** Total environmental pressure also has an effect on the limits of flammability (*see Figure 4-4.2.5*). For a given atmospheric composition, an increase in pressure generally broadens the flammability range, the rich limit being influenced more than the lean limit. For example, the flammability limits for natural gas-air mixtures at 34 atm are 4.45 and 44.20 volume percent compared to 4.50 and 14.20 volume percent at normal atmospheric pressure. A decrease in environmental pressure below 1 atm produces little effect on the limits of flammability until the low pressure limit is reached, whereupon materials become nonflammable.

**4-4.2.6** The low pressure limit is dependent on the particular fuel and oxidant as well as the temperature, size, geometry, and attitude of the confining vessel. The quenching or low pressure limits are represented in Figure 4-4.2.5 by broken lines to indicate their dependency on surroundings.

**4-4.2.7** Under practical application conditions, the fire problem usually involves heterogeneous mixtures rather than homogeneous combustible-oxidant mixtures. One type of heterogeneous system pertains to gaseous fuel-oxidant mixtures and is heterogeneous in view of the concentration gradients that normally exist when the combustible vapor is first introduced into the oxidizing atmosphere. The type of flame that results is a diffusion flame. A heterogeneous system also results when a liquid fuel is injected in the form of a mist into the oxygen-containing atmosphere. These systems are noted in Figure 4-4.2.4.

**4-4.2.8** In the case of the heterogeneous vapor system, both flammable and nonflammable mixtures can be formed at temperatures above the flash point of the liquid

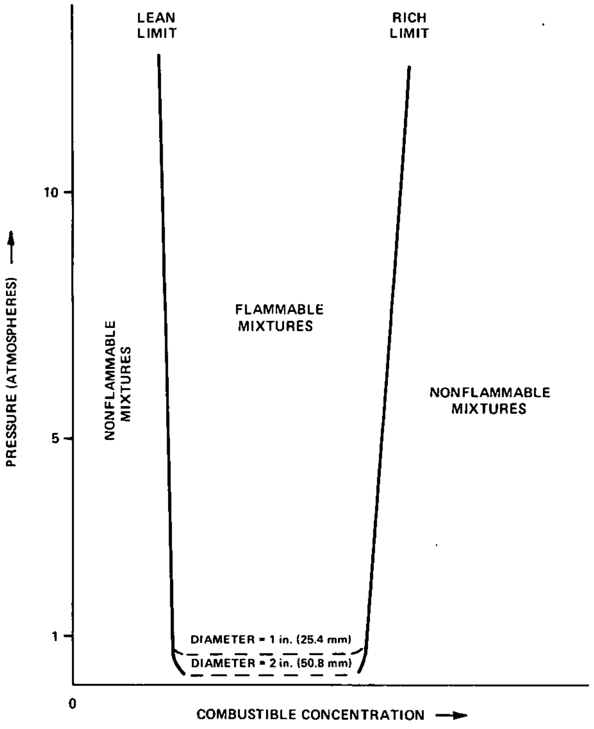

**Figure 4-4.2.5 Effects of pressure on limits of flammability of a combustible vapor in air and of pressure and composition on the quenching diameter.**[8]

from which they are formed. The flammable zones exhibit ignition and burning characteristics similar to flammable homogeneous mixtures. Flammable heterogeneous vapor-mist-oxidant mixtures can be formed at temperatures below the flash point; flammable sprays can be produced over a wide temperature range, both below and above the flash point. Ignition of a flammable mist or spray requires vaporization of the fuel droplets to form flammable gas mixtures; as a result, the ignition energies for these mixtures are higher than those of normal flammable gas mixtures due to the heat of vaporization.

4-4.2.9 For most practical cases, the type of flame that is encountered is a diffusion flame and requires the diffusion of oxidant to the combustible gas at the flame front for its combustion. The rate of burning is primarily dependent on the rate at which the fuel and oxidant are brought together and is influenced by such factors as thermal gradients and turbulence. Increasing the oxidant content, such as in oxygen-enriched atmosphere applications, can result in a significant increase in burning rate.

### 4-4.3 Combustible Solids—Nonmetallics.

4-4.3.1 Burning of solid combustibles requires the consideration of only heterogeneous fuel-oxidant systems. As in the case of flammable liquids and gases, the flame reaction occurs in the gas phase. Once a particular solid combustible has been ignited, propagation of flame requires that a portion of the heat of combustion be fed back to the solid fuel to cause its vaporization or pyrolysis, or both, thereby making additional gaseous fuel available to mix with the oxidant. The flame process is of the diffusion type.

4-4.3.2 Although it is not possible to predict the exact burning behavior of a material in atmospheres of different composition and pressure without actual experimentation, the general effect of these parameters on flame propagation over the surface of a solid combustible, referred to as the flame spread rate, is a factor used to evaluate the fire hazard in different oxygen-enriched atmospheres. This rate is also dependent on direction of propagation, orientation of the combustible, scaling, and nature of the combustible surface (nap burning).

4-4.3.3 The observed effect of atmosphere composition and pressure on the flame spread rate is illustrated in Figure 4-4.3.3. Note that increasing the partial pressure of oxygen at a constant environmental pressure may change the classification of a material from the nonflammable to the flammable category. For materials already in the flammable category based on 21 percent oxygen, further increase in the oxygen partial pressure results in a higher flame spread rate.

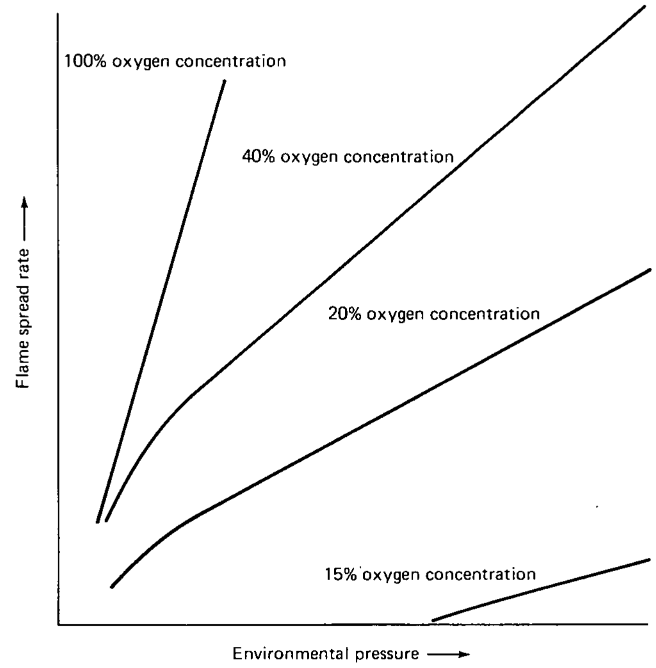

**Figure 4-4.3.3 Effects of atmosphere oxygen content and environmental pressure on flame spread rate.**

4-4.3.4 Fire properties of some nonmetallic materials in different atmospheres have been tabulated in Chapter 5. Perusal of these data clearly indicates that almost all of these materials are flammable in pure oxygen environments.

**4-4.4 Combustible Solids — Metals.** The burning of metals can occur in either the vapor phase or in a condensed phase reaction and therefore can require the consideration of both homogeneous and heterogeneous fuel-oxidant systems. Once a particular metallic combustible has been ignited, propagation of the combustion, whether burning in the vapor phase or condensed phase, requires that a portion of the heat of combustion (assuming the ignition source has been removed) be fed back to the solid fuel to cause it to heat past the ignition point.

**Table 4-5.3 Oxygen Content, Maximum Fuel Consumption, and Resulting Combustion Temperatures and Pressures in Different Atmospheres in a 10.2 $m^3$ (360 cu ft) Volume Enclosure**

| FUELS: | CELLULOSE | | HYDROCARBON | |
|---|---|---|---|---|
| ATMOSPHERE: | 103.4 kPa (15 psi) (Air) | 103.4 kPa (15 psia) (100%—$O_2$) | 103.4 kPa (15 psia) (Air) | 103.4 kPa (15 psia) (100%—$O_2$) |
| Oxygen Content (kg) | 2.9 | 14.5 | 2.9 | 14.5 |
| Maximum Burnable Fuel* (kg) | 1.2 | 11 | 0.36 | 3.3 |
| Heat of Combustion (cal/gm) | ~4000 | | ~11700 | |
| Maximum Heat Release (kcal) | ~4924 | ~43500 | ~4233 | ~38200 |
| Maximum Theoretical Temperature (°C) | 1810 | 5670 | 1390 | 5840 |
| Maximum Pressure Ratio $(P_{final}/P_{initial})$** | 8 | 36 | 7 | 33 |
| Maximum Final Pressure (kPa) | 827 (120 psia) | 3723 (540 psia) | 724 (105 psia) | 3413 (495 psia) |

*Assumes all but 10 volume percent of available $O_2$ can react.
**Does not consider dissociation of product gases.

## 4-5 Effects of Fire in Oxygen-Enriched Atmospheres.

**4-5.1** It has been noted that oxygen-enriched atmospheres usually facilitate the initiation of the combustion process and, once ignition has occurred, the flame reaction proceeds with greater rapidity. Another important consideration in the analysis of the overall fire problem is that oxygen-enriched atmospheres may be encountered under closed-environment (fixed-volume) conditions (e.g., in spacecraft and hyperbaric chambers).[9]

**4-5.2** In confined spaces, the combustion of a relatively small quantity of combustible can result in the rapid generation of extremely high temperatures and increased pressure. The high temperature can result in the ignition of other combustibles some distance from the initial reaction zone, thereby contributing to the rapid spread of the fire. The high temperatures and toxic combustion products that are generated are in themselves potentially lethal to any personnel in the environment, even if they are not engulfed in flames. The increased pressure produced in association with the flame process can also result in the explosive rupture of the chamber.

**4-5.3** The effects of oxygen content and environmental pressure on the quantity of fuel that can be consumed and the resulting maximum theoretical temperatures and pressures that can be attained in air and in several other typical oxygen-enriched atmospheres in a 10.2-$m^3$ (360-$ft^3$) chamber are indicated in Table 4-5.3.

**4-5.3.1** The maximum temperatures and pressures in Table 4-5.3 are recognized as higher than those that would be experienced under true closed-environmental fire conditions. The specific values have been calculated on the following assumptions:

(a) Combustion of the fuel is instantaneous;

(b) None of the heat generated is lost to the walls of the chamber; and

(c) No dissociation of the product gases occurs.

Assumption (c) fails significantly above 1,371°C (2500°F).

**4-5.3.2** Nonmetallic combustibles, such as fabric materials, burn rapidly in 100 percent oxygen, but consumption of the stoichiometric amount of material requires several seconds. This allows a considerable portion of the thermal energy produced to be absorbed by the walls. Experiments conducted with cotton fabric in 34.5 kPa (5 psia), 100 percent oxygen in a 0.045-$m^3$ (1.6-$ft^3$) explosion test chamber, with sample dimensions and test configurations conducive to maximum flame spread, resulted in peak pressures of 241 kPa (35 psia) in 15 seconds after ignition, or approximately 20 percent of the theoretical maximum pressure for cellulose.

**4-5.3.3** Solid metallic materials can burn in OEA, but their flammability depends greatly upon the material, oxygen concentration, oxygen pressure, and test sample temperature and configuration (geometry).[10-14] The consumption of the stoichiometric amount of the material requires several seconds and allows some of the energy produced to be absorbed by the walls of the containment vessel. As a result of the combustion of metals, the temperature and pressure of a containment vessel (of reasonable size) will increase. This increase in pressure occurs even though the oxygen is combined with the metal to form liquid and solid metal oxides; that is, despite the fact that some of the gaseous oxygen is consumed.

### Footnotes to Chapter 4

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[2] Steinberg, T. A., Mulholland, G. P., Wilson D. B., and Benz F. J. "The Combustion of Iron in High-Pressure Oxygen." *Combustion and Flame 89*. Elsevier Science Publishing Co., Inc., 1992, pp. 221-228.

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[4] Mellor, A. M. "Heterogeneous Ignition of Metals: Model and Experiment." Final Report, NASA Grant NSG-641, Princeton University, Princeton, NJ, 1967.

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[7]Tatem, P. A., Gann, R. G., and Carhart, H.W. "Extinguishment of Combustion in Confined Spaces with Nitrogen." *Combustion Science and Technology*, Vol. 7, 1973, p. 213.

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# Chapter 5 Materials for Use in Oxygen-Enriched Atmospheres

*(Footnotes to Chapter 5 can be found at the end of the chapter.)*

## 5-1 General.

**5-1.1** The careful selection of materials for construction and equipment can do much to reduce the fire hazard associated with the use of an OEA. This chapter describes the effect of material properties on the degree of hazard for guidance in the selection of materials that can be used with safety.

**5-1.2** In Chapter 4 it was shown that the use of an OEA accentuates the hazards associated with the use or accidental presence of combustible materials in an OEA as follows:

(a) Combustible materials are ignited more easily in an OEA than in a normal atmosphere, thus increasing the probability of the occurrence of a fire.

(b) Combustible materials burn more rapidly in an OEA than in a normal atmosphere, thus reducing the time available for remedial action before serious damage or injury occurs. Many materials that do not support combustion in a normal atmosphere will burn vigorously in an OEA.

## 5-2 Combustible Gases, Vapors, and Liquids.

### 5-2.1 General.

**5-2.1.1** Evaluation of the hazard of combustible liquids and gases requires a knowledge of their ignition and flammability properties in the oxidant atmosphere of concern. In applications where these combustibles are encountered, the potential fire or explosion hazard can be defined in part by the temperatures required for the formation of flammable mixtures, the temperature and energy needed for ignition of the mixtures, and the critical fuel concentrations (limits) for flame propagation. This information is presented in Table 5-2.1.1 for various representative liquid and gas combustibles in oxygen or air atmospheres, or both. However, the available data are less complete for oxygen than for air for many of the combustibles. In such cases, the degree of fire or explosion hazard in an oxygen environment may be estimated from the data obtained for air and from known oxygen concentration effects for the given class of combustibles.

### 5-2.2 Ignition Temperature and Energy.

**5-2.2.1** The minimum autoignition temperatures (AIT) of most hydrocarbon fuels, solvents, and anesthetic agents fall between 204°C and 538°C (400°F and 1000°F) in air at 1 atmosphere pressure (*see Table 5-2.1.1*). Generally, the AIT of the paraffinic hydrocarbons decrease with increasing molecular weight. A few hydrocarbon-type combustibles, such as ethyl ether, n-amyl ether, and acetaldehyde, can autoignite below 204°C (400°F) in air; carbon disulfide can also ignite at a low temperature [90°C (194°F)]. These AIT are primarily applicable to hot surface ignitions in quiescent atmospheres and where the heat source is relatively large; vessels of Pyrex® or stainless steel usually have the lowest AIT. As a rule, AIT do not vary greatly with fuel concentration except at near-limiting concentrations where they increase noticeably. Fuel injection pressure can also be important; the AIT of many lubricants decrease as much as 102°C (200°F) when the injection pressure is increased from zero to about 6,895 kPa (1000 psi).

(a) Figure 5-2.2.1 shows the noticeable effect that fluid injection pressure can have on the minimum AIT of a diester (MLO-54-581) and several silicate-type (MLO-54-856, MLO-8200, MLO-54-645, MLO-54-540) hydraulic fluids; this figure also illustrates that the AIT of a chlorinated silicone fluid (MLO-53-446) and a mineral oil (MIL-H-5606) are independent of injection pressure to 34,475 kPa (5000 psig).

**Table 5-2.1.1 Ignition and Flammability Properties of Combustible Liquids and Gases in Air and Oxygen at Atmospheric Pressure**

| | Flash Point | Min. Ign. Temperature[2] | | Min. Ign. Energy[3] | | Flammability Limits[4] Vol. % | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Air | | Oxygen | |
| **Combustible** | **Air °C (°F)** | **Air °C (°F)** | **Oxygen °C (°F)** | **Air mJ** | **Oxygen mJ** | **LFL** | **UFL** | **LFL** | **UFL** |
| **Hydrocarbon Fuels** | | | | | | | | | |
| Methane | Gas | 630 (1166) | — | 0.30 | 0.003 | 5.0 | 15 | 5.1 | 61 |
| Ethane | Gas | 515 (959) | 506 (943) | 0.25 | 0.002 | 3.0 | 12.4 | 3.0 | 66 |
| n-Butane | −60 (−76) | 288 (550) | 278 (532) | 0.25 | 0.009 | 1.8 | 8.4 | 1.8 | 49 |
| n-Hexane | −3.9 (25) | 225 (437) | 218 (424) | 0.288 | 0.006 | 1.2 | 7.4 | 1.2 | 52* |
| n-Octane | 13.3 (56) | 220 (428) | 208 (406) | — | — | 0.8 | 6.5 | ≤0.8 | — |
| Ethylene | Gas | 490 (914) | 485 (905) | 0.07 | 0.001 | 2.7 | 36 | 2.9 | 80 |
| Propylene | Gas | 458 (856) | 423 (793) | 0.28 | — | 2.4 | 11 | 2.1 | 53 |
| Acetylene | Gas | 305 (581) | 296 (565) | 0.017 | 0.0002 | 2.5 | 100 | ≤2.5 | 100 |
| Gasoline (100/130) | −45.5 (−50) | 440 (824) | 316 (600) | — | — | 1.3 | 7.1 | ≤1.3 | — |
| Kerosene | 37.8 (100) | 227 (440) | 216 (420) | — | — | 0.7 | 5 | 0.7 | — |
| **Anesthetic Agents** | | | | | | | | | |
| Cyclopropane | Gas | 500 (932) | 454 (849) | 0.18 | 0.001 | 2.4 | 10.4 | 2.5 | 60 |
| Ethyl Ether | −28.9 (−20) | 193 (380) | 182 (360) | 0.20 | 0.0013 | 1.9 | 36 | 2.0 | 82 |
| Vinyl Ether | −30 (< −22) | 360 (680) | 166 (331) | — | — | 1.7 | 27 | 1.8 | 85 |
| Ethylene | Gas | 490 (914) | 485 (905) | 0.07 | 0.001 | 2.7 | 36 | 2.9 | 80 |
| Ethyl Chloride | −50 (−58) | 516 (961) | 468 (874) | — | — | 4.0 | 14.8 | 4.0 | 67 |
| Chloroform | — — — — — — — — — Nonflammable — — — — — — — — — | | | | | | | | |
| Enflurane | >200 (93) | NA | NA | NA | NA | NA | NA | 9.8 | NA |
| Isoflurane | >200 (93) | NA | NA | NA | NA | NA | NA | 8.8 | NF |
| Desflurane | NF | NA | NA | NA | NA | NA | NA | 17.2 | 20.8 |
| Nitrous Oxide | — — — — — — — — — Nonflammable — — — — — — — — — | | | | | | | | |
| **Solvents** | | | | | | | | | |
| Methyl Alcohol | 12.2 (54) | 385 (725) | — | 0.14 | — | 6.7 | 36 | ≤6.7 | 93 |
| Ethyl Alcohol | 12.8 (55) | 365 (689) | — | — | — | 3.3 | 19 | ≤3.3 | — |
| n-Propyl Alcohol | 15 (59) | 440 (824) | 328 (622) | — | — | 2.2 | 14 | ≤2.2 | — |
| Glycol | 111 (232) | 400 (752) | — | — | — | 3.5* | — | ≤3.5 | — |
| Glycerol | 160 (320) | 370 (698) | 320 (608) | — | — | — | — | — | — |
| Ethyl Acetate | −4.4 (24) | 427 (800) | — | 0.48 | — | 2.2 | 11 | ≤2.2 | — |
| n-Amyl Acetate | 24.4 (76) | 360 (680) | 234 (453) | — | — | 1.0 | 7.1 | ≤1.0 | — |
| Acetone | −17.8 (0) | 465 (869) | — | 1.15 | 0.0024 | 2.6 | 13 | ≤2.6 | 60* |
| Benzene | −11.1 (12) | 560 (1040) | — | 0.22 | — | 1.3 | 7.9 | ≤1.3 | 30 |
| Naphtha (Stoddard) | 37.8 (~100) | 232 (~450) | 216 (~420) | — | — | 1.0 | 6 | ≤1.0 | — |
| Toluene | 4.4 (40) | 480 (896 | — | 2.5 | — | 1.2 | 7.1 | ≤1.2 | — |
| Butyl Chloride | −6.7 (20) | 240 (464) | 235 (455) | 0.332 | 0.007* | 1.8 | 10 | 1.7 | 52* |
| Methylene Chloride | — | 615 (1139) | 606 (1123) | — | 0.137 | 15.9* | 19.1* | 11.7* | 68 |
| Ethylene Chloride | 13.3 (56) | 476 (889) | 470 (878) | 2.37 | 0.011* | 6.2 | 16 | 4.0 | 67.5 |
| Trichloroethane | — | 458 (856) | 418 (784) | — | 0.092 | 6.3* | 13* | 5.5* | 57* |
| Trichloroethylene | 32.2 (90) | 420 (788) | 396 (745) | — | 18* | 10.5* | 41* | 7.5 | 91* |
| Carbon Tetrachloride | — — — — — — — — — Nonflammable — — — — — — — — — | | | | | | | | |
| **Miscellaneous Combustible** | | | | | | | | | |
| Acetaldehyde | −27.2 (−17) | 175 (347) | 159 (318) | 0.38 | — | 4.0 | 60 | 4.0 | 93 |
| Acetic Acid | 40 (104) | 465 (869) | — | — | — | 5.4* | — | ≤5.4 | — |
| Ammonia | Gas | 651 (1204) | — | >1000 | — | 15.0 | 28 | 15.0 | 79 |
| Aniline | 75.6 (168) | 615 (1139) | — | — | — | 1.2* | 8.3 | ≤1.2 | — |
| Carbon Monoxide | Gas | 609 (1128) | 588 (1090) | — | — | 12.5 | 74 | ≤12.5 | 94 |
| Carbon Disulfide | −30 (−22) | 90 (194) | — | 0.015 | — | 1.3 | 50 | ≤1.3 | — |
| Ethylene Oxide | <17.8 (<0) | 429 (804) | — | 0.062 | — | 3.6 | 100 | ≤3.6 | 100 |
| Propylene Oxide | −37.2 (−35) | — | 400 (—) | 0.14 | — | 2.8 | 37 | ≤2.8 | — |
| Hydrogen | Gas | 520 (968) | 400 (752) | 0.017 | 0.0012 | 4.0 | 75 | 4.0 | 95 |
| Hydrogen Sulfide | Gas | 260 (500) | 220 (428) | 0.077 | — | 4.0 | 44 | ≤4.0 | — |
| Bromochloromethane | — | 450 (842) | 368 (694) | — | — | NF[5] | NF | 10.0 | 85 |
| Bromotrifluoromethane | Gas | >593 (>1100) | 657 (1215) | | — | NF | NF | NF | NF |
| Dibromodifluoromethane | Gas | 499 (930) | 453 (847) | — | — | NF | NF | 29.0 | 80 |

[1] Data from Footnotes 1 and 2; open cup method.

[2] Data from Footnotes 3, 4, 5, and 6.

[3] Data from Footnotes 7, 8, 9, 10 and 3.

[4] Data from Footnotes 11, 12, 3, 4, and 6.

*Data at 200°F (93°C).

[5] NF — No flammable mixtures found in Footnote 4.

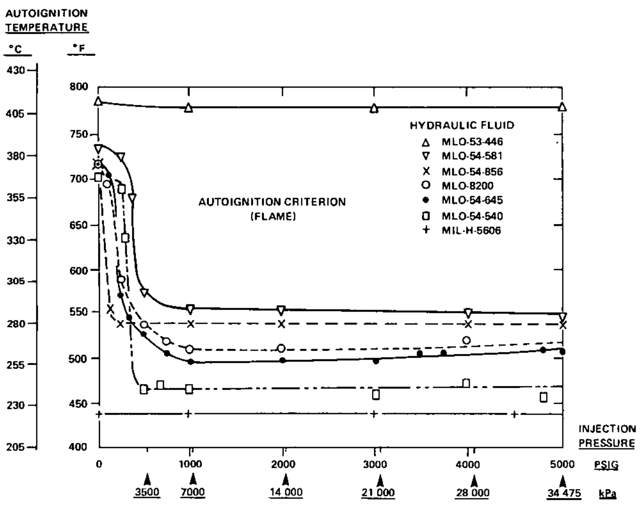

**Figure 5-2.2.1 Minimum autoignition temperatures of seven hydraulic fluids in air at atmospheric pressure and at various injection pressures (200-cc Pyrex® vessel).**[13]

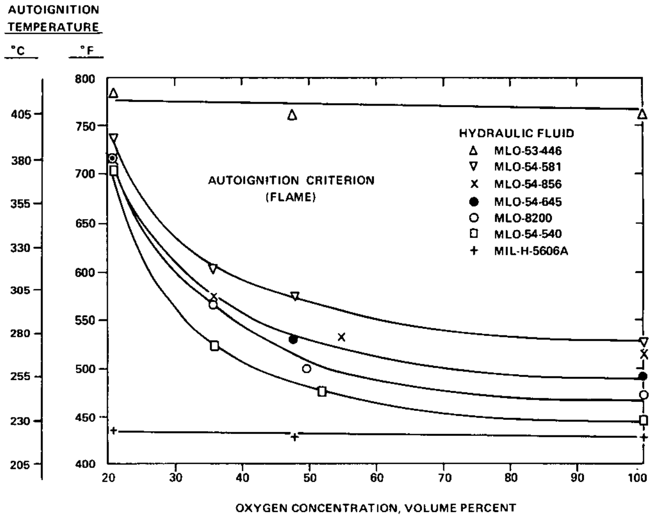

**Figure 5-2.2.2(a) Minimum autoignition temperatures of seven hydraulic fluids at atmospheric pressure in various oxygen-nitrogen atmospheres (200-cc Pyrex® vessel).**[13]

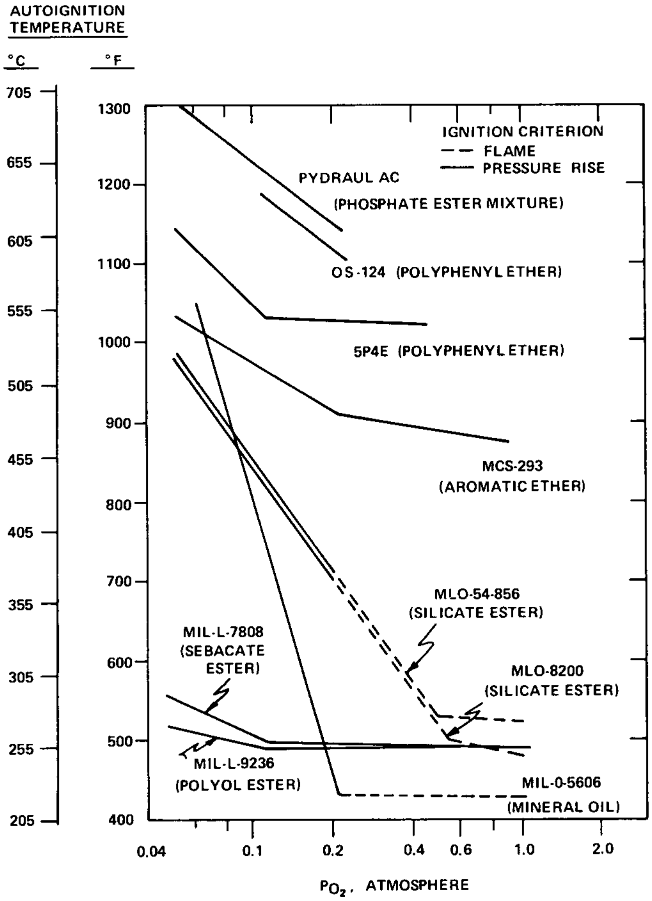

**Figure 5-2.2.2(b) Variation of minimum autoignition temperature with oxygen partial pressure ($P_{O2}$) for various lubricants.**[13]

**5-2.2.2** Although AIT tend to be lower in oxygen than in air, such differences are not significant for many hydrocarbon combustibles. Similarly, the AIT for many combustibles do not vary greatly when the ambient pressure is increased to a few atmospheres. However, at highly reduced pressures (< < 1 atm) or reduced oxygen concentrations (< < 21 percent), AIT tend to be noticeably higher than in air at 1 atm; thus, the autoignition hazard is less severe in such atmospheres. The use of an inert diluent of higher thermal conductivity than nitrogen (e.g., helium) also reduces the autoignition hazard in some instances. Since AIT are normally dependent on oxygen partial pressure, the data obtained at various oxygen percentages can be used to estimate AIT at various total pressures.

(a) In the case of lubricants and hydraulic fluids, the effect of oxygen concentration on AIT tends to be greater than observed for the neat hydrocarbon combustibles in Table 5-2.1.1. Figure 5-2.2.2(a) shows that the AIT for five of the hydraulic fluids decrease between 93°C and 149°C (200°F and 300°F) when the oxygen content is increased from 21 to 100 percent; the AIT of the chlorinated silicone fluid (MLO-53-446) and the mineral oil (MIL-H-5606) are unaffected by such changes in oxygen concentration, similar to when these fluids are subjected to varying injection pressure. A correlation of AIT with oxygen partial pressure is shown in Figure 5-2.2.2(b) for several such combustible fluids at various initial pressures and oxygen concentrations. According to these data, the aromatic ether and chlorinated silicone fluids would be favored over the other fluids for protection against autoignition.

**5-2.2.3** In comparison to autoignition, the spark ignition of a flammable mixture requires much higher temperatures and is governed primarily by the rate of energy input rather than by the heat source temperature. The importance of minimum spark ignition energies is evidenced by the fact that most flammable mixtures of combustibles can be ignited in air or oxygen by the energy dissipated from common electrostatic discharges. The range of ignition energy values provided in Table 5-2.1.1 is from about 0.1 mJ to 3 mJ for most of the hydrocarbon fuels, anesthetics, and solvents, with air as the oxidant. Ammonia and some of the halogenated hydrocarbons (halons) require ignition energies of much higher magnitude (> 1000 mJ). In comparison, such combustibles as acetylene, hydrogen, and carbon disulfide can be ignited with spark energies of only about 0.015 mJ.

**5-2.2.4** Minimum ignition energy values refer to the most ignitible composition of the given fuel vapor-air mixture and are noticeably higher for mixtures that are highly fuel-lean or fuel-rich. In addition, energy values can be expected to be higher at reduced pressures but much lower in oxygen than in air. Many ignition energy data vary inversely with the approximate square of the total pressure. For some liquids and gases, ignition values are as much as about 100 times lower in oxygen. Figure 5-2.2.4 shows the variation of the minimum spark ignition energies of propane-oxygen-nitrogen mixtures with fuel concentration and oxygen concentration at ½ and 1 atmosphere pressure. The substitution of helium for nitrogen results in higher ignition energies but does not eliminate the risk of spark ignitions.

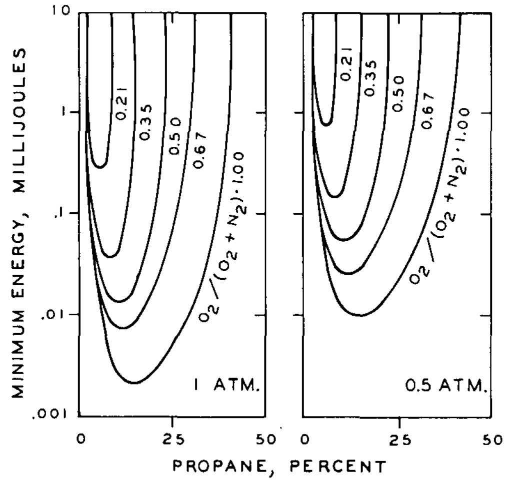

**Figure 5-2.2.4 Effect of oxygen index and ambient pressure on minimum ignition energies.**[9]

### 5-2.3 Combustion.

**5-2.3.1 Nonmetallics.** The extent of combustion or flame propagation depends on a number of factors including the pressure, the temperature, and the composition of the fuel and oxidant. With near-stoichiometric mixtures of hydrocarbon vapors in air, the flames propagate at rates of at least a few feet per second at 1 atmosphere pressure and through apertures as small as about 2.5 mm (0.1 in.) diameter. The rates of flame propagation (flame speeds) normally increase with an increase in chamber diameter. The maximum pressure rises that are produced by the ignition of such mixtures in a large confined space are generally about 689 kPa (100 psig). The explosions are even more severe in oxygen where detonations may occur and the pressure rises and propagation rates are much higher than in air. The transit of a deflagration (subsonic) to a detonation (supersonic) can also occur in air with many fuels if the ratio of the length to the diameter of the reaction chamber is sufficiently great.

**5-2.3.2 Metallics.** As with nonmetals, the extent of combustion or flame propagation for metals depends on a number of factors including the absolute pressure, ambient temperature, fuel and oxidizer composition, geometric shape and temperature of the fuel sample, and direction of combustion front. Depending on these factors, the combustion front in metals can propagate at greatly varying rates. For example, a 3.2-mm (0.13-in.) diameter 316 stainless steel rod burning upward in 6.9 MPa (1000 psia) oxygen will propagate at about 11 mm/s (0.43 in./s), whereas a 3.2-mm (0.13-in.) diameter 6061 aluminum rod will burn at 64 mm/s (2.5 in./s).[14] Since most metals burn in the liquid phase, chamber diameter normally has little effect on the combustion front propagation rate once a minimum chamber diameter is reached [which allows adequate amounts of oxidizer to surround the fuel to ensure stoichiometric combustion without appreciable (< 3%) reduction of oxidizer]. In general, the combustion front propagation rate increases with increasing ambient pressure, oxidizer concentration, ambient temperature, and decreasing sample dimensions.[15,16]

### 5-2.4 Limits of Flammability of Nonmetallic Materials.

**5-2.4.1** The lower or lean limit of flammability is of greatest interest since it defines the minimum combustible concentration required for flame propagation through the particular mixture. The minimum temperature at which a lower limit concentration can exist depends on the volatility of the combustible and corresponds approximately to the flash point of the combustible. Many flammable liquids have flash points in air of less than 38°C (100°F) (*see Table 5-2.1.1*). Thus, the fuel vapor-air mixtures formed at or above the given temperatures would propagate flame if they are ignited. In oxygen, the flash points are slightly lower than those in air. Where fuel mists or foams are formed, the mixtures present may propagate flame at temperatures far below the flash points of the fuels.

**5-2.4.2** The lower limits of most hydrocarbon fuels, anesthetics, and solvents are equal to or less than about 5 volume percent in air or oxygen at 1 atm. Table 5-2.1.1 provides data obtained at ordinary temperatures [≤ 593°C (≤ 1100°F)], except where otherwise noted. Such vapors and gases as ammonia, carbon monoxide, and certain halogenated hydrocarbons have much higher lower limits.

(a) In comparison, the values for most lubricants are less than 1 volume percent because of the high molecular weights of such fluid. At the same time, they need much higher temperatures, e.g., 93°C to 371°C (200°F to 700°F), to form lower limit mixtures than do the paraffins and many other hydrocarbons.[13]

**5-2.4.3** Based on weight, the lower limits of the paraffins correspond to about 45 mg of combustible per liter of air (STP). The upper limits for the combustibles vary over a greater range of fuel concentrations. For the paraffinic hydrocarbons, the values in air are equal to or less than 15 percent. They are as high as 100 percent for materials such as acetylene and ethylene oxide, i.e., their vapors can decompose exothermally and propagate flame in the absence of air or oxygen.

**5-2.4.4** Although most lower limits in oxygen do not differ greatly from those in air, the upper limits are usually much higher in oxygen and tend to be above 50 percent for many materials. Furthermore, some combustibles, such as the "halon" agents (bromochloromethane and dibromodifluoromethane), are flammable in oxygen over a wide range of fuel compositions, whereas they do not appear to be flammable in air. Of the halogenated solvents, trichloroethylene displays the widest range of flammability in air and oxygen, although elevated temperatures are necessary.

**5-2.4.5** Ordinarily, the range of flammable mixtures increases with a moderate increase in pressure or temperature. In particular, the upper limits increase, but the increase is not always noticeable where the fuel vapor pressure is not a limiting factor. The lower limits are least affected by changes in pressure or temperature or by the addition of diluents.

**5-2.4.6** Diluents or inerting agents are frequently used in explosion-preventive measures. Nitrogen is a more effective diluent than helium but not as effective as carbon dioxide [*see Figure 5-2.4.6(a)*] or water vapor. Figures 5-2.4.6(a) and (b) show the complete range of flammable mixture compositions that may be expected with a hydrocarbon fuel, such as cyclopropane in air or oxygen, and various diluents at atmospheric pressure. The minimum oxygen percentage below which most hydrocarbon mixtures are not flammable is about 14 percent with $CO_2$ diluent and 10 to 12 percent with $N_2$ diluent. The corresponding values for hydrogen and carbon monoxide are 6 percent and 5 to 5.5 percent, respectively. In general, most combustible liquids and gases can be expected to form flammable mixtures over a wide range of oxygen or oxygen-diluent concentrations.

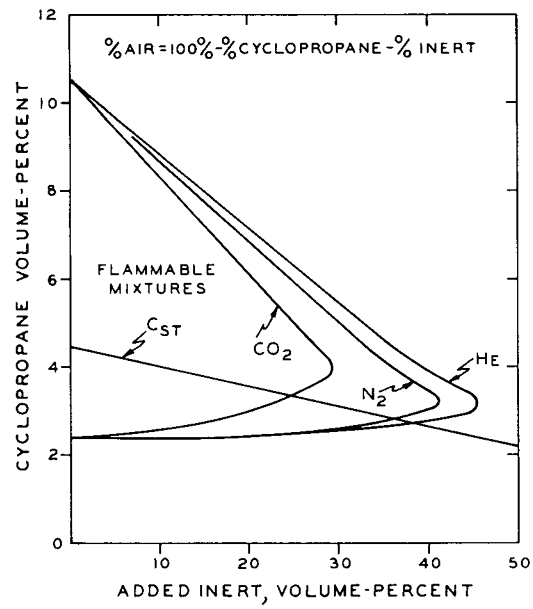

**Figure 5-2.4.6(a) Limits of flammability of cyclopropane-carbon dioxide-air, cyclopropane-nitrogen-air, and cyclopropane-helium-air mixtures at 25°C (86°F) and atmospheric pressure.[6] (Cst = Stoichiometric composition = line defining amount of combustible vapor required for complete combustion.)**

**5-2.5 Limits of Flammability — Metals.** Flammability limits, per se, do not exist for most structural metal alloys, since they burn in the liquid phase rather than the vapor phase. However, two measures of the relative flammability of metals exist that are of practical value. They are the minimum oxygen pressure required to support combustion of a standard sample (threshold pressure) and the minimum oxygen concentration required to support combustion of a standard sample at a given pressure (oxygen index). Data on the threshold pressures and oxygen indices of metals and alloys are provided in 5-3.4.

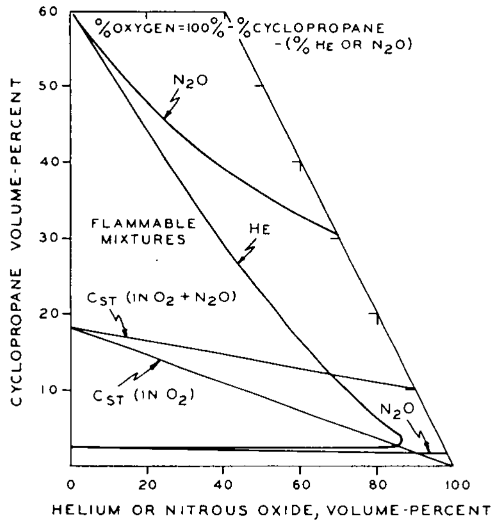

**Figure 5-2.4.6(b) Limits of flammability of cyclopropane-helium-oxygen and cyclopropane-nitrous oxide-oxygen mixtures at 25°C (86°F) and atmospheric pressure.[6] (Cst = Stoichiometric composition = line defining amount of combustible vapor required for complete combustion.)**

## 5-3 Combustible Solids.

### 5-3.1 General.

**5-3.1.1** The combustibility data obtained by different researchers under various conditions of tests make direct comparison and interpretation of the results difficult. Very little, if any, available data seem to exist on large-scale tests of materials under simulated OEA conditions. For any specific material, ignition and flammability data are dependent on such factors as:

(a) Specimen — size, shape, density, color, and surface treatment;

(b) Ignition source — heat flux rate plus time;

(c) Position of the specimen with reference to the ignition source and direction of the gravitational or convective field;

(d) Surroundings — size of enclosure, ambient temperature;

(e) Venting — external airflow; and

(f) Inerting — oxygen deficiency and carbon dioxide buildup.

### 5-3.2 Ignition Temperature and Energy.

**5-3.2.1** Organic solid materials in the form of finely dispersed dust clouds are extremely susceptible to combustion when heated to temperatures of generally less than 538°C (1000°F) and where spark ignition energies are less than 0.1J. The degree of this type of fire hazard has been expressed conveniently in the literature as an explosibility index with a range of 0 to 10+. According to this scale, vinyls and fluorocarbons are outstanding, with an index of less than 0.10, which agrees with other flammability data[17] on these materials.

(a) The index of explosibility is the product of the ignition sensitivity and the explosion severity. The indices are dimensionless quantities and have a numerical value of 1 for a dust equivalent to the standard Pittsburgh Coal. An explosibility index greater than 1 indicates a hazard greater than that for coal dust. The ignition sensitivity is the product of the ignition temperature, multiplied by minimum energy, multiplied by minimum concentration of Pittsburgh Coal dust, divided by the product of ignition temperature, multiplied by minimum energy multiplied by minimum concentration of the sample dust under consideration. The explosion severity is the product of maximum explosion pressure multiplied by maximum rate of pressure rise of the sample dust under consideration, divided by the product of maximum explosion pressure, multiplied by maximum rate of pressure rise of Pittsburgh Coal dust.[17]

**5-3.2.2** Single fibers of organic material, such as those of lint, cotton tufts, and fluffy fabrics, are especially vulnerable to a localized heat source such as an electrical discharge. Single cotton fibers can be ignited by a 0.02J static spark in 100 percent $O_2$ but not in 64 percent $O_2$ in air. Fibers contaminated with greasy substances can be ignited by much weaker sparks.[18]

**5-3.2.3** Textile fabrics, such as used in clothing, can be ignited and burned by high-energy repetitive electrical sparks. For example, both cotton and wool have been ignited with a spark energy as low as 2.3J in 100 percent $O_2$ at atmospheric pressure, whereas, in normal air, a spark energy as high as 193J was required. Silk and polyester fabrics are more difficult to ignite than cotton or wool. Oily fabrics are highly flammable and may be ignited with spark energy as small as $^{1}/_{10,000}$ of that for a clean sample.[19]

**5-3.2.4** Frictional sparks in 100 percent $O_2$ may be much more incendive than in air. For example, a grinding wheel in contact with metal that produces low energy sparks incapable of igniting fuel vapors normally requiring only 0.0003J spark energy in air will ignite textile fabrics in 100 percent $O_2$ due to increased reactivity of the abrasive particles in oxygen. Cotton and wool fabrics can also be ignited by spark from the impact of a hardened steel tool against a rusty steel plate.

**5-3.2.5** Combustible materials, when heated, may self-ignite at relatively low temperatures that approach the spontaneous or autogenous temperatures (SIT) or (AIT) obtained under ideal test conditions. Limited data and theory indicate that the SIT for typical materials, such as polyethylene and polyvinylchloride, decrease linearly with an increase in partial pressure of the oxygen. A decrease of about 93°C (200°F) in SIT is indicated for these materials, with an increase in oxygen partial pressure from 155 mm [21 kPa (3.0 psia)] to 760 mm [101 kPa (14.7 psia) (1 atm)]. Temperatures much higher than those for SIT are indicated to cause hot surfaces to ignite materials by direct contact. For example, polyvinylchloride will not ignite when exposed to a surface temperature of 649°C (1200°F) in air. However, in 100 percent $O_2$ at 1 atm, this material will ignite at about 393°C (740°F).[20]

(a) Other test results show that, for cotton sheeting, the minimum hot plate temperature for ignition decreases from 465°C (869°F) in normal air to 360°C (680°F) in 100 percent $O_2$ at 1 atm. For this same material, decrease in the temperature with increase in the air pressure from 1 atm to 6 atm is about equal to that specified above for 100 percent $O_2$. No ignition for Nomex® was obtained under similar test conditions in normal air. However, ignition does occur at 520°C (968°F) in 100 percent $O_2$ at 1 atm and at 560°C (1,040 °F) in air at 6 atm.[21]

**5-3.2.6** All metals, with the possible exception of the noble metals — gold and platinum — can be expected to ignite in oxygen at some elevated temperature and pressure. Metals most liable to ignition hazards are those configured with high surface-to-volume ratios such as dusts, thin sheets, wires, and wire meshes. When the bulkier structural elements of systems containing pressurized oxygen ignite and burn, the results are often catastrophic, due to the explosion-like release of high pressure gases and ejection of burning debris. Ignition mechanisms include mechanical impact, particle impact, friction, electrical arc and spark, resonance, rupture, exposure of fresh metal surfaces, and promoted ignition. The most ignitible common metals are titanium, magnesium, and lithium; the least ignitible are nickel, copper, and cobalt. Increase in oxygen pressure and content promotes the ignition of metals at lower temperatures.[22]

**5-3.2.6.1** Ignition of metals by frictional heat is a commonly recognized hazard in rotating machinery for oxygen service.[23-26] Frictional ignition is controlled by two factors: the resistance of the material to ignition and combustion due to its chemical composition (chemical kinetics) and the ability of the material to generate heat by friction. The combined effect of these factors is reflected in the product of the contact pressure [P = test specimen contact pressure at ignition (loading force divided by initial contact area)] and the velocity (v = relative velocity between the rubbing components) required for the ignition of metallic test specimens tested in standard configuration and conditions. Table 5-3.2.6.1 shows the Pv product required for ignition of 2.5 cm (1 in.) diameter × 0.25 cm (0.1 in.) wall × 2 cm (0.8 in.) long specimens rotated axially with end rubbing in stagnant 6.9 MPa (1000 psia) oxygen. Tests were conducted by keeping v constant at 22 m/s (72.4 ft/s) and increasing P at a rate of 35 N/s (7.5 lbf/s) until ignition.

(a) When frictional ignition test specimens made from different metals are rubbed together, the metal that is least resistant to ignition by friction tends to control the ignition

**Table 5-3.2.6.1[23,26,27,28] Friction Ignition Test Data for Similar Pairs of Test Specimens**

| Test Materials | Pv Product at Ignition | |
|---|---|---|
| | $W/m^2 \times 10^{-8}$ | (lbf/in.$^2$ × ft/min ×x $10^{-6}$) |
| Inconel MA 754 | 3.96—4.12* | 11.30—11.75[27] |
| Inconel MA 758 | 2.64—3.42 | 7.53—9.76 |
| Nickel 200 | 2.29—3.39 | 6.50—9.66[26] |
| Inconel 600 | 2.00—2.91 | 5.70—8.30[26] |
| Inconel 625 | 1.63—1.73 | 4.65—4.94 |
| Monel® 400 | 1.44—1.56 | 4.12—4.46[26] |
| Monel® K-500 | 1.37—1.64 | 3.91—4.68[26] |
| Inconel 718 | 1.10—1.19 | 3.13—3.37[27] |
| 17-4 PH (H 900) | 1.00—1.21 | 2.87—3.45[28] |
| 304 SS | 0.85—1.20 | 2.33—3.41[27] |
| Brass CDA 360 | 0.70—1.19 | 1.98—3.41[26] |
| 17-4 PH (Cond. A) | 0.61—1.05 | 1.75—2.99[28] |
| 316 SS | 0.53—0.86 | 1.50—2.50[26] |
| Aluminum 6061-T6 | 0.061 | 0.18[26] |
| Ti-6Al-4V | 0.0035 | 0.01[26] |

NOTE: The source of all unannotated data is previously unpublished Frictional Heating Tests performed at NASA White Sands Test Facility.

* This material did not ignite at these Pv products.

threshold.[28] For example, when Monel® 400 and 316 stainless steel are rubbed together, the pair ignites within the range of the Pv products required to ignite the stainless steel, thereby degrading the performance of the Monel® 400.[29]

(b) Figure 5-3.2.6.1 provides the Pv products required for the frictional ignition of three alloys as a function of oxygen pressure. In the case of carbon steel 1015 and 316 stainless steel, there exists a pressure where increasing or decreasing pressure produces increases in the Pv products required for ignition. At the pressure where the minimum Pv product occurs, it is believed that the heat rate produced by the oxidation process is equal to the heat loss rate. The ignition process at pressures lower that this minimum are dominated by oxidation kinetics, whereas, at pressures above this minimum, the ignition process is dominated by heat loss from the material.[26]

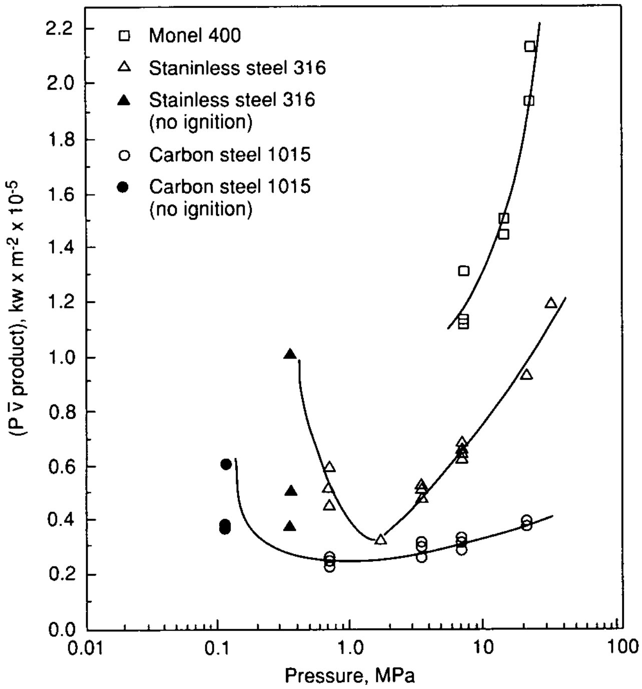

**Figure 5-3.2.6.1 Effect of oxygen pressure on the Pv products required for the frictional ignition of Monel® 400, 316 stainless steel, and carbon steel 1015.**[26]

**5-3.2.6.2** The impact of high-velocity particles on surfaces has been suspected for many years to be the cause of fires in oxygen-enriched atmospheres (OEA).[30-33] Pressure, temperature, particle size, quantity, and type, target material and configuration, and oxygen concentration all affect the likelihood of particle impact ignition. Generally, the likelihood of particle impact ignition increases with increasing particle velocity, target temperature, and oxygen concentration. The ignition/no ignition response of five structural alloys subjected to supersonic impact of single 2000-micron (0.08-in.) diameter aluminum particles in 27 MPa (3900 psia) oxygen is shown in Figure 5-3.2.6.2.[23]

**5-3.2.7** Compared to metals, organic materials ignite and burn at relatively low temperatures and energy inputs. Organics include the vast number and combinations of synthetic plastics, wood and paper products, resins, and natural and synthetic fibers. These materials, unlike metals, are characterized by the occurrence of thermal degradation prior to ignition, whereby combustible gases are generated. This occurs with the more conventional plastics within a narrow range of 204°C to 316°C (400°F to 600°F) corresponding to the flash point temperature for ASTM D1929, *Standard Test Method for Ignition Properties of Plastics*. Of special interest on the subject of ignitibility are the recent developments in heat resistant polymers, which show promise of extending the maximum operating safe temperature range of plastics to 538°C (1000°F).[34]

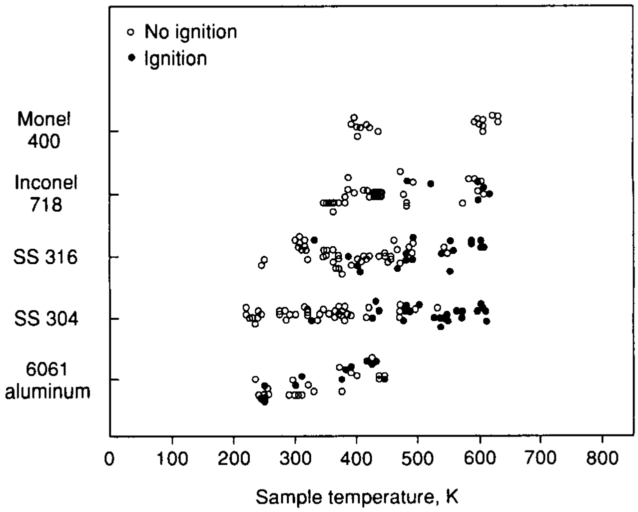

**Figure 5-3.2.6.2 Results of supersonic impact of single 2000-micron (0.08-in.) diameter aluminum particles impacting various alloys in 27 MPa (3900 psia) oxygen.**[23]

**5-3.2.8** An increase in the oxygen concentration of the atmosphere at constant pressure or an increase in the total pressure at constant composition (increased partial pressure of oxygen) results in a significant lowering of the ignition temperature as shown by the data in Table 5-3.2.8.[21]

(a) Fire retardant treatments commonly applied to fabrics for use in a normal atmosphere do not prevent ignition in OEA and may even lower the ignition temperature.

**5-3.2.9** Experiments in which samples of polyethylene and polyvinylchloride were heated in an oxygen atmosphere in a furnace at a temperature slightly below the standard ignition temperature resulted in ignition after delays of an hour or more. The temperature of the sample was observed to rise as much as 38°C (100°F) above the furnace temperature just prior to ignition, indicating the occurrence of an oxidation reaction taking place in the solid sample.[20] The slow oxidation of organic materials subjected to slightly elevated temperatures in an oxygen-enriched atmosphere may be an easily overlooked source of ignition in such systems.

**5-3.2.10** The ignitibility of nonmetallic materials is also affected by the thermal conductivity of the diluent gas used with oxygen. An appreciable increase in energy input is required for ignition where nitrogen is replaced with helium. This can be of some benefit in reducing the possibility of ignition from electrically overheated wiring by greater cooling from exposed hot surfaces in helium.[35] (*Caution — see 5-3.3.6.*)

**Table 5-3.2.8 Minimum Hot Plate Ignition Temperatures of 6 Combustible Materials in Oxygen-Nitrogen Mixtures at Various Total Pressures**

| | | Ignition Temperature, °C | | | |
|---|---|---|---|---|---|
| | | Total Pressure, atmospheres | | | |
| **Material** | **Oxidant** | **1** | **2** | **3** | **6** |
| Cotton sheeting | Air | 465 | 440(425)† | 385 | 365 |
| | 42% $O_2$, 58% $N_2$ | 390 | 370 | 355 | 340 |
| | 100% $O_2$ | 360 | 345 | 340 | 325 |
| Cotton sheeting treated* | Air | 575 | 520(510) | 485(350) | 370(325) |
| | 42% $O_2$, 58% $N_2$ | 390(350) | 335 | 315 | 295 |
| | 100% $O_2$ | 310 | — | 300 | 285 |
| Conductive rubber sheeting | Air | 480 | 395 | 370 | 375 |
| | 42% $O_2$, 58% $N_2$ | 430 | 365 | 350 | 350 |
| | 100% $O_2$ | 360 | — | 345 | 345 |
| Paper drapes | Air | 470 | 455 | 425 | 405 |
| | 42% $O_2$, 58% $N_2$ | 430 | — | 400 | 370 |
| | 100% $O_2$ | 410 | — | 365 | 340 |
| Nomex fabric | Air | > 600 | >600 | > 600 | 560 |
| | 42% $O_2$, 58% $N_2$ | 550 | 540 | 510 | 495 |
| | 100% $O_2$ | 520 | 505 | 490 | 470 |
| Polyvinyl chloride sheet | Air | >600 | — | 495 | 490 |
| | 42% $O_2$, 58% $N_2$ | 575 | — | 370 | 350 |
| | 100% $O_2$ | 390 | — | 350 | 325 |

* Cotton sheeting treated with Du Pont X-12 fire retardant; amount of retardand equal to 12 percent of cotton specimen weight.

† Values in parentheses indicate temperature at which material glowed.

## 5-3.3 Combustion — Nonmetallic Materials.

**5-3.3.1** There is general agreement that nonmetallic materials are made more flammable by increasing the partial pressure of the oxygen in an air mixture rather than by increasing the total pressure of air. Thus, a 42 percent $O_2$ / 58 percent $N_2$ mixture at 1 atm pressure is more hazardous than a 21 percent $O_2$ normal air mixture compressed to 2 atm, although the same amount by weight of oxygen is present in both mixtures. It is also recognized that materials in 100 percent oxygen at 258 mm Hg (5 psia) are more flammable than those in normal air at 1 atm. Small increases in oxygen concentration at atmospheric pressure have a similar effect on the flammability of many materials,[35] as is shown in Table 5-3.3.1. Only glass fiber materials and Teflon® and other fully fluorinated materials, of those tested, appear to be safe for use in OEA. However, caution is necessary. Glass fabrics (and asbestos fabrics) frequently contain an organic sizing material that burns vigorously in OEA. Thin films of Teflon®, Kel-F®, and other fluorocarbons will also sustain combustion in OEA, but thicker sections burn only if strongly heated from an external source.

**5-3.3.2** Chemical additives to solid plastics and textile fabrics, such as halogens, borax, phosphates, and various metal oxides, are effective in reducing both ignitibility and flammability. Impregnating cotton fabric with borax/phosphate compounds is effective in increasing the fire resistance of this material. However, protection is limited to atmospheres with less than 30 percent to 35 percent $O_2$ content.[21,35,36]

**Table 5-3.3.1 Flame Resistance of Materials Held Vertically at One Atmosphere Pressure in $O_2/N_2$ Mixtures**

| NRL Sample Number | Material | Combustion in $O_2/N_2$ Mixtures | | |
|---|---|---|---|---|
| | | 21% $O_2$ | 31% $O_2$ | 41% $O_2$ |
| FM-1 | Rosin-impregnated paper | Burned | | |
| FM-3 | Cotton terry cloth | Burned | | |
| FM-28 | Cotton cloth, white duck | Burned | | |
| FM-4 | Cotton terry cloth, Roxel-treated | No | No | Burned |
| FM-5 | Fleece-backed cotton cloth, Roxel-treated | Surface only | Burned | Burned |
| FM-14 | Cotton O.D. Sateen, Roxel-treated | No | Burned | — |
| FM-15 | Cotton green whipcord, Roxel-treated | No | Burned | — |
| FM-16 | Cotton white duct, Roxel-treated | No | Burned | — |
| FM-17 | Cotton, King Kord, Roxel-treated | No | Burned | — |
| FM-29 | Cotton white duck, treated with 30% boric acid-70% borax | No | Burned | Burned |
| FM-30 | Cotton terry cloth, treated with 30% boric acid-70% borax | No | Burned | Burned |
| FM-6 | Fire resistant cotton ticking | No | Burned | — |
| FM-7 | Fire resistant foam rubber | No | No | Burned |
| FM-9 | Nomex temperature resistant Nylon | No | Burned | — |
| FM-10 | Teflon fabric | No | No | No |
| FM-11 | Teflon fabric | No | No | No |
| FM-12 | Teflon fabric | No | No | No |
| FM-13 | Teflon fabric | No | No | No |
| FM-19 | Verel fabric | No | Burned | Burned |
| FM-22 | Vinyl-backed fabric | No | Burned | Burned |
| FM-23 | Omnicoated Dupont high-temperature fabric | No | Burned* | Burned |
| FM-24 | Omnicoated glass fabric | No | No | Burned* |
| FM-20 | Glass fabric, fine weave | No | No | No |
| FM-21 | Glass fabric, knit weave | No | No | No |
| FM-25 | Glass fabric, coarse weave | No | No | No |
| FM-26 | Glass fabric, coarse weave | No | No | No |
| FM-27 | Aluminized asbestos fabric | No | No | Burned |
| FM-32 | Rubber from aviator oxygen mask | Burned | Burned | Burned |
| FM-33 | Fluorolube grade 362 | No | No | No** |
| FM-34 | Belco no-flame grease | No | No | No** |

*Burned only over igniter.

**White smoke only.

**5-3.3.3** Ignitibility data are given for high temperature wiring operating in 100 percent $O_2$ at 34 kPa (5 psia).[37] Insulation of the wires, consisting of Teflon®, Nomex®, Kapton®, Kynar®, Silicone®, and Polyolefin®, and combinations of these, was subjected to both external heat and internal heat from overloaded electrical wires. Polyolefin® and Silicone® were flammable to the extent that these would not be suitable for use in oxygen. Teflon® burns only under extreme conditions requiring external heating and an intense electrical spark to ignite the combustion vapors. While Kapton® insulation is resistant to ignition in oxygen-enriched atmospheres, it is subject to arc tracking, which may ignite adjacent material.[38,39] Potting compounds, circuit boards, and other components of the electrical system may also contribute to the fuel supply in an OEA.

**5-3.3.4** The rate of flame spread over the surface of a combustible material provides an indication of the speed at which a fire involving the combustible will develop (*see Table 5-3.3.4*). Reported measurements of flame spread rates in an OEA may show wide variations due principally to differences in experimental techniques. Flame spread rates are much greater in the upward direction, due to buoyant convection, than in the horizontal or downward direction.

**Table 5-3.3.4 Effect of Oxygen on Flame Spread Rates over Various Materials (Edges Not Inhibited)**

| | **Flame Spread Rate (mm/s)** | |
|---|---|---|
| **Material** | **In Air** | **In 258 mm Hg Oxygen** |
| Aluminized mylar tape | — | 49.53 |
| Aluminized vinyl tape | NI | 78.74± 10.16 |
| Asbestos insulating tape | NI | 2.03 |
| Butyl rubber | 0.152 | 0.40±0.04 |
| Canvas duck | NP | 6.35 |
| Cellulose acetate | 0.305 | 7.1 |
| Chapstick | NI | 46.23 |
| Cotton shirt fabric | NP | 38.1±1.27 |
| Electrical insulating resin | NI | 6.86 |
| Electrical terminal board | NI | 1.524±.254 |
| Fiberglas@ insulating tape | NI | 106.68±15.24 |
| Foam cushion material | 4.83 | 314.96 |
| Foamed insulation | 0.051 | 55.88±5.08 |
| Food packet, aluminized paper | NI | 7.112±1.27 |
| Food packet, brown aluminum | NI | 17.78±7.62 |
| Food packet, plastic | 8.38 | 13.97 |
| Glass wool | NI | NI |
| Kel-F® | NI | NI |
| Masking tape | 4.32 | 46.228 |
| Natural rubber | 0.254 | 15.49 |
| Neoprene rubber | NI | (8.13±1.0) |
| Nylon 101 | NI | (4.83±1.27) |
| Paint, Capon, ivory | NI | 9.652±1.016 |
| Paint, Pratt & Lambert, grey | NI | 15.24±5.08 |
| Plexiglas® | 0.127 | (8.89±0.25) |
| Polyethylene | 0.356 | (6.35±1.27) |
| Polypropylene | 0.254 | (8.89±0.25) |
| Polystyrene | 0.813 | (20.32±5.08) |
| Polyvinyl chloride | NI | (2.54±0.25) |
| Pump oil | NI | 122.606 |
| Refrigeration oil | NI | 20.828±1.778 |
| Rubber tubing | 0.76 | 6.096 |
| Silicone@ grease | NI | 23.368 |
| Solder, rosin core | NI | 4.572 |
| Sponge, washing | 1.78 | 205.74±2.54 |
| Teflon® pipe sealing tape | NI | NI |
| Teflon® tubing | NI | NI |
| Tygon tubing | 4.57 | 12.7±1.27 |
| Viton A | NI | (.076±.051) |
| Wire, Mil W76B, orange | NI | 14.478±1.27 |
| Wire, Mil W76B, blue | NI | — |
| Wire, Mil W76B, yellow | NI | — |
| Wire, Mil W16878, green | NI | NI |
| Wire, Mil W16878, black | NI | NI |
| Wire, Mil W16878, yellow | NI | NI |
| Wire, Mil 16878, white | NI | NI |
| Wire, misc., white, 3/32 | NI | 8.382 |
| Wire, misc., black, 3/16 | NI | — |
| Wire, misc., brown, 7/32 | NI | 12.954±1.27 |
| Wire, misc., yellow 7/64 | NI | 22.606 |
| Wire, misc., yellow, 5/32 | NI | 10.414 |

NP — No sustained propagation of flame
NI — No ignition of material

**5-3.3.5** The rate of flame spread increases with an increase in the oxygen concentration at constant pressure or with an increase in the total pressure at a constant percentage of oxygen (increased oxygen partial pressure). Table 5-3.3.5 shows typical data for the burning rate of filter paper over a wide range of pressure and atmospheric composition.[40] In many cases, the rate of flame spread at constant atmospheric composition shows a fair correlation with the square root of the total pressure.

**5-3.3.6** At high oxygen concentrations, a flash fire can spread over the surface of fabrics having a nap of fine fibers at a very high rate [508 mm/s (20 in./sec) or higher]. This nap fire is of short duration, but it can ignite more sustained fires at edges, seams, and folds and, thus, spreads the fire very rapidly.[42]

**5-3.3.7** The combustibility of the material is affected by the diluent gas used with oxygen. It has been shown that flame spread rate is directly related to the log function of the heat capacity of the gas mixture, which can be extrapolated to zero flammability. Appreciable increase in the flame spread rate is observed where helium replaces nitrogen in air mixtures.[40,43]

**5-3.3.8** The oxygen index test, ASTM D2863, *Standard Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index)*, and variations of it, have come into wide use in the last few years for their characterizations of the flammability of materials. In the ASTM procedure, a small, vertically oriented sample is burned downward in a candle-like fashion in an oxygen-nitrogen mixture. The composition of the gas mixture is adjusted to determine the minimum percent of oxygen that will begin to support combustion of the sample. This minimum oxygen concentration is called the oxygen index (O.I.). Burning in an upward direction may take place more readily and produce a lower O.I.

The O.I. test, as determined by ASTM D2863, is limited to nonmetals (e.g., plastics) at ambient pressure. However, the O.I. concept is now utilized at elevated pressures (and temperatures) and for metals as well as nonmetals (see 5-3.4 for the oxygen index data of metals). Other means of ignition have also been used, as have other oxidants and diluents.[44,45]

Conceptually, an O.I. is a flammability limit but is more complex than the flammability limit for gas mixtures. Therefore, the oxygen index is only one of several criteria that can be utilized to evaluate the suitability of materials for a specific oxygen application.

Table 5-3.3.8 provides some O.I. data for nonmetals at ambient pressure.

### 5-3.4 Combustion of Metals.

**5-3.4.1** There is general agreement that metals are more flammable in oxygen-enriched environments than in air. For example, a 3.2-mm (0.13-in.) diameter rod of Ti-6Al-4V burned completely when ignited at the bottom in commercially pure oxygen at 0.14 MPa (20 psia), whereas it did not burn at all in air at 34.5 MPa (5000 psia), even though the partial pressure of oxygen was 7.2 MPa (1,045 psia).[47] This leads to the general conclusion that commercially pure oxygen at low pressures is more hazardous than air at relatively higher pressures. Whereas small increases in oxygen concentration at atmospheric pressure render nonmetallic materials dramatically more flammable (*see 5-3.3.1*),

**Table 5-3.3.5[41] Typical Measured Burning Rates for Strips of Filter Paper at 45° Angle**

| Total pressure. atm. abs. | | | Burn Rate, cm/s 0.21 atm. | 0.53 atm. | 1.00 atm. | 4.03 atm. | 7.06 atm. | 10.09 atm. |
|---|---|---|---|---|---|---|---|---|
| ft. of seawater | | | — | — | 0 ft. | 100 ft. | 200 ft. | 300 ft. |
| Gas Composition (dry basis) | | | | | | | | |
| %0$_2$ | %N$_2$ (a) | %He | | | | | | |
| 99.6 | 0.4 | 0.0 | 2.32 | 3.13 | 4.19 | d | d | d |
| 50.3 | 49.7 | 0.0 | 1.13 | 1.44 | 2.36 | 3.72 | 5.10 | 6.34 |
| | | | 1.17 | | | 3.77 | 4.06 | |
| 20.95,b | 79.05 | 0.0 | c | 0.80 | 1.17 | 1.82 | 2.80 | 3.13 |
| | | | | | 1.17 | 1.78 | 2.28 | 3.25 |
| | | | | | 1.10 | | | |
| 49.5 | 0.0 | 50.5 | 1.24 | 1.87 | 2.96 | 4.06 | 4.90 | d |
| | | | | 1.90 | 2.89 | | 4.82 | |
| | | | | | 2.89 | | | |
| 20.3 | 0.0 | 79.7 | c | c | c | 2.23 | 2.61 | 2.49 |
| 47.0 | 24.6 | 28.4 | d | d | 2.74 | 3.66 | 4.41 | 5.53 |
| | | | | | 2.68 | | 4.64 | 6.78 |
| 20.9 | 39.6 | 39.5 | d | d | 1.38 | 2.28 | 2.71 | 3.72 |
| | | | | | 1.38 | 2.28 | 2.83 | 3.13 |
| | | | | | 1.35 | 1.97 | 2.74 | 3.56 |
| | | | | | 1.27 | 2.28 | | 3.33 |
| | | | | | | 1.81 | | 3.00 |
| | | | | | | 1.72 | | |

(a) Includes any argon that was present.
(b) Compressed air.
(c) Sample would not burn, even with brightly glowing igniter grid.
(d) No run was made under these conditions.

relatively large increases in oxygen concentration and increase in total pressure are required to render most structural metals flammable. Two measures of the relative flammability of metals that are of practical value are the minimum oxygen pressure required to support complete combustion of a standard sample (threshold pressure) and the minimum oxygen concentration required to support combustion of a standard sample at a given pressure (oxygen index).

NOTE: Combustion is considered "complete" when the sample burns up to the point where the sample holder influences the combustion process.

**5-3.4.2** The threshold pressures of several alloys configured as 3.2-mm (0.13-in.) diameter rods burning in an upward direction are shown in Table 5-3.4.2(a).[48-53] Because the results of combustion tests are highly configuration-dependent, it should be noted that these threshold pressures are not absolute flammability limits. Changing the configuration of the test samples can dramatically affect the threshold pressures. Table 5-3.4.2(b) shows the threshold pressures of several metal alloys configured as 60 × 60 wire meshes with a wire diameter of 0.18 mm (0.007 in.). The wire mesh test samples were rolled into 6.4-mm (0.25-in.) diameter cylinders, mounted vertically, and ignited at the bottom.[54] By comparing the threshold pressures for 3.2-mm (0.13-in.) diameter rods and the wire meshes, the dramatic effect of configuration becomes evident.

**5-3.4.3** The minimum oxygen concentration required to support combustion of a standard sample (oxygen index) is another important measure of the flammability of metals. The oxygen indices for C-1018 carbon steel tube [25.4-mm (1-in.) outside diameter and 4.8-mm (0.19-in.) wall] are shown in Figure 5-3.4.3(a).[55] For most structural alloys, the oxygen index decreases with increasing pressure.[51, 56-60] The oxygen indices for several alloys configured as 3.2-mm (0.13-in.) diameter rods are shown in Figure 5-3.4.3(b).[57] The oxygen indices of several alloys configured as rods and tubes are shown in Figure 5-3.4.3(c).[58]

**5-3.4.4** The oxygen indices for aluminum alloys are affected by the diluent gas used with oxygen. Figure 5-3.4.4 shows the threshold pressures of two aluminum alloys configured as 6.4-mm (0.25-in.) diameter rods burning upward in downward-flowing gas and shown as a function of the mole percent of nitrogen and argon in oxygen.[56]

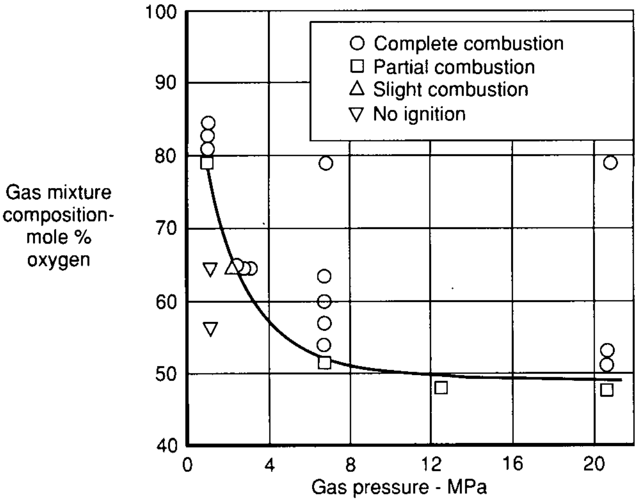

**Figure 5-3.4.3(a)[55]** Effect of pressure on the mole percent of oxygen in nitrogen required to support upward combustion of C-1018 carbon steel tubes [25.4-mm (1-in.) outside diameter and 4.8-mm (0.19-in.) wall].

**Table 5-3.3.8 Oxygen Index for Selected Materials[46]**

| Material | Description | OI$^a$ |
|---|---|---|
| Polyacetal | | 16 |
| Loctite pipe sealant | | |
| Nuclear grade PST® | anaerobic sealant (cured), cup test$^b$ | 17 |
| Type PS/T | anaerobic sealant (cured), cup test$^b$ | 20 |
| Poly(methylmethacrylate) | | |
| Plexiglas® | | 18.5 ± 0.5 |
| ECO/Rubber | epichlorohydrin rubber | 18.5 |
| Silicone® rubber | | |
| RTV 102 | | 23 |
| Silastic@ 732 | | 25 |
| SMS 2454 | | 25 |
| RTV 60 | | 28.5 |
| RTV 560 | | 29 |
| RTV 560 mixture | user-added 50% glass | 36 |
| Silicone® grease | cup test$^b$ | 26 ± 1 |
| Rectorseal® #15 thread sealant | | < 30.0 |
| Durabla gasket | | 28.0 ± .5 |
| Fluorosilicone grease #822 | cup test$^b$ | 30 |
| Blue Gard® gaskets | | |
| Blue Gard® 3000 | nonasbestos gasket | 30.5 ± 0.5 |
| Blue Gard® 3200 | nonasbestos gasket | 31 |
| Blue Gard® 3400 | nonasbestos gasket | 52 |
| Blue Gard® 3200 | nonasbestos gasket | 60 |
| Blue Gard® 3000 | nonasbestos gasket | 62 |
| Blue Gard® 3300 | nonasbestos gasket | 68 |
| Nylon | | |
| Nylon 66 | | 30.5 |
| Nylon 66 (glass-filled) | | 23.5 |
| CYL-SEAL thread sealant | | 38 |
| Polyvinylidene fluoride | | |
| Kynar® | | 39 |
| Fluorocarbon rubber | | |
| Viton® | brown O-ring | '0.5 ± 0.5 |
| Viton®, green | green O-ring | 42 |
| Viton A® | | 57 |
| Viton A® | | 57.5 |
| Viton E-60C® | | 60.5 |
| Viton B®, #V494-70 | | DNP |
| Balston® filters | | |
| Type—Epoxy | cut from cylinder | 42.5 |
| Type Q-fluorocarbon | cut from cylinder | 47 ± 1 |
| Type H-Inorganic | cut from cylinder | DNI |
| Molykote® Z powder | $MOS_2$ cup test$^b$ | 45 |
| Bel-Ray Greases | cup test$^b$ | 57 |
| FC1260 | cup test$^b$ | DNP |
| FC1245 | halocarbon oil/graphite | |
| Key Abso-Lute® | cup test$^b$ | 67 |
| CTFE Lubricants | | |
| Fluorolube GR362 grease | cup test$^b$ | 67 ± 4 |
| Halocarbon 25-20 oil | cup test$^b$ | 75 |
| Halocarbon 11-14S oil | cup test$^b$ | DNP |
| Fluorocarbon FEP | tubing | 77 |
| Fluorocarbon PFA | | 100 |
| Fluorocarbon TFE | | DNP |
| PFPE grease | | |
| Fomblin RT15® | cup test$^b$ | DNP |
| Krytox 283AC® | cup test$^b$ | DNP |
| Krytox GPL 225® | cup test$^b$ | DNP |
| Krytox GPL 205® | cup test$^b$ | DNI |
| Tribolube 13C® | cup test$^b$ | DNP |
| PFPE fluid | | |
| Fomblin Y25® | cup test$^b$ | DNI |
| Krytox GPL 105® | cup test$^b$ | DNP |
| CTFE plastic | | |
| Kel-F 81® | 15% glass filled | DNP |
| Kel-F 81® | nonplasticized | DNP |

**Table 5-3.3.8 (cont.)**

| Material | Description | OI[a] |
|---|---|---|
| Perfluoroelastomer | | |
| Kalrez® 1045 | O-ring | DNP |
| Kalrez® 1050 | O-ring | DNP |
| Kalrez® 4079 | O-ring | DNP |
| Silica gel | cup test[b] | DNI |
| Blue Drierite | cup test[b] | DNI |
| Kaowool Insulation | alumina-silica | DNI |
| Cerawool paper | | DNI |
| Fiberglass/cement board | | DNI |
| Kwik Flux #54® | cup test[b] | DNI |
| Asbestos cement board | | |
| Transite® | | DNI |
| Sindanyo CS51® | | DNI |
| Turnalite TI 150® | | DNI |
| Asbestos paper | 32 lb/100 ft$^2$ | DNI |

[a] DNP (Did not propagate); DNI (Did not ignite).

[b] Cup test performed basically as described by Nelson, G.L., and Webb, J.L. "Oxygen Index of Liquids, Techniques and Application." *Journal of Fire and Flammability*, Vol. 4, July 1973, pp. 210-226.

**Table 5-3.4.2(a)[48-53] Threshold Pressures[a] in Oxygen of 3.2-mm (0.13-in.) Diameter Rods Ignited at the Bottom**

| Material | Threshold Pressure[a] (MPa) | (psia) |
|---|---|---|
| Monel® K-500 | >68.9 | >10,000 |
| Inconel MA754 | >68.9 | >10,000 |
| Monel® 400 | >68.9 | >10,000 |
| Brass 360 CDA | >68.9 | >10,000 |
| Nickel 200 | >55.2 | >8,000 |
| Copper 102 | >55.2 | >8,000 |
| Hastelloy C276 | 20.7 | 3,000 |
| Inconel 600 | 17.2 | 2,500 |
| Inconel 625 | 17.2 | 2,500 |
| Hastelloy C22 | 13.8 | 2,000 |
| Inconel 718 | 6.9 | 1,000 |
| 440C SS | 6.9 | 1,000 |
| 316 SS | 6.9 | 1,000 |
| 304 SS | 6.9 | 1,000 |
| 17-4 PH SS | 6.9 | 1,000 |
| Weldalite 049 | 2.1 | 300 |
| Aluminum 8090 | 2.1 | 300 |
| Aluminum 2219 | 0.2 | 35 |
| HSLA steel[b] | 0.17 | 25 |
| Aluminum 99.9% | 0.17 | 25 |
| Ti-6Al-4V | 0.007 | 1 |

[a] Threshold pressure is the minimum test pressure required to support complete combustion of the test sample. (*See NOTE to 5-3.4.1.*)

[b] Denotes high-strength low-alloy steel.

**Table 5-3.4.2(b)[54] Threshold Pressures[a] in Oxygen of 60 × 60 Wire Meshes Rolled into 6.4-mm (0.25-in.) Diameter Cylinders Ignited at the Bottom**

| Material | Threshold Pressure[a] (MPa) | (psia) |
|---|---|---|
| Nickel 200 | >69 | >10,000 |
| Copper 100 | 0.3 | 47 |
| Monel® 400 | ≤0.085 | 12.4 |
| 316 stainless steel | ≤0.085 | 12.4 |
| 304 stainless steel | ≤0.085 | 12.4 |
| Carbon steel | ≤0.085 | 12.4 |

[a] Threshold pressure is the minimum test pressure required to support complete combustion of the test sample. (*See NOTE to 5-3.4.1.*)

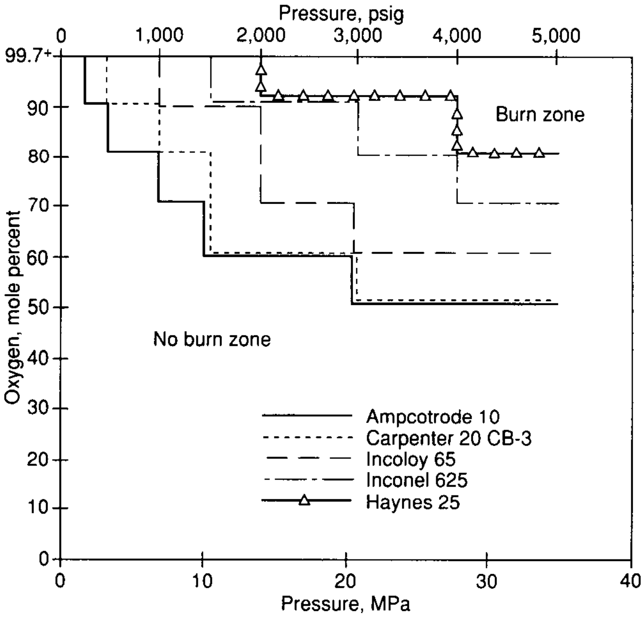

**Figure 5-3.4.3(b)[57] Summary of flammability data showing boundaries between burn and no-burn zones for several engineering alloys configured as 3.2-mm (0.13-in.) diameter rods burning in the upward direction.**

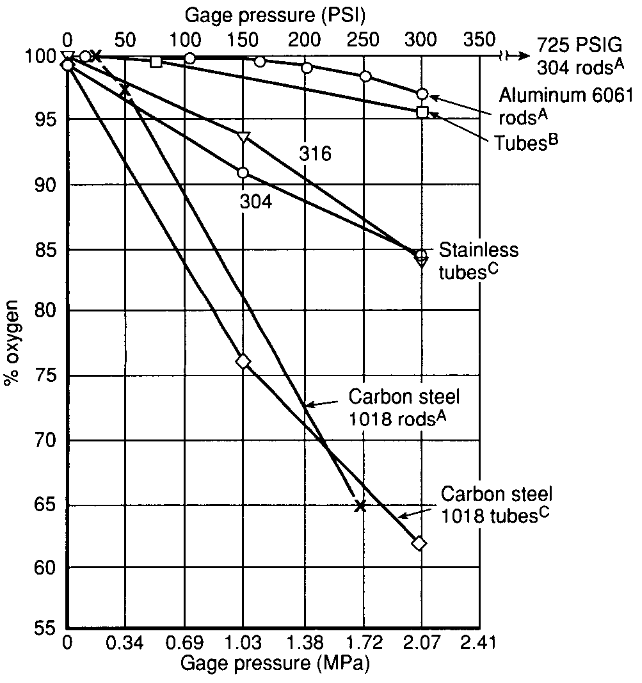

**Figure 5-3.4.3(c)[58]** **Oxygen index of some alloys in various configurations.**

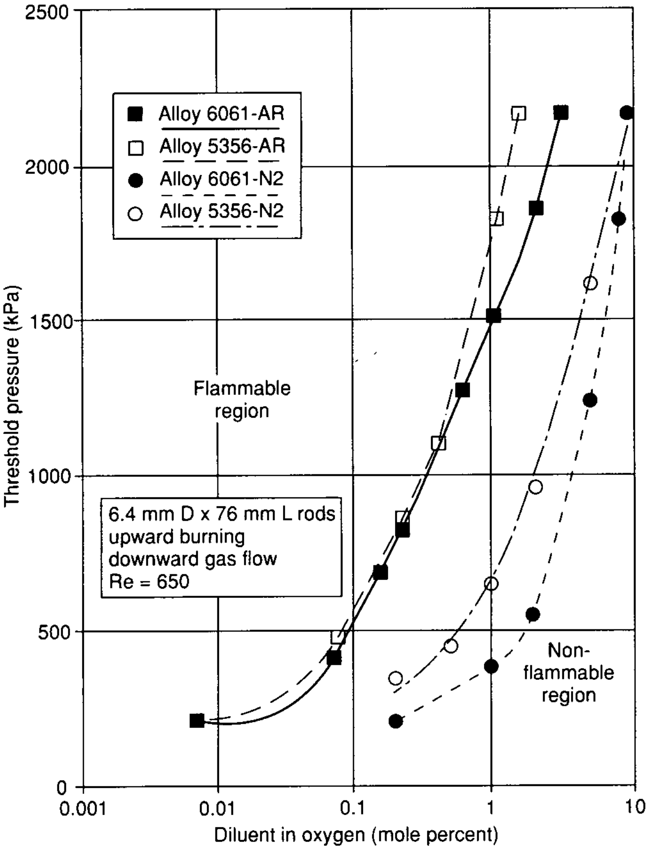

**Figure 5-3.4.4[56]** **Threshold pressures of two aluminum alloys configured as 6.4-mm (0.25-in.) diameter rods burning upward in downward-flowing gas.**

## 5-4 Test Methods.

### 5-4.1 General.

**5-4.1.1** A variety of test methods has been used to evaluate materials for use in OEA, but little progress has been made toward the standardization of such methods. Where possible, it is desirable to pattern such methods after the well-established procedures for the fire hazard rating of materials for use in a normal atmosphere. This is seldom possible because of the need to make measurements over a wide range of pressure and atmospheric composition, the limitations imposed by a pressure chamber of practical size, and the difficulties in providing suitable gas supplies and ignition sources within the test chamber. Almost all testing in OEA has been limited to small specimens using laboratory-scale apparatus. Large-scale testing under conditions that simulate actual fire conditions is only beginning.

**5-4.1.2** The significance of the various properties of a material that contribute to its fire hazard depend significantly on whether the material is in the gaseous, liquid, or solid phase, and it is therefore convenient to discuss test methods under these headings.

**5-4.1.3** The American Society for Testing and Materials Committee G-4 on the Compatibility/Sensitivity of Materials in Enriched Oxygen Atmospheres is developing and promulgating standard test methods, definitions, recommended practices, classifications for determining the compatibility/sensitivity of materials, materials configurations, and applications intended for use in systems subjected to oxygen-enriched atmospheres. The committee's considerations include, but are not limited to, ignition, combustion, off-gassing, reaction products, and decomposition tendencies.

### 5-4.2 Gases.

**5-4.2.1** Minimum ignition energies are usually determined using a capacitance spark-type discharge. Many of the apparatuses are patterned after those of the Bureau of Mines[7,9] in which flanged electrodes are used and in which quenching distances can also be obtained.

**5-4.2.2** Flammability limits can be determined under quiescent conditions by the partial pressure method[11] or under flow conditions. The reaction vessel diameter should be at least 51 mm (2 in.) for determinations at 1 atm. Where wall effects are great, (e.g., at reduced pressures) quenching distance data should be relied on to determine the suitable vessel size. Also, the ignition source should be of sufficient strength to ignite the test mixture.

### 5-4.3 Liquids.

**5-4.3.1** Flash points of combustible liquids are ordinarily determined in air using such apparatuses as the Tag Closed Tester (ASTM D56, *Standard Test Method for Flash Point by Tag Closed Tester*) and the Cleveland Open Tester (ASTM D92, *Standard Test Method for Flash Fire Points by Cleveland Open Cup*). The closed cup method tends to give slightly lower temperature values, i.e., 6°C to 12°C (10°F to 20°F), for most liquids.

**5-4.3.2** Minimum autoignition temperatures in air or oxygen at atmospheric pressure may be determined using the ASTM recommended apparatus (ASTM E659, *Standard Test Method for Autoignition Temperature of Liquid Chemicals*), which is equipped with an open 200-cc Pyrex® Erlenmeyer flask. At reduced pressures or oxygen concentrations, larger test vessels are necessary to avoid possible wall effects. Modified ASTM apparatuses, such as those used by the Bureau of Mines,[8] are suitable for reduced and elevated pressure determinations.

### 5-4.4 Solids.

**5-4.4.1** The National Aeronautics and Space Administration has published procedures for the evaluation of materials for use in spacecrafts.[61] These include:

(a) Combustion of materials;

(b) Heat release rates;

(c) Odor and off-gassing tests of nonmetallic materials;

(d) Electrical wire insulation flammability test;

(e) Mechanical and pneumatic test of materials in gaseous and liquid oxygen;

(f) Combustion of materials in high pressure oxygen; and

(g) Arc tracking of wire insulation.

**5-4.4.2** These NASA procedures are small-scale tests, suitable for use in the evaluation of materials in oxygen-enriched atmospheres. The document contains criteria for the selection of materials based on these data. This NASA document also contains guidelines on conducting large-scale flammability and out-gassing tests.

**5-4.4.3** Spark,[61] hot wire,[35,40] and radiation[43,62] ignition sources have been used to evaluate the ease of ignition of materials in OEA. These are direct adaptations of methods widely used in a normal atmosphere.

**5-4.4.4** An investigation of spontaneous heating in oxygen-enriched atmospheres was carried out using an apparatus based on the ASTM E136, *Standard Test Method for Behavior of Materials in a Vertical Tube Furnace at 750 Degrees C*, noncombustibility apparatus, which is an adaptation of the BS476 apparatus.[20]

**5-4.4.5** Some solid materials exist in such a finely divided form as to be ignitible by a spark discharge. These forms include combustible dusts, such as flour, teased cotton wool, and the nap of flammable fabrics. An appropriate test method is described in 5-4.2.1.

**5-4.4.6** The rate at which flames will spread under a given set of circumstances is the most important property of a solid material in terms of fire hazard. Unfortunately, several of the methods regarded as most reliable for flame spread determinations in a normal atmosphere are not readily applicable at elevated pressures or even in atmospheres of nonstandard composition.

**5-4.4.7** The method applicable to building lining materials and considered to be standard in North America is ASTM E84, *Standard Test Method for Surface Burning Characteristics of Building Materials*, colloquially known as the Tunnel Test. The specimen under test is 7.62-m (25-ft) long and is ignited under controlled draught conditions by a gas flame enveloping the first 1.5 m to 1.8 m (5 ft to 6 ft) of the specimen. It would doubtless be possible to supply a suitably constructed apparatus with a specified oxygen atmosphere at pressures of up to, for example, 3 atm. Specification of the igniting flame would still constitute a problem, however, since flame dimensions and rate of gas supply could not both be maintained invariant regardless of atmospheric constituency and pressure. No laboratory has yet attempted to investigate flame spread in nonstandard atmospheres using a modified ASTM E84 technique.

(a) For building lining materials, the current thinking is that useful flame spread tests necessitate a fairly severe exposure, preferably on a large scale. Atmospheric oxygen depletion and thermal problems are then important.

(b) Another popular test for assessing the flame spread characteristics of building materials is the ASTM E162, *Standard Test Method for Surface Flammability of Materials Using a Radiant Heat Energy Source*. Although the specimen size is not large [457 mm × 152 mm (18 in. × 6 in. )], the test involves irradiation from a 457 mm × 305 mm (18 in. × 12 in.) gas-fired panel, and this feature complicates its application in nonstandard atmospheres.

**5-4.4.8** Where a solid material is of the nature of a fabric or plastic and will not constitute part of a larger assembly when in use, it is easier to devise a test suitable for use at elevated pressures or in otherwise nonstandard atmospheres. One approach is to hang the material vertically, igniting it at the bottom. For ASTM D568, *Standard Test Method for Rate of Burning and/or Extent and Time of Burning of Flexible Plastics in a Vertical Position*, which is intended for measuring the flammability of thin plastics in a normal atmosphere, a specimen length of only 457 mm (18 in.) is specified. A British worker, investigating the effect of pressure and oxygen enrichment, used a specimen 1,829 mm × 38 mm (72 in. × $1\frac{1}{2}$ in.) in a cabinet of 305 mm$^2$ (1 ft$^2$) cross section. An atmospheric flow of 0.03 m/s (5 linear ft/min) was maintained in an attempt to minimize the effects associated with the small dimensions of the compartment. The choice of a substantial vertical dimension minimized the effect of the variation of the atmospheric conditions on the characteristics of the igniting flame.

**5-4.4.9** ASTM D1230, *Standard Test Method for Flammability of Apparel Textiles*, is potentially adaptable for use with nonstandard atmospheres. The upper surface of a 51 mm × 152 mm (2 in. × 6 in.) specimen, with the longer dimension inclined at an angle of 45 degrees to the horizontal, is exposed to ignition by a small pilot flame. Adaptation of an apparatus of this nature to nonstandard atmospheres is a more formidable task than might first be thought. The supply of air required to permit the burning of even an ounce of most combustible materials would necessitate 2.8 m$^3$ (100 ft$^3$) of air if serious oxygen depletion were to be avoided and substantially more if temperature rise were an important consideration. It is also difficult to establish an exposure condition that remains invariant. Thus, if a flame constitutes the exposure and its fuel supply is held constant, its dimensions and temperature will be a function of the atmospheric composition and pressure. Even resorting to electrical heating poses similar problems. The average heating wire is of sufficiently small diameter to make convective cooling significant compared with radiative losses, even at high temperatures. Thus, the temperature attained by a wire subjected to a constant wattage or voltage is dependent on the nature of the atmosphere. Increase in pressure or change of diluent from nitrogen to helium will reduce the temperature of the wire.

(a) Where fabrics are involved, exposure to a small ignition source is satisfactory, thus simplifying development of a test for use in nonstandard atmospheres. The nature of the test chosen is still of great importance, however. It has been found, for example, that the effect of increase in pressure on flammability, as demonstrated by a test such as that of ASTM D1230, is dependent on the inclination of the specimen to the horizontal being greatest at an angle of 45 degrees.[40]

**5-4.4.10** The oxygen index test, ASTM D2863, *Standard Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index)*, has come into wide use in the last few years for determining the characteristics of the flammability of solids. In this procedure, a small, vertically oriented sample is burned downward in a candle-like fashion in an oxygen-nitrogen mixture. The composition of the gas mixture is adjusted to determine the minimum percent of oxygen that will support combustion of the sample. This minimum oxygen concentration is called the oxygen index (O.I.).

An oxygen index of 20.9 indicates that a material will just continue to burn downward in a normal atmosphere. Burning in an upward direction takes place more readily, and it has been found that an O.I. of 26 or 27 is necessary if a material is to be noncombustible in air. Still higher values would be required for materials for use in most OEA. The oxygen index test provides a convenient method for comparing the flammability of similar materials. No correlation with performance under fire conditions is implied. The O.I. may be used as a guide in the selection of materials, which should then be tested under conditions of intended use.

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## Chapter 6 Design of Systems to Function in Oxygen-Enriched Atmospheres

*(Footnotes to Chapter 6 can be found at the end of the chapter.)*

### 6-1 General.

**6-1.1** This chapter discusses the design of systems used to handle, or to function in, oxygen-enriched atmospheres in the various applications described in Chapter 2.

**6-1.2** Because of the inherent fire and explosion hazard associated with their use in oxygen-enriched atmospheres, all components used in systems, such as mechanical and electrical systems, require careful design for the proper functioning of these systems and, where applicable, optimum life safety for all people in the immediate vicinity under all conditions of use.

**6-1.3** Various interested groups have extensively studied fire safety in oxygen-enriched atmospheres, but no formal safety standards have been established, and no test methods have been promulgated for general application. In the interim, certain fire hazard considerations that need to be recognized in some detail are herewith provided as minimum safety guidelines in the design and construction of the component parts of equipment, apparatus, or instruments, including controls for the various utility services required.

**6-1.3.1** These guidelines currently are general in nature, pending further operating experience in the field and translation of certain critical laboratory-scale information into practical application terms.

**6-1.3.2** The extent or intensity of a fire may be minimized by reducing the quantities or effect of one or more factors of combustion. Quantities of exposed combustible materials used or present in oxygen-enriched atmospheres should be kept to the absolute minimum practicable.

### 6-2 Types of Systems Used in OEA.

**6-2.1 Mechanical and Electrical Systems.** Mechanical and electrical systems include the following:

(a) *Air Conditioning.* Heating, cooling, humidity control, purification, filtering, fresh air supply, and forced circulation.

(b) *Hydraulic Services (water and hydraulic fluids).* Acceptable hydraulic fluids (chemically inert in oxygen), water supply and waste piping, valves, temperature controls, pressure regulators, fire extinguishment.

(c) *Compressed Air Supply.* Compressor, cylinder manifold for emergency use, pressure controls, and piping system from supply source to use location.

(d) *Gas Supply.* Cylinders of such compressed gases as oxygen, nitrous oxide, nitrogen, helium, natural air for human breathing, and anesthetic vapors, such as halothane, enflurane, and isoflurane, cylinder storage, cylinder fastenings in storage or in manifold assemblies, piping and fittings with check valves, flow valves, pressure regulators as required for safe transmission of gas from cylinder to terminal at use site, hose and hose connections at use site for attaching dispensing equipment, inhalation devices such as face masks and endotracheal tubes for connecting to dispensing equipment and for supplying air or gaseous mixtures to humans or animals for breathing.

(e) *Suction Apparatus.* Vacuum pump with controls, piping system from pump to use site, pickup hose, and attachments and shutoff valves.

(f) *Electrical-Main and Emergency Systems.* Conduit and conduit fitting sealing compound, insulated conductors, convenience outlets, switches, overcurrent protective devices (fuses, circuit breakers, and relays), temperature indicating and control devices (thermostats and thermistors), lighting (luminaires, lamps, conductors, and switches), electronic monitoring devices (oscilloscope, blood pressure and heartbeat rate, temperature and high-low alarms), medical instruments (defibrillator and recorders), clocks, elapsed time indicators, chamber temperature indicators, and pressure control devices.

(g) *Communication Systems.* Telephone or intercommunication systems, microphone with speaker (receiver) for communication with others in other compartments of chamber, with monitor at outside chamberport, or with others at remote stations; television and radio.

**6-2.2 Combustible Materials (Fuels).** These materials include electrical conductor insulating materials, sealing compound, molded plastic parts of luminaires, switches, receptacles, electric extension cords and communication equipment conductors and parts, clocks, timers, terminal strips, grommets, insulating tape, wood, acrylic and styrene parts of luminaires, rubber and plastic hose for water, air and medical gases, face masks, catheters, endotracheal tubes, surgical drapes, gauze, drainage tubes and containers (plastic), surgical table mattresses and patient grounding and restraining straps, clothing textiles and shoes, personnel grounding straps, eyeglass frames and pocketed materials, paper and writing materials for notes and instructions, laboratory animals (including feed), excreta and bedding, and human bodies.

## 6-3 Systems Design Considerations.

### 6-3.1 General.

**6-3.1.1** The rate of flame spread and ignition susceptibility of materials of construction should be regarded as prime and inseparable considerations in the promotion of safe design of systems associated with oxygen-enriched environments. This also includes the oxygen compatibility (deterioration stability) as well as the careful assessment of any potential ignition sources capable of initiating combustion in such atmospheres.

**6-3.1.2** Risk of fire initiation or fire expectancy should be a matter of prime concern.

**6-3.1.3** Fires in oxygen-enriched environments are of a fundamentally different character than those occurring in a normal atmosphere. The fire-severity potential is high and extensive damage is possible.

**6-3.1.4** The presence of flammable and combustible liquid vapors and gases and particulate solids (dusts) in oxygen-rich atmospheres can result in ultra-rapid combustion with violent explosion.

**6-3.1.5** A large amount of potential (pressurized) energy is stored in even a small amount of compressed gas (contained in a vessel). Sudden release of such energy from failure (rupture) of a large- or moderate-sized housing vessel or chamber [ranging from a few cubic meters (or cubic feet) to several thousand cubic meters (or cubic feet) in volume] or its auxiliary component parts (piping, valves, etc.) could result in widespread injury to personnel and devastating damage to the structures and adjacent exposures.

**6-3.1.6** Similarly, accidental overpressurization and uncontrolled decomposition (with possible vacuum collapse or implosion) due to equipment failure or malfunctioning of mechanical, electrical, and electronic devices should be guarded against with overriding safety controls and interlocks.

**6-3.1.7** Air conditioning services (ventilation, refrigeration, humidity, and air-quality control) in closed systems are essential to the safety of the occupants. It is important, therefore, to guard against excessive oxygen or nitrous oxide leaks around administrating apparatus, as well as near such likely sources as vapors from anesthetic agents, drugs and medical preparations, excess humidity, respired carbon dioxide, and paint fumes and toxic or irritant vapors emitted from thermal decomposition of heated or burning materials.

**6-3.1.8** Inability to escape from such closed chambers poses a serious problem. For the safety of the occupants in the event of emergencies requiring prompt evacuation from such facilities, interconnecting chambers (or safety locks) or compartments (with pressure equalization features) need to be provided that will permit rapid egress and promote prompt outside efforts for rescue action. Rapid decompression needs to be avoided to prevent serious differential pressures between the nasopharynx and sinuses or middle ear; expansion of gas pockets in the gastrointestinal tract; expansion of trapped gas in the lungs; and the development of bends.

**6-3.1.9** Total elimination of combustible materials is the ideal objective, though it may not be totally achieved in practice. It is, therefore, imperative that every possible effort be made to restrict to the barest minimum the quantity of combustibles permitted within the system, vessel or chamber (including interior surface finishes, such as paints, plastic coverings, and acoustical, thermal, and electrical insulation), coverings and housings of servicing apparatus, and instrumentation employed inside the system or chamber. Combustibles used on exterior support systems or units (ventilating, air conditioning purification or filter media, as well as auxiliary power and air-oxygen supplies) and any components associated therewith (including hydraulic fluids, gaskets, packing and joint compounds, lubricants, etc.) should be regarded as potential fuels, until determined otherwise by suitable tests.

**6-3.1.10** Guidelines for the design of systems for oxygen or oxygen-enriched service are provided in ASTM guide G 88.[1] The basic intent of the document is to reduce the severity of the environment by avoiding or minimizing the factors that cause ignition and enhance propagation. It does not address the selection of materials of construction, which can be found in ASTM guides G63 and G94.

### 6-3.2 Materials for Fabrication of Systems.

**6-3.2.1** The fire-safe characteristics of all materials involved in oxygen-enriched environments need to be carefully and completely evaluated under end-use performance. Accelerated (time-temperature concentration) oxygen deterioration and degradation (by high-energy and ionizing radiation) tests for service durability also should be conducted for overall evaluation.

**6-3.2.2** The possibility of evolution of toxic products or irrespirable vapors or gases produced by thermal decomposition or combustion or by generation of ozone and oxides of nitrogen around high-voltage and radiation-equipment also should be considered. Emission of any such noxious substance is particularly dangerous in some chamber installations, since they operate with a recirculating ventilation system that does not introduce the volume of fresh air necessary for effective dilution of such contaminants.

**6-3.2.3** Guidance for selection of suitable fire-safe materials is provided in Chapter 5 of this guide.

(a) Studies on the hazards and fire risks in oxygen-rich gas environments have been reported by both the RAF Institute of Aviation Medicine of the Air Force Department of the Ministry of Defence, Farnsborough, Hants, England,[2,3] and the NASA Lyndon B. Johnson Space Center, Houston, Texas.[4] The latter developed information on the thermal behavior of certain materials and a categorization for their functional application in various environments in an effort to promote crew-bay safety and mission success. The test evaluations for establishing the criteria of acceptability are directed toward flammability and off-gassing properties of nonmetallic materials. The back-up data are developed by the following group of tests:

(a) Flash and fire points;

(b) Upward/downward combustion propagation rates;

(c) Calorific fuel value (heat of combustion);

(d) Electrical wire insulation, coating, and accessory flammability tests;

(e) Electrical overload and hot-wired ignition tests;

(f) Odor and off-gassing (total organic volatile — potentially toxic and objectionable products) tests; and

(g) Carbon monoxide tests.

These test procedures, along with other supplementary tests (electrochemical initiation of wire insulation fire, friction and impact ignition, gap-propagation determination, autogeneous ignition points, etc.) have been reported.[4]

**6-3.2.4** Additional guidance regarding the selection of materials for use in oxygen systems can be found in ASTM guides G63[5] and G94[6] They apply respectively to nonmetallic and metallic materials under consideration for direct or indirect oxygen or oxygen-enriched fluid service. While the intent of ASTM G88 is to reduce the severity of the environment by avoiding or minimizing the factors that cause ignition and enhance propagation (*see 6-3.1.10*), the intent of ASTM G63 and ASTM G94 is to select materials that can withstand that severe environment. The material selection method includes determining the most severe operating conditions of the intended application, evaluating the probability of occurrence for various ignition sources and their severity, evaluating the available ignition and combustion data for the materials under consideration, and assessing the effect on personnel safety, system objectives, and functional capabilities.

### 6-3.3 Electrical Wiring and Equipment.

**6-3.3.1** No electrical equipment should be installed or used in oxygen-enriched atmospheres unless approved for use at the maximum proposed pressure and oxygen concentration. Electrical equipment should be provided with noncombustible insulation, unless the equipment is of construction that has been found by testing, at the maximum pressure and the oxygen concentration encountered in the chamber or system, to confine any burning of the insulation within the enclosure.

NOTE: Most metals burn freely in oxygen-enriched atmospheres (*see 5-3.4*), depending on the concentration and pressure of the oxygen. Electrical contacts may likewise burn away and initiate fires of the nearby insulation or materials unless proven by tests to be suitable for the particular pressure and oxygen concentration in the chamber or system. Apparatus and circuits that have been found to be safe in ordinary atmospheric ambients are not necessarily safe in oxygen concentrations or pressures higher than those of ordinary atmospheres. It is therefore necessary that equipment and circuits be tested for safe use at the maximum pressure and oxygen concentration as well as for the materials that may be in proximity to the electrical equipment or circuits.

**6-3.3.2** Since there are no flexible cords available with noncombustible insulation, it is essential for safe operation that portable equipment be used in oxygen-enriched atmospheres only if required for life safety and under rigorously controlled conditions. Fixed electrical equipment within an oxygen-enriched atmosphere should comply with the requirements of NFPA 70, *National Electrical Code®*, Article 500, Class I, Division 1, and, in addition, equipment installed therein should be approved for use in the specific hazardous atmospheres at the maximum proposed pressure and oxygen concentration.

**6-3.3.3** All electrical wiring installed in a system or chamber should comply with the requirements of the *National Electrical Code*, Article 500, Class I, Division 1. The boxes and fittings should be approved for use in the specific hazardous atmospheres at the maximum pressure and oxygen concentration of the chamber or system.

**6-3.3.4** Raintight fittings, boxes, and equipment should be used if such devices could be exposed to the water from a sprinkler or water spray system protecting the chamber in the event of a fire in the vicinity of the chamber while it is in operation.

**6-3.3.5** All electrical circuits contained within the chamber or system should be supplied from an undergrounded electrical system, fed from isolating transformers located outside the chamber or system, and equipped with a ground-contact indicator with appropriate signal lamps. This indicator should be capable of sensing single or balanced capacitive-resistive faults as well as leakage of current to ground.

### 6-3.4 Prevention of Ignition.

**6-3.4.1** The number and variety of potential ignition sources are discussed in Chapters 4 and 5.

**6-3.4.2** The ideal fire safety aim is total security against all conceivable sources of ignition. Technical service requirements in many complex systems make it difficult to attain such overall control without compounding the problem with another less controllable hazard.

**6-3.4.3** The degree of ignition and fire spread can be greatly reduced (if not eliminated) by various design innovations and applicable "firestopping" techniques, by avoidance of mass concentration of nonmetallic and combustible materials and their close proximity to potential heat sources, or by eliminating all potential propagation paths through geometric configurations and spatial separation with gaps in and around such critical areas of various internal assemblies.

**6-3.4.4** The principle of "thermal damping" through conductive "heat sinks" and similar flame propagation arresting systems, to prevent spread of fire by "flashover" from one area to another, may be a promising solution. Similarly, the practice of using "sealed packaging," inerted compartmentation, fire-resistive encapsulation and electrical mineral insulation, and noncombustible organometallic and ceramic (cermets) coatings should find material application in this extrahazardous area. Potential ignition problem areas might also be monitored by infared thermographic methods, as employed by aircraft designers for reliability inspection, and for protection against fire, overheat, and abnormal thermal gradient behavior in high density packaging of modules of printed circuits.

### 6-4 Cleaning for Oxygen Service.[7]

**6-4.1** All materials that contact oxygen should be cleaned to remove all foreign material. Of particular importance is the removal of lint, dust, and organic matter such as oil and grease. The latter includes fingerprints. These foreign materials are relatively easily ignited in oxygen and oxygen-enriched atmospheres and could result in an explosion or a fire. A fire could, in turn, ignite the oxygen container or piping. (A list of ignition mechanisms is found in 4-3.1.4 and 5-3.2.6.)

**6-4.2** A variety of cleaning methods is used in practice, including caustic or acid solutions, steam (with or without detergents), hot water (with or without detergents), solvents (with or without vapor degreasing equipment), supercritical fluids, electropolishing, and sand or shot blasting. The method selected depends on the equipment available, foreign materials present, undesirable side reactions (acid attack of metals, solvent attack of nonmetals, etc.), level of cleanliness desired, ability to dispose of spent cleaning agents, worker exposure to the cleaning agents, and other factors. The solvent or detergent should not leave a residual material on the cleaned surface.

**6-4.3** The level of cleanliness required typically increases with the pressure of gaseous oxygen, and the required level of cleanliness is always high in liquid oxygen systems. A typical cleaning criterion for industrial gaseous oxygen systems specifies that the remaining organics should not exceed 500 mg/m$^2$ (of oxygen-contacted surfaces). Some organizations, including the military and NASA, use criterion that are much lower.

**6-4.4** Verification of cleanliness is generally accomplished indirectly by one of the following methods:

(a) Direct visual inspection with white light;

(b) Direct visual inspection with UV or black light;

(c) Inspection of a wipe-sample using a clean, lint-free, cotton or linen cloth or a white filter paper (examined under white light or UV light);

(d) Solvent extraction to determine the level of extractable contaminants (nonvolatile residue analysis, volume of residue analysis, spectroscopic technique).

**6-4.4.1** The reported level of residual organics may be misleading since it is an average level for the surface examined. The organic actually may be concentrated in one area.

**6-4.4.2** Shapes such as those of bellows tubing, Bourdon tubes (in pressure gauges), small-diameter piping, deadlegs in piping, and crevices such as those in mated pipe threads are difficult to clean. Explosions from residual cleaning agents have occurred within products having these shapes. It is always desirable to disassemble components fully for cleaning, as this mitigates the hazard of remaining solvent. Adequate rinsing and drying time are important. Cleaned parts should not be handled with bare hands. Cleaned parts should be placed in sealed noncontaminating bags (or otherwise sealed with plugs in the case of long piping runs), and labeled "Cleaned for Oxygen Service."

**6-5 Applicable Standards.** The following standards provide minimum safe practices pending field experience and further technical developments.

**6-5.1** Design and construction of housing vessels and chambers should be in accordance with the applicable provisions of the currently established practices described in the following documents.

(a) *ASME Boiler and Pressure Vessel Code for Unfired Pressure Vessels,* Section VII, American Society of Mechanical Engineers, New York, NY.

(b) NFPA 99, *Standard for Health Care Facilities,* Chapter 19, "Hyperbaric Facilities."

(c) NFPA 99B, *Standard for Hypobaric Facilities.*

**6-5.2** Guidelines for oxygen storage, piping, and some uses are provided in the following standards:

(a) NFPA 50, *Standard for Bulk Oxygen Systems at Consumer Sites.*

(b) NFPA 51, *Standard for the Design and Installation of Oxygen-Fuel Gas Systems for Welding, Cutting, and Allied Processes.*

(c) NFPA 99, *Standard for Health Care Facilities,* Chapter 4, "Gas and Vacuum Systems."

(d) NFPA 99, *Standard for Health Care Facilities,* Chapter 8, "Gas Equipment."

(e) NFPA 99, *Standard for Health Care Facilities,* Chapter 13, "Ambulatory Health Care Center Requirements," 13-4.1, Anesthetizing Locations.

**6-5.3** Guidelines for electrical equipment and instruments are provided in the following standards:

(a) NFPA 70, *National Electrical Code*, Articles 500, 501, and 517.

(b) NFPA 99, *Standard for Health Care Facilities*, Chapter 3, "Electrical Systems."

(c) NFPA 99, *Standard for Health Care Facilities*, Chapter 7, "Electrical Equipment."

**6-5.4** Guidelines for air conditioning and ventilating systems are provided in the following standards:

(a) NFPA 90A, *Standard for the Installation of Air Conditioning and Ventilating Systems.*

(b) NFPA 91, *Standard for Exhaust Systems for Air Conveying of Materials.*

Footnotes to Chapter 6

[1] *Standard Guide for Designing Systems for Oxygen Service*, ASTM G88. 1992 Annual Book of ASTM Standards, Vol. 14.02, American Society for Testing and Materials, Philadephia, 1992.

[2] Denison, D., and Cresswell, A. W. "The Fire Risks to Man of Oxygen Rich Gas Environments." RAF Institute of Aviation Medicine, IAM Report No. 320, April 1965, and IAM Report No. 343, September 1965.

[3] Denison, D. M., and Cresswell, A. W. "The Hazards to Man in Compressed-Air Environments." RAF Institute of Aviation Medicine, Farnborough, Hants, England.

[4] "Procedures and Requirements for the Evaluation of Spacecraft Nonmetallic Materials." MSC-A-A-66-3, Revision A, NASA Manned Spacecraft Center, June 5, 1967.

[5] *Standard Guide for Evaluating Nonmetallic Materials for Oxygen Service*, ASTM G63. 1992 Annual Book of ASTM Standards, Vol. 14.02, American Society for Testing and Materials, Philadelphia, 1992.

[6] *Standard Guide for Evaluating Metals for Oxygen Service*, ASTM G94. 1992 Annual Book of ASTM Standards, Vol. 14.02, American Society for Testing and Materials, Philadelphia, 1992.

[7] *Standard Practice for Cleaning Methods for Material and Equipment Used in Oxygen-Enriched Environments*, ASTM G93. 1992 Annual Book of ASTM Standards, Vol. 14.02, American Society for Testing and Materials, Philadelphia, 1992.

## Chapter 7 Extinguishment of Fires in Oxygen-Enriched Atmospheres

*(Footnotes to Chapter 7 can be found at the end of the chapter.)*

### 7-1 General.

**7-1.1** Fire in oxygen-enriched atmospheres (OEA), because of the extremely fast burning rate of most combustibles and because of the extremely fast pressure rise generated in enclosed spaces, places new requirements on extinguishing systems. In general, these requirements cannot be met simply by extending materials and techniques currently used in fighting fires in ordinary air at normal atmospheric pressure.

**7-1.1.1** Of particular significance is the greatly increased intensity of burning and rate of flame spread, regardless of whether enrichment is attained by increased air pressure, increased ratio of oxygen to inert gases, or a combination of both. Furthermore, materials normally considered to be nonflammable may become flammable at high concentrations of oxygen. These include some gases and volatile liquids that are used as fire extinguishing agents on fires in normal atmospheres.

**7-1.1.2** It is probably neither possible nor practicable to conduct sufficient laboratory tests or gain sufficient field experience to allow the development of rigid specifications for fire extinguishing equipment and systems for all situations. There is sufficient information available, however, to provide helpful guidelines in designing fire protection systems. Each installation will have its own particular requirements. The completed fire extinguishing facilities provided should be tested for adequacy under the anticipated conditions of use.

**7-1.2** Instruction of personnel in handling fire emergencies is equally as important as providing adequate extinguishing equipment. In most systems using OEA, all personnel within the affected space will have primary duties quite different from those of fire fighting. Access to the affected space by professional fire fighters will usually require far too much time to prevent extensive damage and injuries. It is imperative that all persons working with a system containing an OEA be thoroughly instructed in the nature of the hazard and in the operation of the fire fighting equipment provided.

**7-1.3** Because of the explosive nature of fires involving metals in pressurized oxygen systems, fire extinguishing systems have little effect. Fire protection measures should therefore be concentrated on limiting the spread of fire from involved components to other portions of the system. For oxygen-enriched fires at atmospheric pressure involving metals (e.g., shop turnings), the fire will burn more intensely in OEA, and fire extinguishing systems need to react rapidly and effectively.[1]

### 7-2 Fire Extinguishing Agents.

#### 7-2.1 Special Requirements.

**7-2.1.1** It has been found that even modest oxygen enrichment of the atmosphere can greatly increase burning rates of common combustibles and that, in 100 percent oxygen, many ordinarily slow burning materials are consumed almost explosively. Hence, fire extinguishants for use in OEA need to act rapidly to be effective.

**7-2.1.2** Tests have shown that clothing burning in 100 percent oxygen may produce very serious injury to the wearer in as little as 2 seconds.

**7-2.1.3** Other experiences, not involving clothing, have indicated that a fire in 100 percent oxygen may burn for about 30 seconds and still be effectively controlled.

**7-2.1.4** Fires in air compressed to a few atmospheres burn more slowly than those in pure oxygen but still are much more intense than those burning in air at ordinary pressures. In any event, the requirement for rapid extinguishment is much greater in OEA.

**7-2.1.5** It is assumed, for purposes of this chapter, that OEA areas will be inhabited for at least part of the time. Therefore, fire extinguishing agents should be inherently nontoxic, and they should not produce significant amounts of toxic breakdown products when used. The toxic properties of various agents are more fully discussed in 7-2.3 and 7-2.4.