

NFPA 53

Recommended Practice on Materials, Equipment, and Systems Used in Oxygen-Enriched Atmospheres

1999 Edition



National Fire Protection Association, 1 Batterymarch Park, PO Box 9101, Quincy, MA 02269-9101
An International Codes and Standards Organization

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NFPA 53

Recommended Practice on Materials, Equipment, and Systems Used in Oxygen-Enriched Atmospheres

1999 Edition

This edition of NFPA 53, *Recommended Practice on Materials, Equipment, and Systems Used 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 16–18, 1998, in Atlanta, GA. It was issued by the Standards Council on January 15, 1999, with an effective date of February 4, 1999, and supersedes all previous editions.

This edition of NFPA 53 was approved as an American National Standard on February 4, 1999.

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, 1990, and 1994.

The 1994 edition reflected a complete review of the contents of the document and incorporated much new information gained by research at the National Aeronautic and Space Administration from 1984 to 1994.

The 1999 edition changed the document from a guide to a recommended practice. Also some minor changes were made to the definitions of oxygen-enriched atmosphere and ignition temperature.

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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

Chapter 1 Introduction	53- 4	5-10 Applicable Standards	53- 8
1-1 Scope	53- 4	Chapter 6 Fire Extinguishment	53- 9
1-2 Purpose	53- 4	6-1 Oxygen Supply	53- 9
1-3 Application	53- 4	6-2 Extinguishing Systems	53- 9
1-4 Types of Systems That Are Used in Oxygen-Enriched Atmospheres	53- 4	6-3 Fixed Systems	53- 9
1-5 Interpretations	53- 4	6-4 Water Hose	53- 9
Chapter 2 Definitions	53- 4	6-5 Diluents	53- 9
2-1 Official NFPA Definitions	53- 4	6-6 Limiting Fire Spread	53- 9
2-2 Definitions of Terms Used in This Document	53- 5	6-7 Nontoxic Agents	53- 9
Chapter 3 Materials Selection	53- 6	6-8 Wetting	53- 9
3-1 General	53- 6	6-9 Instructions and Drills	53- 9
3-2 Nonmetals	53- 6	Chapter 7 Referenced Publications	53- 9
3-3 Metals	53- 6	Appendix A Explanatory Material	53-10
Chapter 4 Component Selection	53- 6	Appendix B Training and Education	53-13
4-1 Material Recommendations	53- 6	Appendix C Utilization of Oxygen-Enriched Atmospheres	53-14
4-2 General Design Recommendations	53- 6	Appendix D Fire Experience	53-19
4-3 Specific Component Design Guidelines	53- 6	Appendix E Fundamentals of Ignition and Combustion in Oxygen-Enriched Atmospheres	53-27
4-4 Components	53- 7	Appendix F Material for Use in Oxygen-Enriched Atmospheres	53-33
Chapter 5 System Design	53- 7	Appendix G Referenced Publications	53-52
5-1 Design Considerations	53- 7	Index	53-53
5-2 Worst-Case Conditions	53- 7		
5-3 Fire-Stopping Techniques	53- 7		
5-4 Personnel Qualifications	53- 8		
5-5 Oxygen Transmission	53- 8		
5-6 Shutoff	53- 8		
5-7 Electrical Equipment	53- 8		
5-8 Cleaning for Oxygen Service	53- 8		
5-9 Combustibles	53- 8		

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NOTICE: An asterisk (*) following the number or letter designating a paragraph indicates that explanatory material on the paragraph can be found in Appendix A.

Information on referenced publications can be found in Chapter 7 and Appendix G.

Chapter 1 Introduction

1-1 Scope. This document establishes recommended minimum criteria for the safe use of oxygen (liquid/gaseous) and the design of systems for use in oxygen and oxygen-enriched atmospheres.

1-2 Purpose. The purpose of this recommended practice is to provide information for the selection of materials, components, and design criteria that can be used safely in oxygen and oxygen-enriched atmospheres.

1-3 Application. This recommended practice is applicable to the selection of materials and components, and to the design of new systems associated with oxygen-enriched atmospheres (OEA). Such applications include, but are not limited to, gas and compressed air supplies, spaceflight operations, industrial processes, welding applications, self-contained breathing apparatus (SCBA), self-contained underwater breathing apparatus (SCUBA), medical applications (including home assisted-breathing apparatus), underwater tunneling and caisson work, and commercial and military aviation.

1-4 Types of Systems That Are Used in Oxygen-Enriched Atmospheres. Mechanical and electrical systems that can be found in OEA 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.* Uses of gas in oxygen-enriched atmospheres are as follows:
 1. Cylinders of compressed gases, such as oxygen, nitrous oxide, nitrogen, helium, and natural air, for human breathing
 2. Anesthetic vaporizers such as halothane, enflurane, and isoflurane
 3. 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, and hose and hose connections at use site for attaching dispensing equipment
 4. 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 heart rate, and 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 outside of chamberport, or with others at remote stations; and television and radio

1-5 Interpretations. The National Fire Protection Association does not approve, inspect, or certify any installation, procedure, equipment, or material. With respect to this recommended practice, and to fire and associated hazards in oxygen-enriched atmospheres, its role is limited solely to an advisory capacity. The acceptability of a particular material, component, or system for use in an oxygen-enriched atmosphere is solely a matter between the user and the provider. However, to assist in the determination of such acceptability, the National Fire Protection Association has established interpretation procedures. These procedures are outlined in the *NFPA Regulations Governing Committee Projects*.

Chapter 2 Definitions

2-1 Official NFPA Definitions.

Approved.* Acceptable to the authority having jurisdiction.

Authority Having Jurisdiction.* The organization, office, or individual responsible for approving equipment, an installation, or a procedure.

Code.* A standard that is an extensive compilation of provisions covering broad subject matter or that is suitable for adoption into law independently of other codes and standards.

Guide. A document that is advisory or informative in nature and that contains only nonmandatory provisions. A guide may contain mandatory statements such as when a guide can be used, but the document as a whole is not suitable for adoption into law.

Labeled. Equipment or materials to which has been attached a label, symbol, or other identifying mark of an organization that is acceptable to the authority having jurisdiction and concerned with product evaluation, that maintains periodic inspection of production of labeled equipment or materials, and by whose labeling the manufacturer indicates compliance with appropriate standards or performance in a specified manner.

Listed.* Equipment, materials, or services included in a list published by an organization that is acceptable to the authority having jurisdiction and concerned with evaluation of products or services, that maintains periodic inspection of production of listed equipment or materials or periodic evaluation of services, and whose listing states that either the equipment, material, or service meets identified standards or has been tested and found suitable for a specified purpose.

Recommended Practice. A document that is similar in content and structure to a code or standard but that contains only nonmandatory provisions using the word “should” to indicate recommendations in the body of the text.

Shall. Indicates a mandatory requirement.

Should. Indicates a recommendation or that which is advised but not required.

Standard. A document, the main text of which contains only mandatory provisions using the word “shall” to indicate requirements and which is in a form generally suitable for mandatory reference by another standard or code or for adoption into law. Nonmandatory provisions shall be located in an appendix, footnote, or fine-print note and are not to be considered a part of the requirements of a standard.

2-2 Definitions of Terms Used in This Document.

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

Autoignition or Autogenous Ignition Temperature. See definition of *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.

Contaminant. A foreign or unwanted substance that can have deleterious effects on system operation, life, or reliability.

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.

Diluent. A gas used to dilute or reduce the concentration of oxygen.

Fire. A chemical reaction between a fuel and an oxidant.

Flame Propagation Rate. 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, and 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 ignitable 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.

Hyperbaric. Pressure greater than ambient.

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.

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

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

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

Oxidant.* A chemical compound that supports combustion.

Oxidation. 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 and 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 its partial pressure exceeds 21.3 kPa (160 torr).

Pressure.* The force per unit of area. Values in this recommended practice are based on the unit of pressure derived from the International System of Units (SI), which is the pascal (Pa) or newton per square meter (N/m²).

Pressure, Absolute. The total pressure being measured that equals gauge pressure plus atmospheric pressure.

Pressure, Gauge. Pressure measured with reference to atmospheric pressure that equals absolute pressure minus atmospheric pressure.

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

Spontaneous Ignition Temperature. See definition of *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 definition of *Flammable Limits*.

Worst-Case. The maximum concentration, pressure, temperature, or flow-rate that can occur with a reasonable single-point failure or upset.

Chapter 3 Materials Selection

3-1* General.

3-1.1* The rate of flame propagation and ignition susceptibility of materials of construction should be regarded as prime considerations in the promotion of safe design of systems associated with oxygen-enriched environments.

3-1.2 The oxygen compatibility characteristics of all materials involved in oxygen-enriched environments should be carefully and completely evaluated under end-use conditions. 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.

3-1.3 When selecting materials for oxygen service, situational or configurational flammability should be evaluated.

3-2 Nonmetals.

3-2.1* The use of nonmetals in oxygen systems should be limited and their quantity and exposure to oxygen should be minimized.

3-2.2* When selecting materials, application-specific material tests and configurations should be considered.

3-2.3* When selecting a material for oxygen systems, its ability to undergo specific cleaning procedures to remove contaminants, particles, and combustible materials, without damage, should be considered.

3-2.4 When selecting nonmetals for high-pressure oxygen systems, the material's susceptibility to ignition and the possible ignition sources in the system at the use pressures should be given equal consideration with the structural requirements. Criteria for selection of a material for oxygen service should also include the following:

- (a) Few reactions when tested by mechanical impact
- (b) A high autoignition temperature (AIT)
- (c) A low heat of combustion
- (d) A high oxygen index
- (e) A low flame temperature
- (f) A low burn rate
- (g) A low flame propagation rate

3-3 Metals.

3-3.1 Selection of the proper metals in an oxygen system should be coupled with good design practice to minimize the hazards of ignition and combustion of the metal.

3-3.2* The oxide coating of a metal should be considered when selecting it.

3-3.3* The use of aluminum alloys in lines, valves, and other components should be avoided whenever possible.

3-3.4* High-pressure oxygen systems fabricated from aluminum should be designed with extreme care to eliminate particles. Filters should be fabricated of materials less ignitable than aluminum.

3-3.5 Systems that use large areas of aluminum alloys in oxygen storage tanks should be designed to ensure that aluminum particles cannot cause ignition of other metallic materials downstream from the aluminum.

3-3.6 The use of cadmium, beryllium, magnesium, mercury, and titanium metals in oxygen systems should be restricted.

3-3.7* The ignitibility of other metals and alloys in high-pressure oxygen systems and their ability to propagate fire after ignition should be compared to the flammability properties of the common structural materials described in 3-3.6 before determining how suitable they are for use in high-pressure oxygen systems.

3-3.8 The use of nickel, copper, and their alloys is preferred in oxygen systems.

Chapter 4 Component Selection

4-1 Material Recommendations. Designers of equipment for oxygen use should thoroughly understand the reactivity of selected materials in oxygen-enriched environments. The designer should attempt to avoid using flammable materials; however, many materials that are flammable at operating conditions can safely be used in some applications by carefully avoiding ignition sources. The designer should not compromise safety to reduce material costs.

4-2* General Design Recommendations. Designs should consider system dynamics, component interactions, and operational constraints in addition to component design requirements to prevent conditions leading to fires in oxygen-enriched atmospheres (OEA).

4-3 Specific Component Design Guidelines. Oxygen system designers should

- (a)* Minimize the amount of organic, nonmetallic materials and their exposure to oxygen flow
- (b)* Limit gaseous oxygen pressurization rates
- (c)* Limit gaseous oxygen flow velocities
- (d)* Minimize mechanical impact
- (e)* Minimize frictional heating in oxygen
- (f)* Minimize ignition from particle impact
- (g)* Eliminate burrs and avoid sharp edges
- (h)* Minimize use-generated particles during manufacture, assembly, and operation
- (i)* Avoid rotating valve stems and sealing configurations that require rotation on assembly
- (j)* Minimize electrical arcing
- (k)* Avoid blind passages
- (l)* Avoid crevices for particle entrapment and resonant cavities (Phillips)
- (m) Design dynamic seals to minimize particle generation and to minimize coefficients of friction and surface finishes, and choose seal configurations to minimize particle generation that can cause particle impact ignitions
- (n)* Limit fluid-induced vibrations (over all operating ranges)
- (o)* Consider the effects of single-point seal failures
- (p)* Eliminate rotation of seals and rotation against seats
- (q)* Avoid thin walls
- (r)* Be cautious of single-barrier failures
- (s)* Allow sufficient seal squeeze to avoid O-ring extrusion
- (t)* Use metal-to-metal seals in some cases
- (u) Consider the effects of long-term operation, including the following:
 - 1.* Permanent deformation (cold flow) of seals
 - 2.* Seal extrusion (avoid extrusion-generated particles)

3.* High-temperature excessive oxidation of copper

- (v) Design equipment so that power losses, control pressure leakage, or other loss of actuation sources return the equipment to a fail-safe position to protect personnel and property in an accident
- (w)*Consider the effects of thermal expansion

4.4 Components.

4.4.1 Valves.

4.4.1.1 All valves should be accessible for operation and maintenance and should be protected from accidental damage.

4.4.1.2 Valves in gaseous oxygen distribution systems should be kept to a minimum and should be of good quality. All valve materials must be suitable for oxygen. Stems, packing glands, and other parts vital to proper valve operation should be made of materials that will not readily corrode.

4.4.1.3 Isolation valves should operate either fully open or fully closed and not in a throttling or regulating mode.

4.4.1.4 Where required, a bypass should be provided around isolation valves. The bypass should be of suitable materials. If remotely operated bypass valves are used, the valves should be fail-safe in case of power loss and should close on a system emergency shutdown signal.

4.4.2 Pressure-Relief Devices and Piping.

4.4.2.1 Relief valves or rupture disks should be installed on tanks, lines, and component systems to prevent overpressurization. The capacity of a pressure-relief device should be equal to that of all the vessel and piping systems it is to protect. These devices should be reliable and the settings secured against accidental alteration.

4.4.2.2 Relief valves and similar devices should not be considered secondary and passive components in the test hardware design. It should be assumed that the valves will function at some time. Personnel safety and hardware damage should be primary design considerations.

4.4.2.3 Relief valves should be functionally tested to verify that design requirements are satisfied, including testing in both the static and dynamic states.

4.4.2.4 Relief valve riser pipes on high-pressure oxygen systems should be analyzed for resonant tuning. Piping lengths should be changed if resonant tuning is determined.

4.4.2.5 All sections of the pipeline system should be adequately protected by pressure-relief devices and should have an adequate manual vent valve to allow for blowdown and purging. All components in any oxygen system that should be permitted to be removed for inspection, maintenance, or replacement, should be provided with a vent valve for blowdown and purging.

4.4.2.5.1 Safety valves, vent valves, and associated piping should be constructed of compatible materials.

4.4.2.5.2 Downstream relief devices and any vent lines should be built from the most ignition-resistant materials available and should be positioned in remote locations or isolated from personnel by barriers or shields.

4.4.2.6* Piping, tubing, and fittings should be suitable for the intended oxygen service.

4.4.2.7 Safety devices should be checked before use to prevent possible installation of incorrect pressure-rated devices.

4.4.2.8 The minimum relieving capacities of the safety devices should be as determined by the flow formulas in applicable codes and specifications (for example, Schmidt and Forney, and National Academy of Sciences). Safety relief valves and frangible disks should be designed and installed in accordance with applicable codes and specifications (for example, 49 CFR and CGA S-1.2, *Pressure Relief Device Standards — Part 2 — Cargo and Portable Tanks for Compressed Gases*).

4.4.2.9 Flexible Piping and Tubing.

4.4.2.9.1 Proper restraining cables and anchoring cables should be required for flexible hose.

4.4.2.9.2 Stainless steel tubing, which can be formed into loops to provide enough flexibility for easy hookup, should be an acceptable practice.

4.4.2.9.3 Flexible metal tube or pipe such as bellows sections should also be acceptable. All-metal bellows are difficult to clean and cleaning fluids cannot be completely rinsed off, leading to corrosion. Polytetrafluoroethylene-lined flexible hose can be used if particular care is exercised to ensure that pneumatic impact ignitions cannot occur. The risks can be minimized if procedures are written so as to avoid operator error and to incorporate a long, nonignitable metallic housing at the downstream end of the flexible hose in the design.

Chapter 5 System Design

5-1 Design Considerations. In the design of systems associated with oxygen-enriched atmospheres (OEA), the following should be considered:

- (a) Characteristics of construction materials include ignition susceptibility, flame spread rate, and smoke development
- (b) Risk of fire initiation include ignition sources such as heat from compression of gases, friction, mechanical impact, and electrical arc or spark
- (c) Presence of potential energy sources, such as compressed gases
- (d) Removal or elimination of foreign materials or contaminants
- (e) Physical environment surrounding the system
- (f) Personnel safety

5-2 Worst-Case Conditions. The characteristics of all materials to be used in oxygen-enriched atmospheres should be evaluated for use under worst-case conditions, such as maximum pressure, temperature, and flow.

5-3 Fire-Stopping Techniques. When designing an oxygen-enriched system, fire-stopping techniques should be used where appropriate to minimize ignition potential and fire spread. These techniques include the following:

- (a) Avoidance of mass concentration of combustible materials near potential heat or ignition sources
- (b) Spatial separation and configuration to minimize or eliminate flame propagation paths
- (c) Thermal damping by judicious placement of fire-resistant heat-sink masses
- (d) Flashover barriers

- (e) Sealed packaging, such as inerted compartments and fire-resistant encapsulation
- (f) Automatic fire detection and suppression such as infrared thermography, fire detectors, and fixed suppression systems

5-4* Personnel Qualifications. The design of an oxygen-enriched system should only be undertaken by qualified personnel.

5-5 Oxygen Transmission. Systems used in the transmission of oxygen should be cleaned prior to use and on a routine basis to remove contaminants.

5-6* Shutoff. A manual emergency oxygen shutoff should be provided that is accessible.

5-7 Electrical Equipment.

5-7.1* No electrical equipment should be installed or used in OEA unless approved for use at the maximum proposed pressure and oxygen concentration. Electrical equipment should be provided with noncombustible insulation to confine any burning of the insulation within the enclosure, unless the equipment is of construction that has been found, through testing, at the maximum pressure and the oxygen concentration encountered in the chamber or system.

5-7.2* Fixed electrical equipment within an OEA 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.

5-7.3 All electrical wiring installed in a system or chamber should comply with the requirements of NFPA 70, *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.

5-7.4 Raintight fittings, boxes, and equipment should be used if such devices could be exposed to the water from a sprinkler or water spray system that is protecting the chamber in the event of a fire in the vicinity of the chamber while it is in operation.

5-7.5 All electrical circuits contained within the chamber or system should be supplied from an isolated electrical system, fed from isolation transformers located outside the chamber or system, and equipped with a line isolation monitor 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.

5-7.6 Electrical wiring in high concentrations of gas oxygen should be encased in hermetically sealed conduits or conduits inerted with helium or nitrogen gas. The instruments, switches, flow sensors, and electrical devices should be designed in modular structure, hermetically sealed, and inerted with nitrogen or helium gas.

5-8* Cleaning for Oxygen Service.

5-8.1* All hardware that is exposed to OEA should be cleaned to remove contaminants.

5-8.2* The solvent or detergent should not leave a residual material on the cleaned surface.

5-8.3* A typical cleaning criterion for industrial gaseous oxygen systems specifies that the remaining organics should not exceed 500 mg/m² of oxygen-contacted surfaces.

5-8.4* Verification of cleanliness should be accomplished by one or more of the following methods:

- (a) Direct visual inspection with white light
- (b) Direct visual inspection with ultraviolet (UV) or black light
- (c) Inspection of a wipe sample using a clean, lintfree cotton or linen cloth or a piece of white filter paper examined under white or UV light
- (d) Solvent extraction to determine the level of extractable contaminants include nonvolatile residue analysis, volume of residue analysis, and spectroscopic technique
- (e) Aqueous cleaning and verification processes

5-8.5* Cleaned parts should be placed in sealed noncontaminating bags, or sealed with plugs in the case of long piping runs, and labeled "Cleaned for Oxygen Service." Cleaned parts should not be handled with bare hands.

5-9* Combustibles. It is highly recommended that every possible effort be made to restrict the quantity of combustibles permitted within the system, vessel, chamber, surrounding physical environment (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.

5-10 Applicable Standards.

5-10.1 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
- (b) NFPA 99, *Standard for Health Care Facilities*, Chapter 19, "Hyperbaric Facilities"
- (c) NFPA 99B, *Standard for Hypobaric Facilities*
- (d) API 620, *Recommended Rules for Design and Construction of Large, Weld, Low-Pressure Storage Tanks*
- (e) CGA pamphlets as follows:
 1. P-1, *Safe Handling of Compressed Gases in Containers*
 2. S-1.1, *Pressure Relief Device Standards — Part 1 — Cylinders for Compressed Gases*
 3. S-1.2, *Pressure Relief Device Standards — Part 2 — Cargo and Portable Tanks for Compressed Gases*
 4. S-1.3, *Pressure Relief Device Standards — Part 3 — Stationary Storage Containers for Compressed Gases*

5-10.2 Oxygen storage, piping, and uses should be in accordance with 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"; Chapter 8, "Gas Equipment"; Chapter 12, "Hospital Requirements"; and 12-4.1, "Anesthetizing Locations"
- (d) CGA G-4, *Oxygen*

- (e) ANSI B-31.3, *American National Standard Code for Process Piping*
- (f) ANSI B-31.5, *American National Standard Code for Pressure Piping, Refrigeration Piping*
- (g) ANSI B-31.8, *American National Standard Code for Pressure Piping, Gas Transmission and Distribution Piping Systems*
- (h) U.S. *Code of Federal Regulations* as follows:
 1. 49 *CFR* 173.301
 2. 49 *CFR* 173.302
 3. 49 *CFR* 173.337
 4. 49 *CFR* 178.37
 5. 49 *CFR* 178.45

5-10.3 Electrical equipment and instruments should be in accordance with 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," and Chapter 7, "Electrical Equipment"
- (c) NFPA 496, *Standard for Purged and Pressurized Enclosures for Electrical Equipment*

5-10.4 Air-conditioning and ventilating systems should be in accordance with 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 Vapors, Gases, Mists, and Noncombustible Particulate Solids*

Chapter 6 Fire Extinguishment

6-1 Oxygen Supply. The oxygen supply should be discontinued in the event of a fire.

6-2* Extinguishing Systems. Due to the rapid flame spread in oxygen-enriched atmospheres (OEA), fire-extinguishing systems should be capable of fast automatic actuation by fire detectors as well as by manual actuation.

6-2.1 Automatic actuation should occur in less than 1 second of detection of flame.

6-2.2 Manual actuation of the fire-extinguishing system should be provided.

6-3 Fixed Systems. Fixed systems should utilize an extinguishing agent acceptable for use on fires in OEA.

6-4 Water Hose. In addition to an automatic, fixed extinguishing system in occupied areas, a manually operated water hose not less than 19-mm ($3/4$ -in.) inside diameter, and with an effective nozzle pressure of not less than 345 kPa (50 psi) above the ambient pressure, should be available.

6-5 Diluents. In unoccupied areas, diluents (e.g., carbon dioxide, nitrogen) can be used.

6-6* Limiting Fire Spread. Fire protection measures should be concentrated on limiting the spread of fire from involved components to other portions of the system.

6-7 Nontoxic Agents. Fire-extinguishing agents should be inherently nontoxic and should not produce significant amounts of toxic breakdown products when used.

6-8* Wetting. Where the combustible is present in more than one layer, all layers should be wetted by the water.

6-9 Instructions and Drills. All personnel working in a space containing OEA should be instructed in the special hazards involved, and the differences between fire in OEA and fire in ordinary air should be emphasized. Each person working in an OEA system should be assigned a specific fire emergency duty. Other personnel working in associated monitoring areas should likewise be instructed and assigned specific duties appropriate to a fire emergency. The instruction should be augmented by frequent drills so that proper action can be taken immediately upon the occurrence of a hazardous condition. Such instruction and drill should be so comprehensive and specific that no time is lost in decision-making or considering alternative procedures. (See *Appendix B*.)

Chapter 7 Referenced Publications

7-1 The following documents or portions thereof are referenced within this recommended practice and should be considered as part of its recommendations. The edition indicated for each referenced document is the current edition as of the date of the NFPA issuance of this recommended practice. Some of these documents might also be referenced in this recommended practice for specific informational purposes and, therefore, are also listed in *Appendix G*.

7-1.1 NFPA Publications. National Fire Protection Association, 1 Batterymarch Park, P.O. Box 9101, Quincy, MA 02269-9101.

NFPA 50, *Standard for Bulk Oxygen Systems at Consumer Sites*, 1996 edition.

NFPA 51, *Standard for the Design and Installation of Oxygen-Fuel Gas Systems for Welding, Cutting, and Allied Processes*, 1997 edition.

NFPA 70, *National Electrical Code*®, 1999 edition.

NFPA 90A, *Standard for the Installation of Air Conditioning and Ventilating Systems*, 1996 edition.

NFPA 91, *Standard for Exhaust Systems for Air Conveying of Vapors, Gases, Mists, and Noncombustible Particulate Solids*, 1999 edition.

NFPA 99, *Standard for Health Care Facilities*, 1999 edition.

NFPA 99B, *Standard for Hypobaric Facilities*, 1999 edition.

NFPA 496, *Standard for Purged and Pressurized Enclosures for Electrical Equipment*, 1998 edition.

7-1.2 Other Publications.

7-1.2.1 ANSI Publications. American National Standards Institute, Inc., 11 West 42nd Street, 13th floor, New York, NY 10036.

ANSI B-31.3, *American National Standard Code for Process Piping*, 1996.

ANSI B-31.5, *American National Standard Code for Pressure Piping, Refrigeration Piping*, 1992.

ANSI B-31.8, *American National Standard Code for Pressure Piping, Gas Transmission and Distribution Piping Systems*, 1995.

7-1.2.2 API Publication. American Petroleum Institute, 1220 L Street, NW, Washington, DC 20005.

API 620, *Recommended Rules for Design and Construction of Large, Weld, Low-Pressure Storage Tanks*, 1996.

7-1.2.3 ASME Publication. American Society of Mechanical Engineers, 345 East 47th Street, New York, NY 10017.

ASME *Boiler and Pressure Vessel Code for Unfired Pressure Vessels*.

7-1.2.4 CGA Publications. Compressed Gas Association, 1725 Jefferson Davis Highway, Arlington, VA 22202-4100.

CGA G-4, *Oxygen*, 1994.

CGA P-1, *Safe Handling of Compressed Gases in Containers*, 1991.

CGA S-1.1, *Pressure Relief Device Standards — Part 1 — Cylinders for Compressed Gases*, 1994.

CGA S-1.2, *Pressure Relief Device Standards — Part 2 — Cargo and Portable Tanks for Compressed Gases*, 1995.

CGA S-1.3, *Pressure Relief Device Standards — Part 3 — Stationary Storage Containers for Compressed Gases*, 1995.

7-1.2.5 U.S. Government Publications. U.S. Government Printing Office, Washington, DC 20402.

Title 49, *Code of Federal Regulations*, Part 173.301, 1997.

Title 49, *Code of Federal Regulations*, Part 173.302, 1997.

Title 49, *Code of Federal Regulations*, Part 173.337, 1997.

Title 49, *Code of Federal Regulations*, Part 178.37, 1997.

Title 49, *Code of Federal Regulations*, Part 178.45, 1997.

7-1.3 Additional References.

National Academy of Sciences, 1973.

Phillips, 1975.

Schmidt and Forney, 1975.

Appendix A Explanatory Material

Appendix A is not a part of the recommendations of this NFPA document but is included for informational purposes only. This appendix contains explanatory material, numbered to correspond with the applicable text paragraphs.

A-2-1 Approved. The National Fire Protection Association does not approve, inspect, or certify any installations, procedures, equipment, or materials; nor does it approve or evaluate testing laboratories. In determining the acceptability of installations, procedures, equipment, or materials, the authority having jurisdiction may base acceptance on compliance with NFPA or other appropriate standards. In the absence of such standards, said authority may require evidence of proper installation, procedure, or use. The authority having jurisdiction may also refer to the listings or labeling practices of an organization that is concerned with product evaluations and is thus in a position to determine compliance with appropriate standards for the current production of listed items.

A-2-1 Authority Having Jurisdiction. The phrase “authority having jurisdiction” is used in NFPA documents in a broad manner, since jurisdictions and approval agencies vary, as do their responsibilities. Where public safety is primary, the authority having jurisdiction may be a federal, state, local, or other regional department or individual such as a fire chief; fire marshal; chief of a fire prevention bureau, labor department, or health department; building official; electrical inspector; or others having statutory authority. For insurance purposes, an insurance inspection department, rating bureau, or other insurance company representative may be the authority having jurisdiction. In many circumstances, the property owner or his or her designated agent assumes the role of the authority having jurisdiction; at government installations, the commanding officer or departmental official may be the authority having jurisdiction.

A-2-1 Code. The decision to designate a standard as a “code” is based on such factors as the size and scope of the document,

its intended use and form of adoption, and whether it contains substantial enforcement and administrative provisions.

A-2-1 Listed. The means for identifying listed equipment may vary for each organization concerned with product evaluation; some organizations do not recognize equipment as listed unless it is also labeled. The authority having jurisdiction should utilize the system employed by the listing organization to identify a listed product.

A-2-2 Ignition Energy, Minimum. 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.

A-2-2 Ignition Temperature. 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.

A-2-2 Oxidant. Examples of oxidants include nitrous oxide, nitric oxide, and chlorates.

A-2-2 Pressure. A newton is that force that causes a mass of 1 kilogram to accelerate 1 meter per second.

One atmosphere = 33 feet of water (39.2°F) = 14.7 pounds per square inch (psi) = 760 millimeters of mercury (mm Hg) (0°C) = 760 torr = 101,325 newtons per square meter (N/m²) = 101,325 pascals.

A-3-1 See Appendix F for additional guidance.

A-3-1.1 Other considerations include the deterioration stability as well as the careful assessment of any potential ignition sources capable of initiating combustion in such atmospheres.

A-3-2.1 Nonmetals are more susceptible to ignition than metals (most nonmetals are flammable in oxygen at 1 atm or greater). In many instances, failures of metallic components are caused by a polymer ignition, which provides sufficient energy for the metal to ignite.

A-3-2.2 Materials in an oxygen environment below their autoignition temperature (AIT) do not ignite without an ignition source. The rate of energy input has to exceed the rate of heat dissipation before ignition can occur. Ignition temperature is dependent on the property of the material, the configuration, the environment (temperature, pressure, oxygen concentration, and fuel characteristics), and the dynamic conditions for flow systems.

Nonmetals, such as polymers, generally ignite at lower temperatures and pressures than metals; nonmetals can burn at oxygen pressures lower than 7 kPa (1 psia). The primary concern with nonmetals in oxygen systems is that, if ignited, they might cause damage to the oxygen system or injury to persons in the vicinity. Some damage that might result includes propagation of the fire to metallic components, loss of function arising from system leaks, and toxic combustion and pyrolysis products entering the oxygen system.

In general, bulk metals are not easily ignited. When ignited, however, burning metals can cause more damage than burning nonmetals because of their higher flame temperatures and because they usually produce liquid combustion products that spread fires readily. Also, metals comprise the major system components, such as valve bodies and pressure vessels, so that when they ignite and burn, oxygen is released to the surrounding areas in an explosive manner.

A-3-2.3 For more information, see ASTM G 93, *Standard Practice for Cleaning Methods and Cleanliness Levels for Material and Equipment Used in Oxygen Enriched Environments*, and CGA G-4.1, *Cleaning Equipment for Oxygen Service*.

A-3-3.2 The resistance to ignition for metals can be enhanced by a protective oxide coating on the metal surface.

A-3-3.3 Aluminum alloys in high-pressure oxygen ignite easily, burn rapidly, and have very high heats of combustion. Aluminum is easily ignited by friction because the wear destroys its protective oxide layer, therefore, aluminum should not be used in systems where frictional heating is possible.

A-3-3.4 Nickel, silver, bronze, or Monel® alloys are recommended, although Monel® wire meshes are known to be flammable in elevated-pressure oxygen environments, (Stoltzfus, Lowrie, and Gunaji). Aluminum alloys are more suitable for static components at low oxygen flow rates, such as oxygen storage tanks, than for components with internal movement and variable flow rates such as valves and regulators.

A-3-3.7 Many other metals and alloys exist that have mechanical properties suited to applications in high-pressure oxygen systems. New alloys are continually being developed, and some are being designed that resist ignition and do not support self-sustained combustion in high-pressure oxygen systems.

A-4-2 The use of ignition- and burn-resistant materials for components in oxygen systems will not eliminate fires in OEA. For more information, see ASTM G 63, *Standard Guide for Evaluating Nonmetallic Material for Oxygen Service*; ASTM G 88, *Standard Guide for Designing Systems for Oxygen Service*; and ASTM G 94, *Standard Guide for Evaluating Metals for Oxygen Service*, for guidelines on material use.

A-4-3(a) Organic, nonmetallic materials exposed to oxygen flow can be readily heated through rapid compression of the gas (Shelly, Christianson, and Stoltzfus) or readily ignited through kindling-chain reactions. Minimizing organic, non-metallic materials' exposure by shielding with surrounding metals can significantly reduce ignition hazards.

A-4-3(b) Organic, nonmetallic materials, such as seals, coatings, and lubricants, are susceptible to ignition from heating caused by rapid pressurization. For example, Teflon®-lined flexible hose are sensitive to this ignition mode, and, therefore, their use with rapid pressurization applications is discouraged (Janoff et al). Pressurization rates of valve and regulator actuators should be minimized. In some applications, flow-metering devices are prudent for manually actuated valves, especially for quarter-turn ball valves.

A-4-3(c) Limiting flow velocities minimizes erosion problems and reduces the risk of particle impact ignitions. Although each material and configuration combination needs to be reviewed individually, fluid velocities above 30.5 m/sec (100 ft/sec) should receive special attention, especially at flow restrictions (Williams, Benz, and McIlroy; Benz, Williams, and Armstrong; and CGA G-4.4, *Industrial Practices for Gaseous Oxygen Transmission and Distribution Piping Systems*).

A-4-3(d) Mechanical impact can cause ignition of contaminants and organic, nonmetallic materials. Relief valves, shut-off valves, regulators, and subminiature parts should especially be reviewed for this hazard.

A-4-3(e) Frictional heating, such as heating that occurs with bearings, pistons, and pump impellers, can cause ignitions

(Dees and Peterson). Any contamination near the heated region can also be ignited. Frictional heating hazards can be reduced by carefully controlling surface finishes, coefficients of friction, alignment, and flow-induced cooling. Frictional heating has also been found to ignite materials in cryogenic applications.

A-4-3(f) The risk of particle impact ignitions can be reduced if potential impact surfaces are designed with shallow impact angles to reduce the kinetic energy absorbed by the impact surface upon impact (Christianson and Plante).

A-4-3(g) Burrs and sharp edges on equipment provide ignition sources for particle impact and the ingredients for kindling-chain combustion propagation (Christianson and Plante). Removal of this material is standard shop practice and is essential to avoid oxygen-enriched ignitions.

A-4-3(h) These particles could be a source of particle impact ignition. Designs should have provisions to minimize particle generation through the normal operation of valve stems, pistons, and other moving parts. Bearings, bushings, and configurations can be used to keep particles away from oxygen-wetted regions. Additionally, proper assembly, cleaning, and maintenance practices should minimize contamination.

A-4-3(i) Rotating valve stems and seals can gall and generate particles.

A-4-3(j) Electrical arcs in oxygen-enriched environments can lead to heating and subsequent ignition.

A-4-3(k) Long, narrow passages, or blind passages, are difficult to clean and to inspect for cleanliness. Additionally, these passages can provide a location for particles to accumulate during operation of the equipment. This contamination can make the equipment susceptible to particle impact, rapid compression, and resonant cavity ignitions.

A-4-3(l) Cavities, especially those formed at the intersection of mating parts in assemblies, create a location where contamination can accumulate and increase ignition risks, as in blind passages.

A-4-3(n) Vibrations can cause fretting, galling, impacting, and particle generation in components and systems. Check valve chatter and valve poppet oscillations are examples of this phenomenon. Particle accumulations will increase the risk of particle impact ignitions.

A-4-3(o) Seals will degrade with time and use. Eventually, they can be expected to fail to seal the contained fluid. When this happens, the effects of an oxygen-enriched external environment, high-velocity leakage, and loss of mechanical integrity must be addressed.

A-4-3(p) Sealed parts that require rotation at assembly, such as O-rings on threaded shafts, can generate particles that can migrate into the flow stream. Particle generation also occurs in ball valves where operation of the valve rotates a ball on a nonmetallic seat.

A related phenomenon that can be described as feathering occurs when valve stems are rotated against some nonmetallic seats. Because of the mechanical properties of some nonmetallic materials, a thin, featherlike projection of material is extruded from the seat. The feathered material is more ignitable than the seat itself.

Nonmetallic materials subject to feathering should be used with caution for seals and seats in rotating configurations. Ball

valves are not recommended for oxygen systems because of their tendency to generate particles and their fast opening times that create rapid pressurization of systems.

A-4-3(q) The walls between inner cavities or passageways and the outer surface of component housings can become so thin that stress concentrations result when pressure is introduced. Because geometries both inside and outside can be complex, it might not be obvious from drawings or even from direct inspection that such thin, highly stressed areas exist. If such walls become too thin, they might rupture under pressure loading. The energy released by the rupture can raise the temperature in the rupture zone. The failed section can expose bare, jagged metal that can oxidize rapidly and heat enough to ignite and burn.

A-4-3(r) A single-barrier failure is defined as a leak in which only the primary containment structure is breached. Such a leak introduces oxygen into a region not normally exposed to oxygen. The materials or configuration of parts in this region might not be compatible with high-pressure oxygen.

Any situation in which a single barrier can fail should be analyzed during the design phase. The single-barrier failure analysis might consist of an engineering evaluation of the configuration, including an analysis of the compatibility of materials exposed by the failure with the high-pressure oxygen. The purpose of the analysis should be to determine if a barrier failure is credible and if exposure of incompatible materials can create a hazard. If the hazard cannot be assessed adequately by analysis, a configurational test can be performed.

A-4-3(s) Standard manufacturers' dimensions and tolerances should be incorporated into designs unless an unusual overriding design constraint demands the change. Additionally, the dimensions of all parts in the valve assembly should be carefully inspected. Ideally, adequate gland size should be provided in the initial design.

A-4-3(t) Polymeric materials cannot be used as seals in valves that control the flow of hot oxygen because they lose sealing properties, ignite easily, and wear rapidly.

High pressures and high flow rates can produce side loads and oscillations on the poppet seal that can cause metal deterioration by fretting or galling. (Galling is the more severe condition, because it involves smearing and transferring material from one surface to another.) Fretting and galling can cause several problems in oxygen systems. The valve poppet might seize, resulting in loss of function. The frictional heat of the fretting or galling can lead to ignition of the valve. The particles generated by the fretting or galling can cause malfunction or ignition of another component downstream.

Where possible, the valve poppet should be designed for symmetrical flow so that no oscillatory side loads are created. The symmetrical flow centers the poppet in the bore and maintains design clearances between the poppet and bore surfaces.

For gaseous systems, it might be possible to reduce the volumetric flow rate, and thus the magnitude of oscillations and side loads, by installing an orifice. The orifice should be downstream of the poppet to minimize the pressure differential across the poppet. It is also possible to flexure-mount the poppet in the bore and to incorporate labyrinth seal grooves in the poppet surface.

To minimize the possibility of ignition, poppet and bore materials should be relatively resistant to ignition caused by

frictional heating. Both can be hardened by nitriding or a similar process to minimize material loss by fretting or galling.

A-4-3(u)1 Cold flow is a concern, especially for organic, non-metallic materials with little resiliency. With applied loads, these materials permanently deform, usually resulting in sealing loss.

A-4-3(u)2 Generally, seals with low hardnesses tend to provide better sealing. However, the softer seals will not withstand high temperatures and pressures. When such seals fail, they often extrude, generating particles. Pressure and thermal reversal cycles can also result in seal extrusion. Although silicone seals are not recommended, they can be found in existing oxygen systems. If found, careful examination during maintenance procedures is recommended. Excessive cross-linking of silicone elastomers in oxygen environments can occur, leading to embrittlement and degradation.

A-4-3(u)3 Copper is often used for oxygen seals. It can provide a very reliable seal; however, at extremely high temperatures, the copper oxide that forms on exposed surfaces can dislodge from the substrate. The oxide is then likely to become a source of particles.

A-4-3(w) Buckling can create component failures.

A-4-4.2.6 Materials are described in Chapter 3 and Appendix F. Systems built entirely of suitable materials can still develop the following problems if the pressurized gas flow is either started or stopped abruptly.

- (a) Abruptly starting or stopping pressurized gas flow can result in compression heating at elbows, dead ends, and valves. The resulting temperature rise can be sufficient to ignite all polymeric materials commonly used in gaseous oxygen systems.
- (b) Mechanical shock to the system can dislodge solid particles. If these particles are caught up in the flow and impinge on a surface, hot spots will result that can cause ignition.

A-5-4 See Appendix B for information on the training and education of personnel.

A-5-6 An automatic shutoff can also be provided.

A-5-7.1 Most metals burn freely in OEA (*see F-3.4*), depending on the concentration and pressure of the oxygen. Electrical contacts can 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 conditions 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 might be in proximity to the electrical equipment or circuits.

A-5-7.2 Because there are no flexible cords available with non-combustible insulation, it is essential for safe operation that portable equipment be used in OEA only if required for life safety and under rigorously controlled conditions.

A-5-8 See ASTM G 93, *Standard Practice for Cleaning Methods and Cleanliness Levels for Material and Equipment Used in Oxygen Enriched Environments*.

A-5-8.1 Of particular importance is the removal of lint, dust, and organic matter such as oil and grease. The latter includes fingerprints. These contaminants 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 E-3.1.4 and F-3.2.6.)

A-5-8.2 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 (e.g., acid attack of metals and solvent attack of nonmetals), level of cleanliness desired, ability to dispose of spent cleaning agents, worker exposure to the cleaning agents, and other factors.

A-5-8.3 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. Some organizations, including the U.S. military and the National Aeronautics and Space Administration (NASA), use criteria that are more stringent.

A-5-8.4 The reported level of residual organics can be misleading since it is an average level for the surface examined. The organic level actually might be concentrated in one area.

A-5-8.5 Shapes such as those of bellows tubing, Bourdon tubes in pressure gauges, small-diameter piping, dead-legs in piping, and crevices in mated pipe threads, and so forth are difficult to clean. Explosions from residual cleaning agents have occurred within products having these shapes. It is always advised to fully disassemble components for cleaning, since this mitigates the hazard of remaining solvent. Adequate rinsing and drying time are important.

A-5-9 Total elimination of combustible materials is the ideal objective, though it might not be totally achieved in practice. Combustibles used on exterior support systems or units, such as ventilating, air-conditioning purification, or filter media, as well as auxiliary power and air-oxygen supplies, and any components associated therewith, including hydraulic fluids, gas-kets, packing and joint compounds, and lubricants, should be regarded as potential fuels, until otherwise determined by suitable tests.

A-6-2 Fire-extinguishing systems for use in OEA face many requirements in addition to those required for conventional systems because of ignition susceptibility, increased flame spread rate and burning intensity, and the flammability of normally flame-resistant materials. Therefore, fire-extinguishing agents have to act rapidly to be effective. To protect occupants and real property, they should be inherently nontoxic and should not produce toxic or corrosive decomposition products. In general, these new requirements cannot be satisfied by the simple extension of traditional extinguishment techniques. Emergency personnel should receive special instruction and training, and special extinguishing agents and systems should be selected.

Water has shown to be an effective extinguishing agent in OEA when applied in sufficient quantities. Water at a spray density of 50 L/min/m² (1¹/₄ gpm/ft²) applied for 2 minutes will extinguish cloth burning in 100 percent oxygen at atmospheric pressure. The application method of the water is all-

important. Water extinguishing systems should be carefully designed such that all protected space is covered by the minimum spray density and that water is distributed to a depth sufficient to extinguish stratified fires in nonhomogeneous materials — for example, layers of cloth in clothing. New technology in the use of high-expansion, water-based foams has resulted in improved extinguishing properties. However, the applicability of this agent to each particular candidate system should be carefully evaluated with regard to the available space, required time, and application methods. More data has become available on the use of low-expansion foam and dry chemical extinguishing agents in normal atmospheres, but their applicability in OEA is still unknown.

A-6-6 Because of the explosive nature of fires involving metals in pressurized oxygen systems, fire-extinguishing systems have little effect. For oxygen-enriched fires at atmospheric pressure involving metals (e.g., shop turnings), the fire will burn more intensely in OEA. Fire-extinguishing systems need to react rapidly and effectively. (Topscott et al.)

A-6-8 It has been noted that the underlayer of two layers of cloth can continue to burn even though the outer layer has been wetted and extinguished.

Appendix B Training and Education

This appendix is not a part of the recommendations of this NFPA document but is included for informational purposes only.

B-1 Training. Personnel should be properly trained in the use of oxygen and oxygen systems and be familiar with the following specific areas.

B-1.1 Personnel who handle and use oxygen or design equipment for oxygen systems must be familiar with its pertinent physical, chemical, and hazardous properties. Personnel should know what materials are compatible with oxygen and the cleanliness requirements of oxygen systems. They should also be qualified to recognize system limitations and how to respond properly to all foreseeable failure modes.

B-1.2 Personnel should be thoroughly familiar with the use and care of protective and safety equipment and with first aid techniques.

B-1.3 Operators should be trained in the selection of proper equipment for handling liquid oxygen and gaseous oxygen and in the procedures for handling spills and leaks and disposing of oxygen. Personnel involved in design and operations should adhere to accepted standards and guidelines and comply with established regulatory codes.

B-2 Education. To aid in the education of designers, the ASTM Committee G-04 has developed a standards technology training course, "Controlling Fire Hazards in Oxygen Handling Systems," which is accompanied by a course textbook, *Fire Hazards in Oxygen Systems*. This course was developed by committee members from oxygen manufacturers, government agencies, equipment suppliers, and users. The course is based on the experience of committee individuals and their respective organizations. Course content was derived from all of the following documents:

- (a) Compressed Gas Association G-4.1, *Cleaning Equipment for Oxygen Service*

- (b) Compressed Gas Association G-4.4, *Industrial Practices for Gaseous Oxygen Transmission and Distribution Piping Systems*
- (c) Compressed Gas Association Video AV-8, "Characteristics and Safe Handling of Cryogenic Liquid Gaseous Oxygen"
- (d) Compressed Gas Association P-14, *Accident Prevention in Oxygen-Rich and Oxygen-Deficient Atmospheres*
- (e) Compressed Gas Association E-2, *Hose Line Check Valve Standards for Welding and Cutting*
- (f) European Industrial Gas Association 33/86/E, *Cleaning Equipment for Oxygen Service*
- (g) European Industrial Gas Association 5/75/E, *Code of Practice for Supply Equipment and Pipeline Distributing Non-Flammable Gases and Vacuum Services for Medical Purposes*
- (h) European Industrial Gas Association 6/77, *Oxygen Fuel Gas Cutting Machine Safety*
- (i) European Industrial Gas Association 8/75/E, *Prevention of Accidents Arising from Enrichment or Deficiency of Oxygen in the Atmosphere*
- (j) European Industrial Gas Association 12/80/E, *Pipelines Distributing Gases and Vacuum Services to Medical Laboratories*
- (k) European Industrial Gas Association 10/81/E, *Reciprocating Compressors for Oxygen Service*
- (l) European Industrial Gas Association 27/82/E, *Turbo Compressors for Oxygen Service, Code of Practice*
- (m) NFPA 53, *Recommended Practice on Materials, Equipment, and Systems Used in Oxygen-Enriched Atmospheres*
- (n) NFPA 50, *Standard for Bulk Oxygen Systems at Consumer Sites*
- (o) NFPA 51, *Standard for the Design and Installation of Oxygen-Fuel Gas Systems for Welding, Cutting, and Allied Processes*
- (p) NFPA 99, *Standard for Health Care Facilities*
- (q) ASTM G 63, *Standard Guide for Evaluating Nonmetallic Material for Oxygen Service*
- (r) ASTM G 88, *Standard Guide for Designing Systems for Oxygen Service*
- (s) ASTM G 93, *Standard Practice for Cleaning Methods and Cleanliness Levels for Material and Equipment Used in Oxygen Enriched Environments*
- (t) ASTM G 94, *Standard Guide for Evaluating Metals for Oxygen Service*
- (u) ASTM G 128, *Guide for the Control of Hazards and Risks in Oxygen-Enriched Atmospheres*

Appendix C Utilization of Oxygen-Enriched Atmospheres

This appendix is not a part of the recommendations of this NFPA document but is included for informational purposes only.

C-1 General.

C-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 appendix 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.

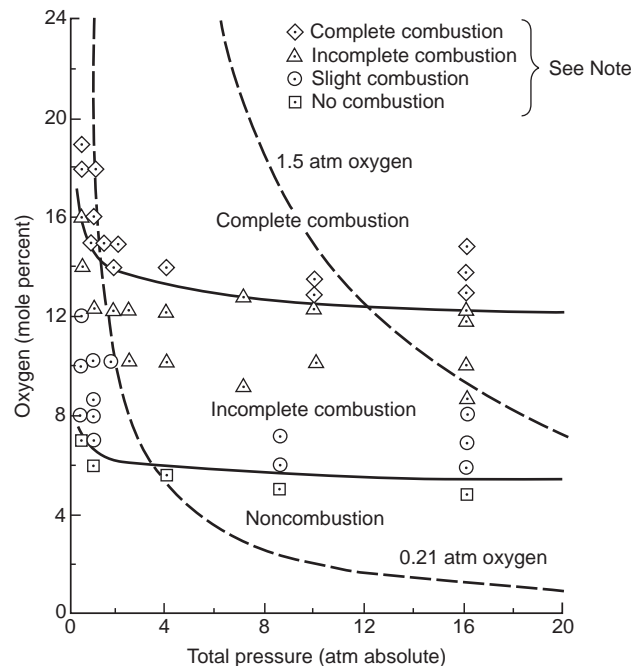
C-1.2 The degree of fire hazard of an oxygen-enriched atmosphere varies with the concentration of oxygen present, the diluent gas, and the total pressure. An oxygen-enriched atmosphere is defined as any atmosphere in which the concentration of oxygen exceeds 21 percent by volume or the partial pressure of oxygen exceeds 160 torr (21.3 kPa). Other oxidants include nitrous oxide, nitric oxide, and chlorates. In most commonly encountered oxygen-enriched atmospheres, an increased fire hazard is produced by the increased partial pressure of oxygen (e.g., in an atmosphere of compressed air) or by the absence of the diluting effect of an inert gas (e.g., in pure oxygen at a pressure $1/5$ atm). 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 (21.3 kPa). For example, a 4 percent oxygen mixture in nitrogen or helium at a total pressure of 12 atm will not support the combustion of paper even though the partial pressure of oxygen is 365 torr (48.6 kPa). 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.

C-1.2.1 Table C-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.

C-1.2.2 Figures C-1.2.2(a) and C-1.2.2(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.

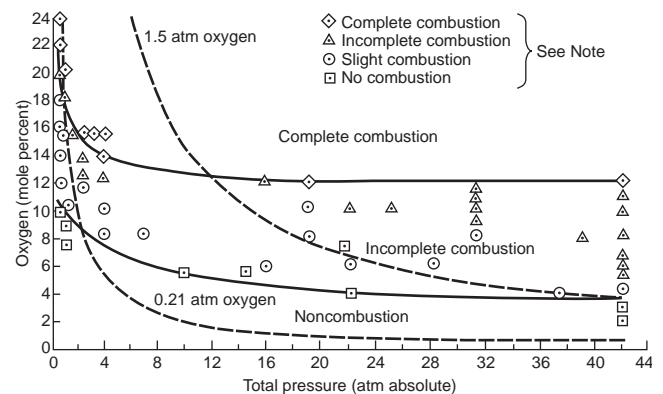
Table C-1.2.1 Partial Pressure of Oxygen in a Rarefied or Compressed-Air Atmosphere

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	Air or Sea Water m	ft	mm Hg or torr ^a	% by Volume
1/5	152	2.9	20	11,735	38,500	32	100.0 ^b
1/3	253	4.9	33.8	8,832	27,500	53	62.7 ^b
1/2	380	7.3	50.3	5,486	18,000	80	42.8 ^b
2/3	506	9.8	67.6	3,353	11,000	106	31.3 ^b
1	760	14.7	101.4	Sea level		160	20.9
2	1,520	29.4	202.7	-10	-33	320 ^b	10.5
3	2,280	44.1	304.1	-20	-66	480 ^b	6.9
4	3,040	58.8	405.4	-30	-99	640 ^b	5.2
5	3,800	73.5	506.8	-40	-132	800 ^b	4.2

^aThis column shows the increased available oxygen in compressed-air atmospheres.^bOxygen-enriched atmosphere.

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 C-1.2.2(a) Illustration of varying degrees of combustion in an oxygen-nitrogen oxygen-enriched atmosphere. [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 C-1.2.2(b) Illustration of varying degrees of combustion in an oxygen-helium oxygen-enriched atmosphere. [1]

C-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 commercial and military aviation. Such atmospheres are inherent to oxygen processing, transporting, and storage facilities. Oxygen-enriched atmospheres can develop inadvertently at any time when oxygen or compressed air is transported, stored, or utilized.

C-1.4 Oxygen is stored either in its liquid state or as a compressed gas. Compressed-gas storage pressures are variable and can be as high as 52 MPa (gauge pressure of 7500 psi). The den-

sity of oxygen in such conditions is high, and the fire hazard within pressure-containing components is greatly increased.

C-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.

C-1.4.2 Most common textile materials, including clothing, that become contaminated with oxygen are susceptible to rapid combustion. However, 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 Appendix F.)

C-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.

C-1.5 Nitrous oxide, a stable, nontoxic oxide of nitrogen, is widely employed 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 can develop in situations in which nitrous oxide is employed.

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

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

C-2.1 Preparation of oxygen conventionally involves the compression of air, followed by cooling and re-expansion, 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 can be stored as a compressed gas or as a liquid. Oxygen is also separated from air by adsorption and membrane-based systems.

C-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.

C-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 during transfer from the tank can create oxygen-enriched atmospheres.

C-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.

C-2.4 Leakage or venting of oxygen from any storage or dispensing equipment can create an oxygen-enriched atmosphere. (See C-8.1.)

C-2.5 Contamination of any pressure-containing component of an oxygen storage or dispensing system with any flammable or combustible substance, such as oil, grease, solvents, dust,

lint, or any organic substance, can produce a serious fire or explosion hazard.

C-2.6 Consult NFPA 50, *Standard for Bulk Oxygen Systems at Consumer Sites*, for the installation of storage systems.

C-3 Medical Applications.

C-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 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), some of which are flammable in air, but all of which are flammable in the oxygen-enriched atmosphere of operating rooms. Therefore, the operating room environment continues to present fire hazards.

C-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 widely practiced. Most hospitals of larger size are equipped with central oxygen piping systems for use in patient care facilities throughout the hospital. Recognizing the potential hazards of oxygen-enriched atmospheres created by such use, NFPA 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*.

C-3.2.1 Since ambulatory patients as well as hospital patients might 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.

C-3.2.2 Chapter 13, "Ambulatory Health Care Center Requirements," of NFPA 99, *Standard for Health Care Facilities*, covers nonhospital use.

C-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 can create a hazardous oxygen-enriched atmosphere.

C-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 is sealed and pressurized, sometimes to 4 atm 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 flamma-

bility-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 atm). (See Chapter 19, "Hyperbaric Facilities," of NFPA 99, *Standard for Health Care Facilities*.)

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.

C-4 Industrial Applications.

C-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 can place severe demands on equipment, materials, and systems. Elevated temperatures, high corrosivity, and reduced contamination levels are factors, in addition to flammability, that need to be considered, because they could limit the options of materials selection for oxygen services in advanced applications.

C-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 products include alcohols, aldehydes, and syngases. Elevated-temperature stability, corrosion resistance, and oxygen compatibility can limit use to certain alloys that are resistant to ignition and combustion in oxygen.

C-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. Oxygen-fuel burners are used to reheat ingots and slabs and to preheat ladles. Oxygen-fuel burners are also used in glass furnaces. Generally, materials selection issues and operating practices have been well defined in the steel industry.

C-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 and Allied Processes*, cover such applications.

C-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.

C-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 might be experienced in certain wastewaters that contain both oxygen and ozone. Ozone will aggressively attack certain nonmetallics.

C-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.

C-4.8 Ultra-high purity (UHP) oxygen is used to manufacture microchips in the semiconductor industry. The need 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 can 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 F-3.4.4.)

C-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 might also increase. Materials selection issues are similar to those encountered in various other processes where oxygen and aqueous environments are involved.

C-4.10 As a result of new technologies, the oxygen concentration of systems originally designed for air can be increased by a small percentage to increase efficiency. Such systems, which might not have been cleaned initially for oxygen service or designed with oxygen-compatible or combustion-resistant materials, would be unique. The systems should be treated on an individual basis with respect to issues such as cleaning, filtration, degree to which the oxygen levels are increased, and so forth.

C-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, and 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.

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

- (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 can be reduced without the nitrogen from air)
- (f) Previously unobtainable production from mineral or oil deposits

Service environments might 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 system design problems in advanced oxygen applications for safe operation.

C-4.13 Large users of oxygen are generally supplied by a pipeline from a nearby oxygen plant that uses cryogenic distillation. Smaller user requirements can 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, and so forth, are well established for oxygen supply systems.

C-5 Caisson Work and Underwater Tunneling. When driving a tunnel under or setting a foundation on a river bed, it might 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 1 atm to compensate [see Table C-1.2.1]. An oxygen-enriched atmosphere exists within the compartment while it is pressurized.

C-6 Space and Deep-Sea Exploration.

C-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.

C-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.

C-6.3 The practice of using aviator breathing oxygen (ABO) for spacecraft life-support systems has been the normal practice in the past and might 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 extravehicular activity (EVA), the orbiter atmosphere is changed to a 30 percent oxygen atmosphere at 70.3 kPa (10.2 psia). 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.

C-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 occupied only when a shuttle is docked for the first 5 to 6 years of operations. Once the space station is permanently occupied, it is expected to operate at 1 atm 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 atm at 21 percent oxygen concentration and used only in an emergency.

C-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 situation 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.

C-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 (21.3 kPa).

C-7 Commercial and Military Aviation.

C-7.1 All high-altitude commercial aircraft of moderate and large size are equipped with emergency oxygen breathing sys-

tems for use in case of failure of normal equipment. 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 (gauge pressure of 1800 psi to 2200 psi) in storage cylinders and from 103 kPa to 483 kPa (gauge pressure of 15 psi to 70 psi) in the dispensing system.

C-7.1.1 Use of such a system during flight can 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.

C-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.

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

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

C-8 Inadvertent Utilization.

C-8.1 An inadvertent oxygen-enriched atmosphere can be created due to use 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.

C-8.1.1 An oxygen-enriched atmosphere can 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.

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

C-8.1.3 An oxygen-enriched atmosphere can 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.

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

C-9 Reference.

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

Appendix D Fire Experience

This appendix is not a part of the recommendations of this NFPA document but is included for informational purposes only.

D-1 Introduction.

D-1.1 This appendix is a compilation of reports of fires and explosions involving both intentional and inadvertent oxygen-enriched atmospheres (OEA) that have been reported to NFPA.

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

D-1.3 The purpose of this appendix is to present examples that illustrate the common manner in which ostensibly diverse circumstances result in similar accidents. Because the sources of data vary, 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.

D-2 Utilization of OEA.

D-2.1 Oxygen Production, Transportation, and Transfer.

D-2.1.1 A reciprocating oxygen transfer pump, operating at 6895 kPa (gauge pressure of 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). The loss estimate was \$20,000.

D-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.

D-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 6.7 m to 11 m (22 ft to 36 ft), was insulated with a fine granular and noncombustible material. The adjacent insulation silo was also destroyed. The loss estimate was \$830,000.

D-2.1.4 Probably as the result of 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. The loss estimate was \$125,000.

D-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 can be reduced to finely divided palladium metal or palladium hydride.

If liquid oxygen 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 liquid oxygen is inadvertently introduced into the vacuum space.

D-2.1.6 A seismic survey vessel was destroyed and three individuals were killed as a consequence of an incident involving a 7570.8-L (2000-gal) liquid oxygen tank carried on board the ship for seismic experiments. The investigation concluded that excessive force applied to a valve stem sheared the stem collar. The internal tank pressure was approximately 413.7 kPa (gauge pressure of 60 psi.)

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 oxygen hazards, and the absence of fail-safe backup shutoff valves. The loss estimate was \$1,250,000.

D-2.1.7 A 4921-L (1300-gal) aluminum liquid oxygen tank truck exploded shortly after a delivery to 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 3.6 kg (8 lb) of aluminum from the pump were consumed. All submerged pumps were removed from service and replaced with external pumps.

D-2.1.8 A liquid oxygen tank truck exploded after making a delivery to a hospital. Two individuals were killed. Approximately 73.5 kg (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 buildup provided a kindling chain, causing further participation of aluminum in the scenario.

D-2.2 Medical.

D-2.2.1 Improper maintenance of a device used with oxygen led to this fire. A humidifier was used alongside a 2-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.

D-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 positively reveal 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.

D-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.

D-2.2.4 A tracheotomy was being performed on a 33-year-old ventilator-dependent woman with multiple medical problems. She was anesthetized with intravenous agents and ventilated with 100 percent oxygen via a polyvinylchloride (PVC) endotracheal tube that 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 1 month later from underlying multiple medical problems. [1]

D-2.2.5 During a tonsillectomy on a 4-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 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 5 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]

D-2.2.6 A 56-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 CO₂ laser. The anesthetic gases were administered via an endotracheal tube, specifically manufactured for CO₂ 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 CO₂ laser had most likely perforated the cuff and then ignited the silicone rubber in the oxygen- and nitrous oxide-enriched atmosphere. [3]

D-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 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]

D-2.2.8 The creation of an oxygen-enriched atmosphere, caused by an open oxygen source and a spark from the operative site, 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. The following two possibilities are likely:

- (a) The nap fibers on the reusable drape burned.
- (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]

D-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]

D-2.2.10 Improper use of an oxygen concentrator caused the following 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]

D-2.3 Cutting and Welding.

D-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. The loss estimate was \$100,000.

D-2.3.2 A pressure gauge, previously used to test the pressure in a hydraulic system, was 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.

D-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 the 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 probably saved his life and, without question, his eyes were saved by the goggles he was wearing.

D-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 pressure-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.

D-2.3.5 A welder and his assistant 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 the 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 assistant managed to escape. The welder was found cremated in his protective suit.

D-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.

D-2.4 Industrial Processing.

D-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 5 weeks cost \$300,000, and damage was estimated at \$350,000.

D-2.4.2 An electrical failure caused a reducing valve to open in an oxygen plant permitting oxygen to enter a nitrogen stream that lead 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 $3\frac{1}{2}$ 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. The loss estimate was \$485,000.

D-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.

D-2.5 Laboratories.

D-2.5.1 A high-pressure oxygen valve ruptured, discharging oxygen gas and metal debris on 300-V dc power cables. The debris broke the insulation, causing arcing. The 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. The loss estimate was \$160,000.

D-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 disposed of into a floor drain. The resulting mixture was ignited by hot surfaces, damaging equipment and metal partitions. The loss estimate was \$65,000.

D-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.

D-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.

D-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.

D-2.6 Space.

D-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. The loss estimate was \$7,186,000.

D-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.

D-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 the following:

- (a) Sealed cabin pressurized with an oxygen atmosphere
- (b) 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

D-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. The composition of the insulation has yet to be determined. 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.

D-2.6.5 The same chamber under the same atmosphere conditions described in D-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-V 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® insulation might 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.

D-2.6.6 During the launch preparation of an Apollo spacecraft, liquid oxygen was directed 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 liquid oxygen storage area preparatory to vehicle liquid oxygen 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 and smoke began issuing from under 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/sec (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 concentration might 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.

D-2.6.7 A space shuttle extravehicular mobility unit (space suit 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 D-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 the following:

- (a) Rupture of a thin, internal section of the aluminum body
- (b) Ignition of a silicone O-ring by compression heating of the oxygen
- (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.

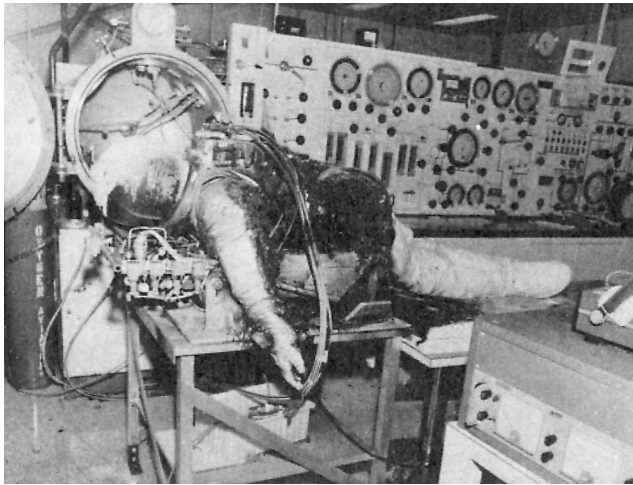


Figure D-2.6.7 This space suit was destroyed in a fire. No one was in the suit at the time of the fire. (Courtesy of NASA/Johnson Space Center.)

D-2.7 Aircraft Oxygen Systems.

D-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 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. The loss estimate was \$177,000.

D-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 jet 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.

D-2.7.3 In January, 1984, the Royal Australian Air Force experienced a ground fire that destroyed a \$6 million P3B Orion

aircraft. The incident occurred during removal of an onboard oxygen cylinder that was 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]

D-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 (2¹/₂-in.) fog lines before extinguishment could be secured, but major damage had been caused, and the aircraft was written off as a total loss.

D-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.

D-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. The fire department used foam to good advantage through openings that the fire had made in the roof and through a cabin window. Extinguishment was achieved 1¹/₂ hours after the fire started.

D-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.

D-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 marking, 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.

D-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 3- to 4-ft 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 side 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 (1850 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 reported that, as he was about to leave the area, he saw a flash of white light that enveloped the oxygen system's 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]

D-2.8 Deep Sea.

D-2.8.1 An accident occurred in a chamber with an internal atmosphere of 100 percent oxygen at 34 kPa (5 psia). Four men were 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 also 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 referenced material number 62 in Appendix F.)

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 ignitable combustibles, such as grease or molten plastics, which can act as localized ignition sources.

D-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 a plastic cover, at least two pillows, reading matter, toilet paper, and the filter paper (possibly 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 gauge pressure of 276 kPa (gauge pressure of 40 psi) 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 (gauge pressure of 43 psi). 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-minute 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. Shortly thereafter, a flash engulfed the compartment and smoke prevented further observation.

The pressure in the inner lock jumped to over 758 kPa (gauge pressure of 110 psi), which is 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 (gauge pressure of 58 psi).

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 the department's 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 gaining access to the chamber.

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.

D-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.

D-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.

D-2.9 Other.

D-2.9.1 A diesel-engine shrimp boat had a compressed-air starter. The compressed air was lost through leakage. 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. Then 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.

D-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.

D-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.

D-2.9.4 The following documented fires in piping systems associated with Navy hypobaric chamber complexes show the need for cleanliness, materials compatibility, and awareness to fires in oxygen systems:

- (a) February 26, 1974, fire in oxygen manifold, Cherry Point, NC
- (b) July 2, 1975, fire in oxygen manifold, device 9A9, Pensacola, FL
- (c) April 11, 1978, fire in shutoff and check valve, device 9A1B, serial #6, Whidbey Island, WA
- (d) April 16, 1980, explosion and fire in oxygen manifold, device 9A9, Pensacola, FL

Documented fires in the oxygen manifolds of Navy altitude chambers have been traced to contamination that was most likely introduced into the system during maintenance activities. The potential for fire and explosion in high-pressure oxygen systems is heightened by the presence of contaminants. More recent evaluation (1986, 1987, and 1993) of oxygen systems in Navy altitude chambers has uncovered unacceptable levels of contaminants including mercury, lead, and hydrocarbons. The fire incidents and further discovery of contamination underscore a need for continuous monitoring of oxygen purity as well as ongoing training of staff assigned to operate and maintain these devices.

Three men became very sick while breathing oxygen in the altitude chamber at MCAS Cherry Point on February 26, 1974. Upon investigation, two valves were found to have been damaged by flash fires resulting from the introduction of an unapproved lubricant. The system was also highly contaminated

with Freon 113. The fires in the two damaged valves were attributed to impact of the unapproved lubricant with pure oxygen. The subsequent laboratory investigation concluded that "the flash fire resulted in the partial decomposition of Teflon and Freon 113 in presence of hot metal. This could result in phosgene-like contaminants.

The July 2, 1975, fire in the oxygen manifold of device 9A9 in Pensacola, FL, was, upon investigation, found to be due to contamination introduced during maintenance of a ball valve. The contaminant entered the downstream check valve where it caused an explosion and fire. The investigation revealed that maintenance actions included installation of spare parts not "cleaned for oxygen use." The ultimate cause of the incident was documented as "...personnel assigned to maintain and operate the oxygen supply were as a result of oversight, lack of training or experience, not knowledgeable/careful enough in the use of their equipment," and that "...it must be assumed that the individuals simply had not been afforded enough proper training in the hazards of high-pressure gaseous oxygen and the handling/maintenance therefore.

The April 11, 1978, release of oxygen and acrid gas from the oxygen manifold of device 9A1B at NAS Whidbey Island was attributed to defective parts installed in the system. As with other fires in oxygen manifolds of Navy altitude chambers, contamination of oxygen was listed as the primary suspected cause. No contamination was found in the oxygen from the bottles in use at the time of the incident. The only source of potential contamination, then, was the components of the oxygen manifold itself.

The April 16, 1980, fire in the oxygen manifold of the 9A9 altitude chamber at NAS Pensacola was caused by contamination introduced during maintenance. A ball valve not "cleaned for oxygen use" had been installed in the manifold. The contaminants were ignited, possibly due to adiabatic compression, causing a high-pressure oxygen leak and fire. One man was injured as a result of the flames. Operators and maintenance personnel interviewed after the fire had not been properly trained in use and maintenance of high-pressure oxygen systems, had not been assigned fire billets, and were unaware of previous fires in oxygen manifolds, including one on the same device 5 years prior to this incident.

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Appendix E Fundamentals of Ignition and Combustion in Oxygen-Enriched Atmospheres

This appendix is not a part of the recommendations of this NFPA document but is included for informational purposes only.

E-1 General.

E-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.

E-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 OEA 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.

E-2 Properties of Atmospheres.

E-2.1 The chemical composition of OEA 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 some of the constituents might be found in the various OEA under consideration. The specific properties of these constituents are indicated in Table E-2.1.

Table E-2.1 Properties of Standard and Oxygen-Enriched Atmosphere Constituents

Constituent	Molecular Formula	Molecular Weight (0 = 16.00)	Melting Point (°C)	Boiling Point (°C)	Density (gm/L)	Thermal Conductivity X*	C _p 25°C (cal/gm)	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 5.2 atm	-78.5 Subl.	1.9768	39.67	0.202	1.303
Sodium or neon	Na Ne	20.183	-248.67	-245.9	0.835	115.71	0.246	1.64
Helium	He	4.003	-272.2 26 atm	-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 ₂ O	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)(cm²)(°C/cm) × 10⁻⁶

E-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 from the fuel. 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.

E-3 Ignition Mechanisms.

E-3.1 General.

E-3.1.1 Flames involve strongly exothermic reactions between oxidants and fuels, producing combustion and pyrolysis 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.

E-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.

E-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.

E-3.1.4 The minimum ignition energy for combustion will vary with the type of ignition source, the specific chemical 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 the following six types:

- Electrical sources, such as electrostatic and break (arc) sparks
- Hot surfaces, such as friction sparks and heated wires
- Heated gases, independent of surfaces, generated by adiabatic compression or jets of hot gas, including pilot flames
- Exothermic chemical reactions
- Mechanical sources, such as frictional heating and particle impact
- Laser sources

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

E-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.

E-3.2.2 Figure E-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.

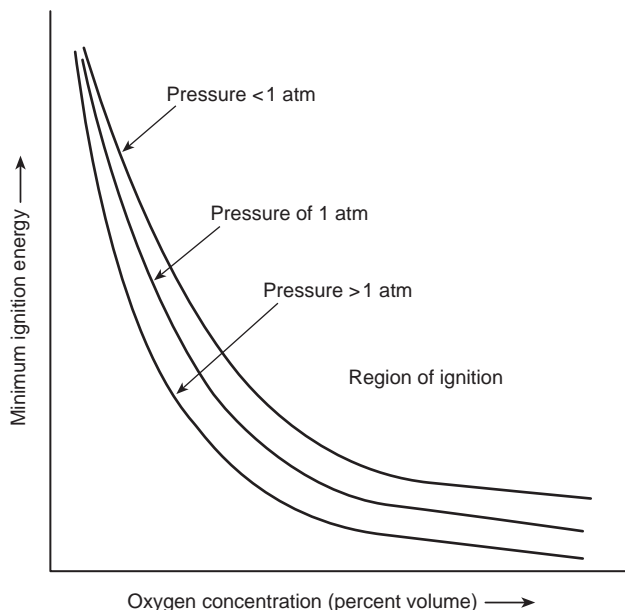


Figure E-3.2.2 Minimum ignition energy behavior of combustibles in oxygen-diluent atmospheres at different pressures.

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

E-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.

E-3.3.2 The specific effect on ignition energy requirements by the typical ignition sources will vary with the particular inert gas selected. This effect 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 atmo-

sphere because of the higher thermal conductivity and lower heat capacity per equivalent volume of helium. [6]

E-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 molecule. Helium is an exception to this trend. Due to its very high thermal conductivity, the flame propagation rate in helium dilution is higher than would be expected by examining heat capacity ranking alone.

E-4 Combustion Mechanisms.

E-4.1 General.

E-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 on 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 recommended practice.

E-4.1.2 It is important to review the essential features of the combustion process to obtain a better appreciation of the fire hazard problem under various OEA. 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.

E-4.2 Combustible Gases, Vapors, and Liquids.

E-4.2.1 In Section E-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 occurs, 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.

E-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., uniformly 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.

E-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.

E-4.2.4 Note in Figure E-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 provides effective fire control, and as long as the oxygen partial pressure is about 0.14 atm, the environment remains habitable.

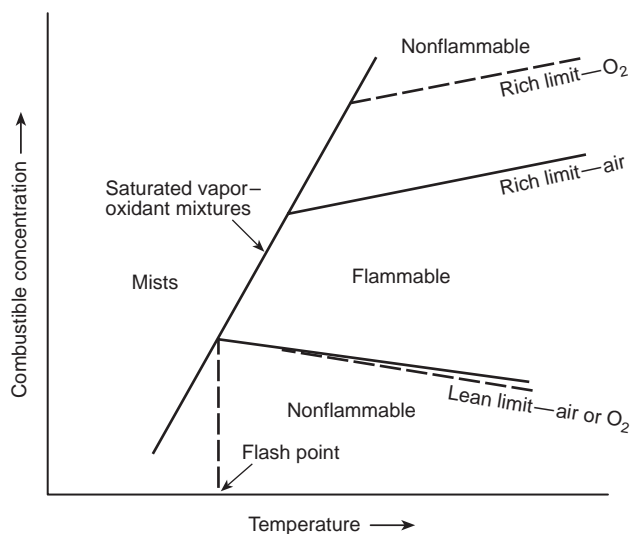


Figure E-4.2.4 Effects of temperature on the limits of flammability of a combustible vapor in air and oxygen. [7]

E-4.2.5 Total environmental pressure also has an effect on the limits of flammability (see Figure E-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.

E-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-

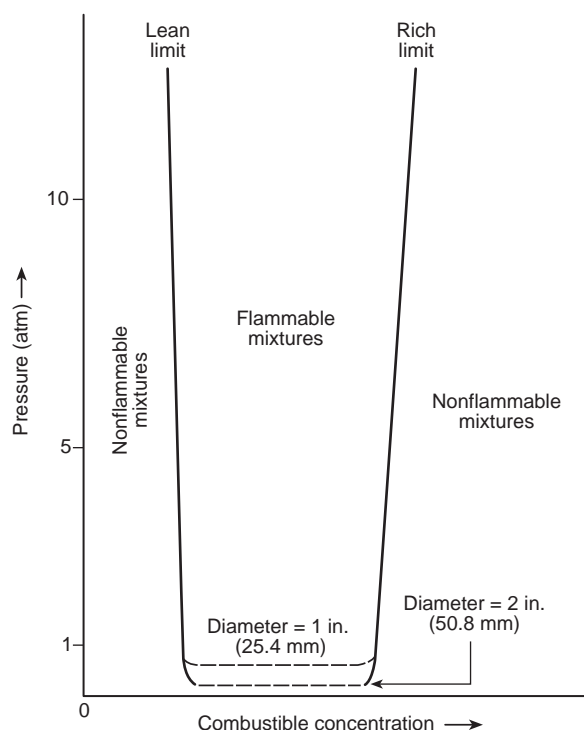


Figure E-4.2.5 Effects of pressure on limits of flammability of a combustible vapor in air and of pressure and composition on the quenching diameter. [8]

pressure limits are represented in Figure E-4.2.5 by broken lines to indicate their dependency on surroundings.

E-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 E-4.2.4.

E-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 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.

E-4.2.9 For most practical cases, the type of flame 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 factors such 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.

E-4.3 Combustible Solids — Nonmetallics.

E-4.3.1 The 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.

E-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 OEA. This rate is also dependent on direction of propagation, orientation of the combustible, scaling, and nature of the combustible surface (nap burning).

E-4.3.3 The observed effect of atmosphere composition and pressure on the flame spread rate is illustrated in Figure E-4.3.3. Note that increasing the partial pressure of oxygen at a constant environmental pressure can change the classification of a material from the nonflammable category 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.

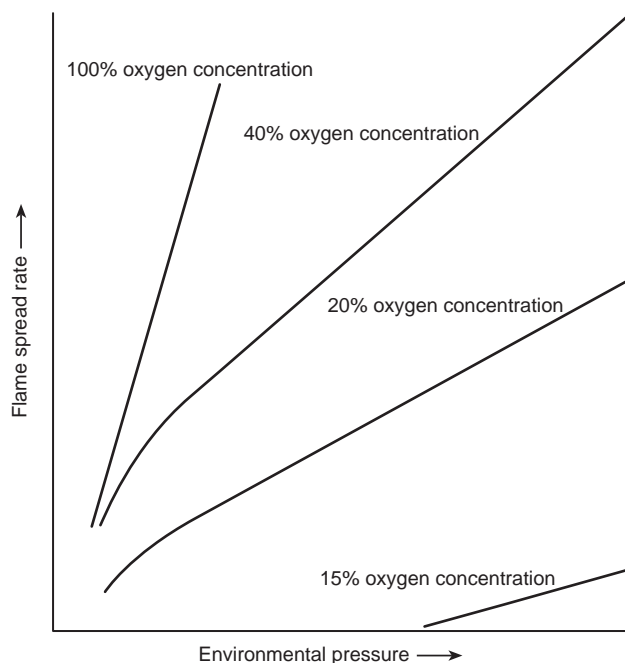


Figure E-4.3.3 Effects of atmosphere oxygen content and environmental pressure on flame spread rate.

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

E-4.4 Combustible Solids — Metals. The burning of metals can occur either in 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.

E-5 Effects of Fire in Oxygen-Enriched Atmospheres.

E-5.1 It has been noted that OEA 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 OEA can be encountered under closed-environment (fixed-volume) conditions (e.g., in spacecraft and hyperbaric chambers). [9]

E-5.2 In confined spaces, the combustion of a relatively small quantity of combustibles 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.

E-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-m³ (360-ft³) chamber are indicated in Table E-5.3.

E-5.3.1 The maximum temperatures and pressures in Table E-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:

- Combustion of the fuel is instantaneous
- None of the heat generated is lost to the walls of the chamber
- No dissociation of the product gases occurs

NOTE: Assumption (c) fails significantly above 1371°C (2500°F).

Table E-5.3 Oxygen Content, Maximum Fuel Consumption, and Resulting Combustion Temperatures and Pressures in Different Atmospheres in a 10.2-m³ (360-ft³) Volume Enclosure

Atmosphere	Cellulose Fuels		Hydrocarbon Fuels	
	103.4 kPa (15 psia) (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 ¹ (kg)	1.2	11	0.36	3.3
Heat of combustion (cal/gm)	~4,000		~11,700	
Maximum heat release (kcal)	~4,924	~43,500	~4,233	~38,200
Maximum theoretical temperature (°C)	1,810	5,670	1,390	5,840
Maximum pressure ratio (P _{final} /P _{initial}) ²	8	36	7	33
Maximum final pressure (kPa)	827 (120 psia)	3,723 (540 psia)	724 (105 psia)	3,413 (495 psia)

¹Assumes all but 10 volume percent of available O₂ can react.

²Does not consider dissociation of product gases.

E-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 consumption 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-m³ (1.6-ft³) 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.

E-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.

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Appendix F Material for Use in Oxygen-Enriched Atmospheres

This appendix is not a part of the recommendations of this NFPA document but is included for informational purposes only.

F-1 General. See also Chapter 3.

F-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 oxygen-enriched atmosphere (OEA). This appendix describes the effect of material properties on the degree of hazard for guidance in the selection of materials that can be used with safety.

F-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.

F-2 Combustible Gases, Vapors, and Liquids.

F-2.1 General. 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 F-2.1 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 can be estimated from the data obtained for air and from known oxygen concentration effects for the given class of combustibles.

Table F-2.1 Ignition and Flammability Properties of Combustible Liquids and Gases in Air and Oxygen at Atmospheric Pressure

Combustible	Flash Point ¹		Minimum Ignition Temperature ²				Minimum Ignition Energy ³		Flammability Limits ⁴ Vol. %			
	Air		Air		Oxygen		Air	Oxygen	Air		Oxygen	
	°C	°F	°C	°F	°C	°F	mJ	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 ⁵
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	—	—	—	—	—	—	—	—	—	—	—	—
Enflurane	>200	93	NA	NA	NA	NA	NA	NA	NA	NA	9.8	NA

(continues)

Table F-2.1 Ignition and Flammability Properties of Combustible Liquids and Gases in Air and Oxygen at Atmospheric Pressure (continued)

Combustible	Flash Point ¹		Minimum Ignition Temperature ²				Minimum Ignition Energy ³		Flammability Limits ⁴ Vol. %			
	Air		Air		Oxygen		Air	Oxygen	Air		Oxygen	
	°C	°F	°C	°F	°C	°F	mJ	mJ	LFL	UFL	LFL	UFL
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 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 ⁵
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 ⁵	1.8	10	1.7	52 ⁵
Methylene chloride	—		615	1139	606	1123	—	0.137	15.9 ⁵	19.1 ⁵	11.7 ⁵	68
Ethylene chloride	13.3	56	476	889	470	878	2.37	0.011 ⁵	6.2	16	4.0	67.5
Trichloroethane	—		458	856	418	784	—	0.092	6.3 ⁵	13 ⁵	5.5 ⁵	57 ⁵
Trichloroethylene	32.2	90	420	788	396	745	—	18 ⁵	10.5 ⁵	41 ⁵	7.5	91 ⁵
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	—	≤5.4	—
Ammonia	Gas		651	1204	—		>1000	—	15.0	28	15.0	79
Aniline	75.6	168	615	1139	—		—	—	1.2 ⁵	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	—
Bromo- chloromethane	—		450	842	368	694	—	—	NF ⁶	NF	10.0	85
Bromotrifluoro- methane	Gas		>593	>1100	657	1215	—		NF	NF	NF	NF
Dibromodifluoro- methane	Gas		499	930	453	847	—	—	NF	NF	29.0	80

¹Data from Footnotes 1 and 2; open-cup method.²Data from Footnotes 3, 4, 5, and 6.³Data from Footnotes 7, 8, 9, 10, and 3.⁴Data from Footnotes 11, 12, 3, 4, and 6.⁵Data at 200°F (93°C).⁶NF — No flammable mixtures found in Footnote 4.

F-2.2 Ignition Temperature and Energy.

F-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 atm pressure (see Table F-2.1). Generally, the AIT of the paraffinic hydrocarbons decreases 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 0 to about 6895 kPa (gauge pressure of 1000 psi).

Figure F-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 (gauge pressure of 5000 psi).

F-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.

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 F-2.1. Figure F-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 F-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.

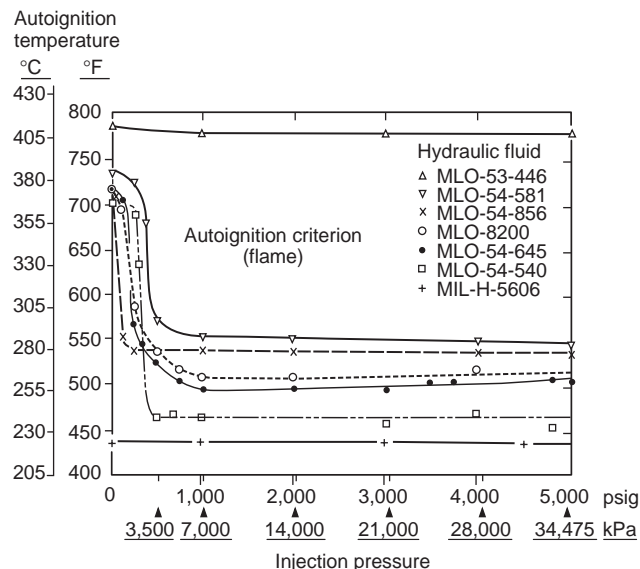


Figure F-2.2.1 Minimum autoignition temperatures of seven hydraulic fluids in air at atmospheric pressure and at various injection pressures (200-cm³ Pyrex® vessel). [13]

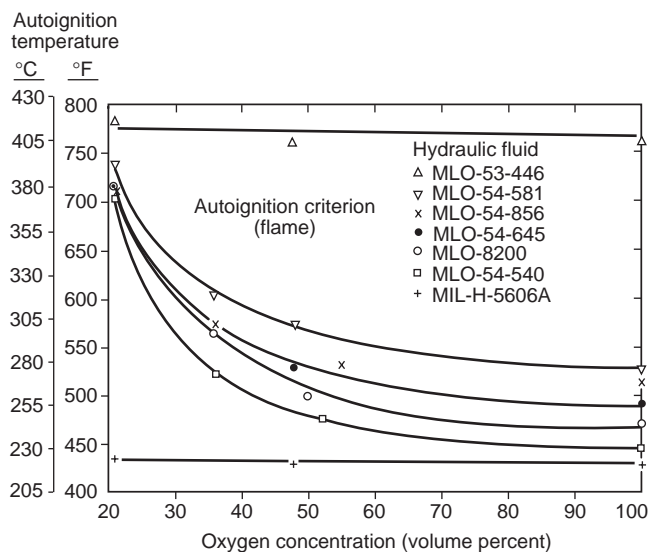


Figure F-2.2.2(a) Minimum autoignition temperatures of seven hydraulic fluids at atmospheric pressure in various oxygen-nitrogen atmospheres (200-cm³ Pyrex® vessel). [13]

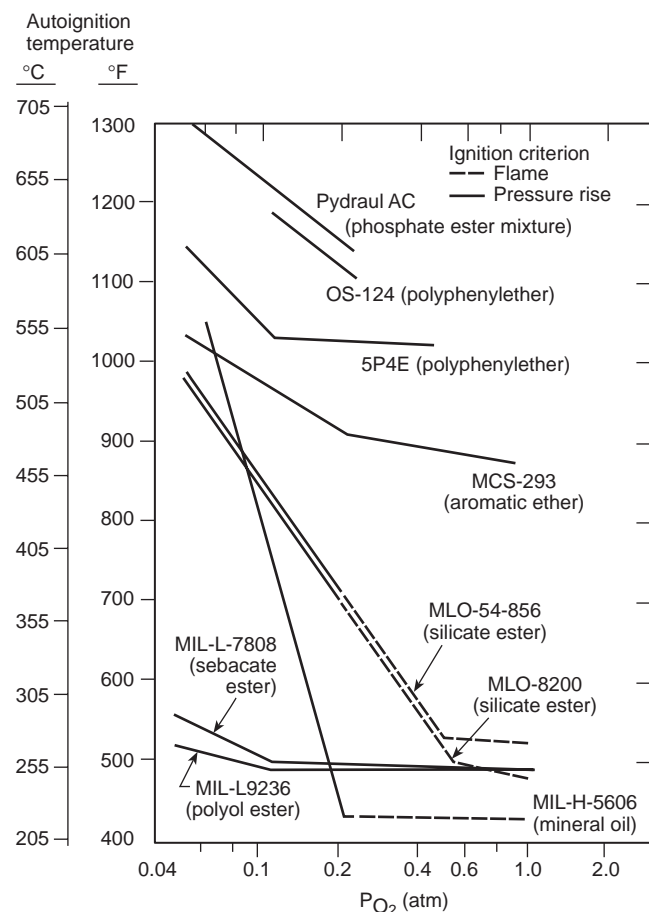


Figure F-2.2.2(b) Variation of minimum autoignition temperatures with oxygen partial pressure (P_{O_2}) for various lubricants. [13]

F-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 F-2.1 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.

F-2.2.4 Minimum ignition energy values refer to the most ignitable 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 F-2.2.4 shows the variation of the minimum spark

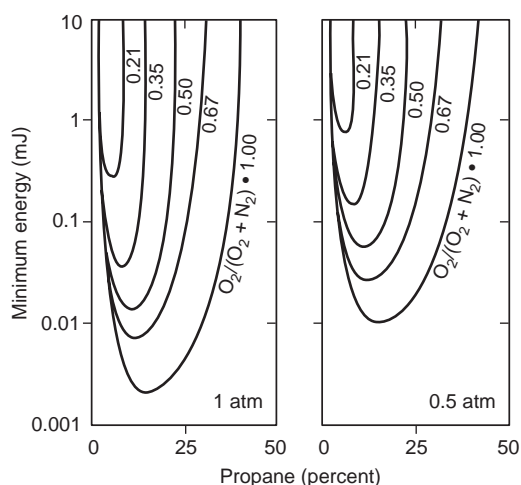


Figure F-2.2.4 Effect of oxygen index and ambient pressure on minimum ignition energies. [9]

ignition energies of propane-oxygen-nitrogen mixtures with fuel concentration and oxygen concentration at 0.5 and 1 atm pressure. The substitution of helium for nitrogen results in higher ignition energies but does not eliminate the risk of spark ignitions.

F-2.3 Combustion.

F-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 atm 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 (gauge pressure of 100 psi). The explosions are even more severe in oxygen where detonations might 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.

F-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/sec (0.43 in./sec), whereas a 3.2-mm (0.13-in.) diameter 6061 aluminum rod will burn at 64 mm/sec (2.5 in./sec). [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 percent) 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]

F-2.4 Limits of Flammability of Nonmetallic Materials.

F-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 F-2.1). 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 can propagate flame at temperatures far below the flash points of the fuels.

F-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 F-2.1 provides data obtained at ordinary temperatures [$\leq 593^{\circ}\text{C}$ ($\leq 1100^{\circ}\text{F}$)], except where otherwise noted. Vapors and gases, such as ammonia, carbon monoxide, and certain halogenated hydrocarbons, have much higher lower limits.

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, lubricants need much higher temperatures, for example, 93°C to 371°C (200°F to 700°F), to form lower limit mixtures than do the paraffins and many other hydrocarbons. [13]

F-2.4.3 Based on weight, the lower limits of the paraffins correspond to about 45 mg (0.00158 oz) 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. The values are as high as 100 percent for materials such as acetylene and ethylene oxide. That is, their vapors can decompose exothermally and propagate flame in the absence of air or oxygen.

F-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.

F-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.

F-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 F-2.4.6(a)] or water vapor. Figures F-2.4.6(a) and (b) show the complete range of flammable mixture compositions

that might 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.

F-2.5 Limits of Flammability — Metals. Flammability limits, as such, 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. The measures 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 F-3.4.

F-3 Combustible Solids.

F-3.1 General. 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 the following:

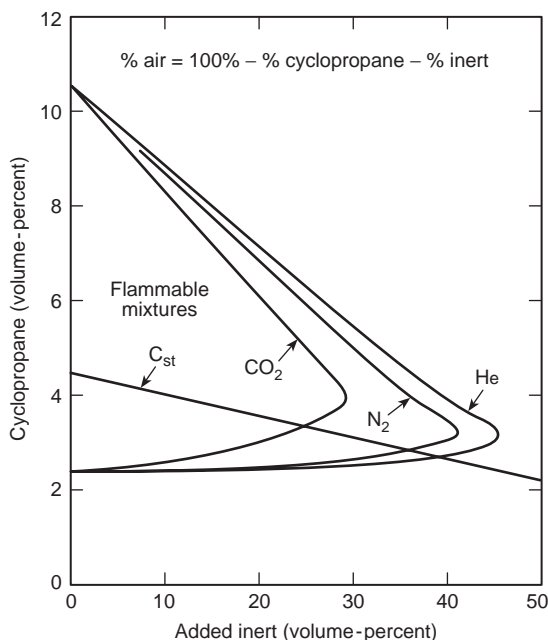


Figure F-2.4.6(a) Limits of flammability of cyclopropane-carbon dioxide-air, cyclopropane-nitrogen-air, and cyclopropane-helium-air mixtures at 25°C (86°F) and atmospheric pressure. [6] (C_{st} = stoichiometric composition = line-defining amount of combustible vapor required for complete combustion.)

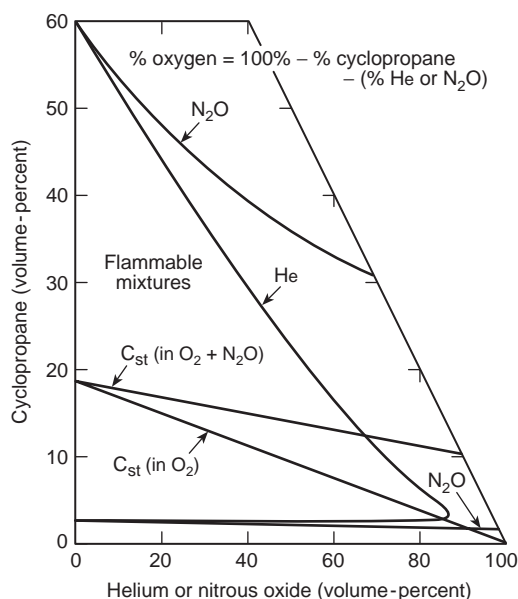


Figure F-2.4.6(b) Limits of flammability of cyclopropane-helium-oxygen and cyclopropane-nitrous oxide-oxygen mixtures at 25°C (86°F) and atmospheric pressure. [6] (C_{st} = stoichiometric composition = line-defining amount of combustible vapor required for complete combustion.)

- (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 and ambient temperature
- (e) Venting — external airflow
- (f) Inerting — oxygen deficiency and carbon dioxide buildup

F-3.2 Ignition Temperature and Energy.

F-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 0.1 J. 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.

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 Dust. 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]

F-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 0.02 J static spark in 100 percent oxygen but not in 64 percent oxygen in air. Fibers contaminated with greasy substances can be ignited by much weaker sparks. [18]

F-3.2.3 Textile fabrics, such as those 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 2.3 J in 100 percent oxygen at atmospheric pressure, whereas, in normal air, a spark energy as high as 193 J was required. Silk and polyester fabrics are more difficult to ignite than cotton or wool. Oily fabrics are highly flammable and can be ignited with a spark energy as small as 1/10,000 of that for a clean sample. [19]

F-3.2.4 Frictional sparks in 100 percent oxygen can be much more incandescence 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 0.0003 J spark energy in air will ignite textile fabrics in 100 percent oxygen due to increased reactivity of the abrasive particles in oxygen. Cotton and wool fabrics can also be ignited by a spark from the impact of a hardened steel tool against a rusty steel plate.

F-3.2.5 Combustible materials, when heated, can self-ignite at relatively low temperatures that approach the spontaneous ignition temperatures (SIT) or autogenous ignition temperatures (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 oxygen at 1 atm, this material will ignite at about 393°C (740°F). [20]

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 oxygen 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 for 100 percent oxygen. 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 oxygen at 1 atm and at 560°C (1040°F) in air at 6 atm. [21]

F-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 explosionlike 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 ignitable common metals are titanium, magnesium, and lithium; the least ignitable are nickel, copper, and cobalt. Increase in oxygen pressure and content promotes the ignition of metals at lower temperatures. [22]

F-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 F-3.2.6.1 shows the P_v product required for ignition of 2.5 cm (1 in.) diameter \times 0.25 cm (0.1 in.) wall \times 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/sec (72.4 ft/sec) and increasing P at a rate of 35 N/sec (7.5 lbf/sec) until ignition. [22]

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

Test Materials	P_v Product at Ignition	
	$W/m^2 \times 10^{-8}$	$lbf/in.^2 \times ft/min \times 10^{-6}$
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 P_v products.

F-3.2.6.1.1 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 igni-

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

F-3.2.6.1.2 Figure F-3.2.6.1 provides the P_v 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 P_v products required for ignition. At the pressure where the minimum P_v 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 than 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]

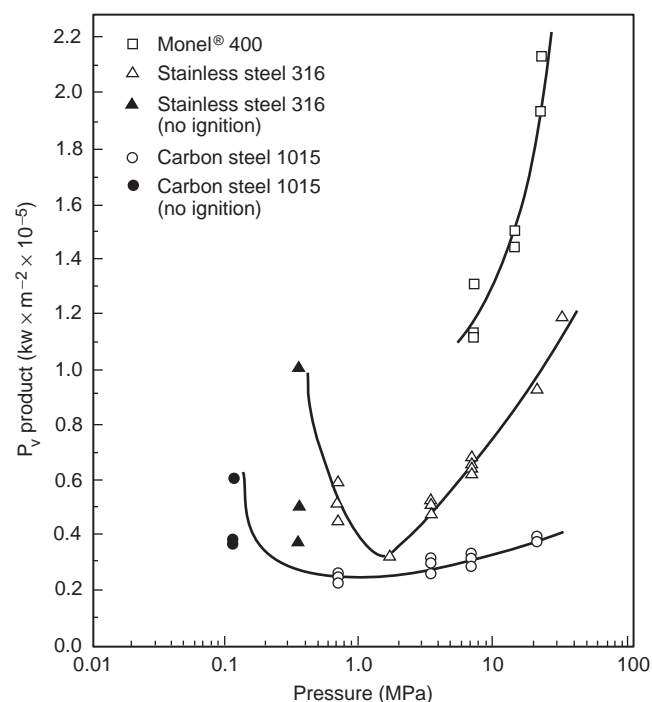


Figure F-3.2.6.1 Effect of oxygen pressure on the P_v products required for the frictional ignition of Monel® 400, 316 stainless steel, and carbon steel 1015. [26]

F-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 F-3.2.6.2. [23]

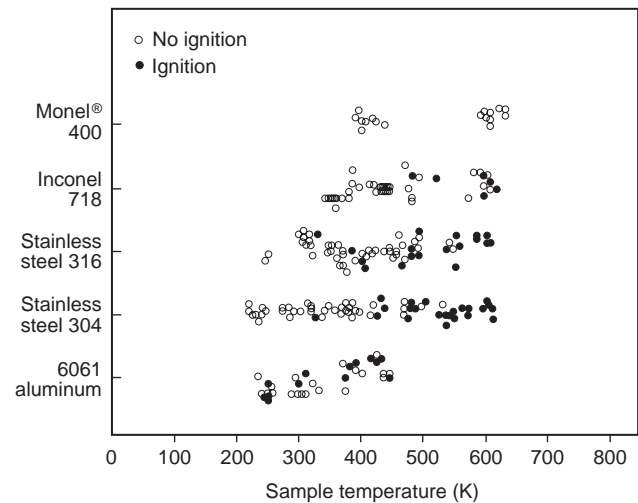


Figure F-3.2.6.2 Results of supersonic impact of single 2000-micron (0.08-in.) diameter aluminum particles impacting various alloys in 27 MPa (3900 psia) oxygen. [23]

F-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 thermal degradation 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 D 1929, *Standard Test Method for Determining Ignition Temperature 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]

F-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 F-3.2.8. [21]

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

Table F-3.2.8 Minimum Hot Plate Ignition Temperatures of Six Combustible Materials in Oxygen-Nitrogen Mixtures at Various Total Pressures

Material	Oxidant	Ignition Temperature, °C			
		Total Pressure, atmospheres			
		1	2	3	4
Cotton sheeting	Air	465	440 (425) ^a	385	365
	42% O ₂ , 58% N ₂	390	370	355	340
	100% O ₂	360	345	340	325
Cotton sheeting, treated ^b	Air	575	520 (510) ^a	485 (350) ^a	370 (325) ^a
	42% O ₂ , 58% N ₂	390 (350) ^a	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

^aValues in parentheses indicate the temperature at which material glowed.
^bCotton sheeting treated with DuPont® X-12 fire retardant; amount of retardant equal to 12 percent of cotton specimen weight.

F-3.2.9 Experiments in which samples of polyethylene and polyvinyl chloride 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 can be an easily overlooked source of ignition in such systems.

F-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 increase 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] (As a cautionary note, see F-3.3.6.)

F-3.3 Combustion — Nonmetallic Materials.

F-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 mixture of 42 percent O₂ and 58 percent N₂ at 1 atm pressure is more hazardous than a 21 percent oxygen 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 F-3.3.1. Only glass fiber materials, 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.

Table F-3.3.1 Flame Resistance of Materials Held Vertically at One Atmosphere Pressure in O₂/N₂ 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 duck, 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

Table F-3.3.1 Flame Resistance of Materials Held Vertically at One Atmosphere Pressure in O₂/N₂ Mixtures (continued)

NRL Sample Number	Material	Combustion in O ₂ /N ₂ Mixtures		
		21% O ₂	31% O ₂	41% O ₂
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 ¹	Burned
FM-24	Omnicoated glass fabric	No	No	Burned ¹
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 ²
FM-34	Belco no-flame grease	No	No	No ²

¹Burned only over igniter.

²White smoke only.

F-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 oxygen content. [21, 35, 36]

F-3.3.3 Ignitibility data are given for high-temperature wiring operating in 100 percent oxygen at 34 kPa (5 psia). [37] The 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 might ignite adjacent material. [38, 39] Potting compounds, circuit boards, and other components of the electrical system can also contribute to the fuel supply in an OEA.

F-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 F-3.3.4). Reported measurements of flame spread rates in an OEA show wide variations principally due 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.

F-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 F-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.

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

Material	Flame Spread Rate (mm/sec)	
	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 ± 0.254
Fiberglass 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)

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

Material	Flame Spread Rate (mm/sec)	
	In Air	In 258 mm Hg Oxygen
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	(0.076 ± 0.051)
Wire, Mil W76B, blue	NI	—
Wire, Mil W76B, orange	NI	14.478 ± 1.27
Wire, Mil W76B, yellow	NI	—
Wire, Mil W16878, black	NI	NI
Wire, Mil W16878, green	NI	NI
Wire, Mil W16878, yellow	NI	NI
Wire, Mil 16878, white	NI	NI
Wire, misc., black, ³ / ₁₆	NI	—
Wire, misc., brown, ⁷ / ₃₂	NI	12.954 ± 1.27
Wire, misc., white, ³ / ₃₂	NI	8.382
Wire, misc., yellow, ⁷ / ₆₄	NI	22.606
Wire, misc., yellow, ⁵ / ₃₂	NI	10.414

Note: NP — No sustained propagation of flame; NI — no ignition of material.

Table F-3.3.5 Typical Measured Burning Rates for Strips of Filter Paper at 45 Degree Angle [41]

Total Pressure Gas Composition (dry basis)			Burn Rate, cm/sec					
			0.21 atm	0.53 atm	1.00 atm	4.03 atm	7.06 atm	10.09 atm
atm abs ft of seawater			—	—	0 ft	100 ft	200 ft	300 ft
% O 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	

(continues)

Table F-3.3.5 Typical Measured Burning Rates for Strips of Filter Paper at 45 Degree Angle [41] (continued)

			Burn Rate, cm/sec					
Total Pressure		atm abs ft of seawater	0.21 atm —	0.53 atm —	1.00 atm 0 ft	4.03 atm 100 ft	7.06 atm 200 ft	10.09 atm 300 ft
Gas Composition (dry basis)								
% O ₂	% N ₂ ^a	% He						
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
					1.38	2.28	2.71	3.72
20.9	39.6	39.5	d	d	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		

^aIncludes any argon that was present.^bCompressed air.^cSample would not burn, even with brightly glowing igniter grid.^dNo run was made under these conditions.

F-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/sec (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]

F-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]

F-3.3.8 The oxygen index test, ASTM D 2863, *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 can take place more readily and produce a lower O.I.

The O.I. test, as determined by ASTM D 2863, 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 F-3.4 for the O.I. 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 O.I. is only one of several criteria that can be utilized to evaluate the suitability of materials for a specific oxygen application.

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

F-3.4 Combustion of Metals.

F-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 (1045 psia). [47] This example 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 F-3.3.1*), 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.