FIRE HAZARDS OF OXYGEN AND OXYGEN-ENRICHED ATMOSPHERES

Doc 04/18

Revision of Doc 04/09
FIRE HAZARDS OF OXYGEN AND OXYGEN-ENRICHED ATMOSPHERES

As part of a programme of harmonization of industry standards, the European Industrial Gases Association (EIGA) publication, EIGA Doc 04, *Fire hazards of oxygen and oxygen enriched atmospheres*, has been used as the basis of an internationally harmonized gas association’s publication on this subject.

This publication is intended as an international harmonized publication for the worldwide use and application by all members of Asia Industrial Gases Association (AIGA), Compressed Gas Association (CGA), European Industrial Gases Association, and the Japan Industrial and Medical Gases Association (JIMGA). Regional editions have the same technical content as the EIGA edition, however, there are editorial changes primarily in formatting, units used and spelling. Regional regulatory requirements are those that apply to Europe.

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Note: Technical changes from the previous edition are underlined
1 Introduction

This publication explains the fire hazards resulting from handling oxygen and the relevant protective measures that should be taken.

2 Scope and purpose

The intent of this publication is to provide personnel working with oxygen, or potentially in or near oxygen-enriched atmospheres, with a high level of awareness of the fire and explosion hazards associated with these conditions. Oxygen levels less than 19.5% constitute an oxygen-deficient atmosphere and may only be entered using special precautions. See CGA SB-2, Oxygen-Deficient Atmospheres, or EIGA Doc 44, Hazards of inert gases and oxygen depletion [1, 2].

Appendix A is a summary of the information in this publication suitable to be produced as a pamphlet to be handed to those involved in daily operations involving oxygen or used as a supplement to safety presentations.

Appendix B lists some incidents that have taken place in recent years that can be used as examples underlining the hazards of oxygen and oxygen-enriched atmospheres.

3 Definitions

For the purpose of this publication, the following definitions apply:

3.1 Publication terminology

3.1.1 Shall

Indicates that the procedure is mandatory. It is used wherever the criterion for conformance to specific recommendations allows no deviation.

3.1.2 Should

Indicates that a procedure is recommended.

3.1.3 May

Indicates that the procedure is optional.

3.1.4 Will

Is used only to indicate the future, not a degree of requirement.

3.1.5 Can

Indicates a possibility or ability.

3.2 Technical definitions

3.2.1 Oxygen-enriched atmosphere

Air and gas mixtures in which the oxygen concentration by volume exceeds 23.5% at sea level or whose partial pressure of oxygen exceeds 175 torr (mm Hg) [3].

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References are shown by bracketed numbers and are listed in order of appearance in the reference section.
3.2.2 Pressure

Bar shall indicate gauge pressure unless otherwise noted – i.e. “bar, abs” for absolute pressure and “bar, dif” for differential pressure.

4 General properties

Oxygen, which is essential to life, is not flammable in itself, but supports and accelerates combustion. The normal oxygen concentration in atmospheric air is approximately 21% by volume.

4.1 Oxygen supports and accelerates combustion

Most materials burn fiercely in oxygen; the reaction can even be explosive.

As the oxygen concentration in air increases, the potential fire risk increases and combustion is accelerated.

4.2 Oxygen gives no warning

Oxygen is colourless, odourless, and has no taste; hence, the presence of an oxygen-enriched atmosphere cannot be detected by normal human senses. Oxygen also does not give any obvious physiological effects that could alert personnel to the presence of oxygen enrichment.

Increasing the oxygen concentration of the air at atmospheric pressure does not constitute a significant health hazard.

4.3 Oxygen is heavier than air

Oxygen can accumulate in low lying areas such as pits, trenches, or underground rooms because it is heavier than air. This is particularly relevant when liquid oxygen is spilled. In this case, the generated cold gaseous oxygen is three times heavier than air.

5 Fire hazards with oxygen

5.1 Necessary conditions for a fire

In general, for a fire or explosion to occur three elements are required: combustible material, oxygen, and an ignition source.

The fire triangle is the usual way of representing these conditions as shown in Figure 1:

When one of the three elements is missing, a fire cannot occur.
5.2 Oxygen

Oxygen reacts with most materials. The higher the oxygen concentration and pressure in the atmosphere or in an oxygen system then:

- combustion reaction or fire will be more vigorous;
- ignition temperature and the ignition energy to promote the combustion reaction is much lower; and
- temperature of the flame is higher and consequently the destructive capability of the flame is greater.

Most causes of oxygen fires can be categorised as follows:

- oxygen enrichment of the atmosphere;
- improper use of oxygen;
- incorrect design of oxygen systems;
- incorrect operation and maintenance of oxygen systems; and
- use of materials incompatible with oxygen service.

Oxygen fires can be caused by one or more of the above conditions.

5.2.1 Oxygen enrichment of the atmosphere

Oxygen enrichment of the atmosphere can be the result of:

- Leaking pipe connections or flanges. This can be particularly hazardous in areas where there is not sufficient ventilation thus causing the oxygen concentration to increase;
- Opening of oxygen systems under pressure. A sudden release of oxygen under pressure can result in a relatively large jet of escaping oxygen. This can result in a jet flame and a projection of molten material;
- Oxygen used in cutting and welding processes. In processes such as cutting, gouging, scaring and thermal lancing, oxygen is used in quantities greater than necessary for the burning process. The unused oxygen remains in the atmosphere, and if ventilation is inadequate the air can become enriched with oxygen;
- Oxygen used in metallurgical processes. Incorrect practice when using blowpipes can lead to oxygen enrichment, especially in confined spaces;
- Desorption. Oxygen can be released in appreciable quantities when cold materials that have absorbed oxygen such as absorbents (molecular sieve, silica gel, etc.) or insulation materials are warmed to room temperature;
- Cryogenic liquid spill. A spill of liquid oxygen creates a dense cloud of oxygen-enriched air when evaporating. In an open space, hazardous oxygen concentration usually exists only within the visible cloud associated with the spill. The cold gas can collect in nearby low-lying spaces such as ditches or drains, which are not well ventilated; atmospheric checks should be carried out on any such nearby spaces after a spill;
- Liquefaction of air. When using cryogenic gases with boiling points lower than oxygen, for example, nitrogen, hydrogen and helium, oxygen enrichment can also occur. Ambient air will condense on uninsulated equipment where the temperature is lower than the liquefaction
temperature of air (approximately –193 °C). This can also occur on pipework lagged with an open cell insulant. The liquid air can contain up to 50% oxygen and, if this liquid drips off and evaporates, the oxygen concentration in the remaining portion can be greater than 80%; or

- Oxygen vents. Areas near oxygen vents can be particularly hazardous. A sudden release of oxygen can occur without warning. The non-cryogenic production of oxygen or nitrogen can involve an occasional or continuous venting of oxygen. See EIGA Doc 154, Safe Location of Oxygen and Inert Gas Vents [4].

5.2.2 Improper use of oxygen

Serious incidents have been caused by the use of oxygen for applications for which it was not intended.

Examples of improper use of oxygen include:

- powering pneumatic tools;
- inflating vehicle tyres and rubber boats;
- pressurising and purging systems;
- replacing air or inert gas;
- cooling or refreshing the air in confined spaces;
- blowing oxygen inside clothing, for example, by a welder in an attempt to create a cooling breeze;
- removing dust from benches, machinery, and clothing;
- starting diesel engines;
- cleaning; or
- ventilating.

In each case, the fire and explosive risk is the same and results from exposing combustible materials such as flammable gases, flammable solids, rubbers, textiles, oils and greases to oxygen.

5.2.3 Design of oxygen systems

The correct design of oxygen installations is critical. Inadequate designs can and have led to serious incidents.

Examples of inadequate design include:

- Using rapidly opening (ball) valves. This can lead to ignition caused by the heat generated by high velocity gas or adiabatic compression (see the following);
- Allowing too high a gas velocity, which can cause ignition of incompatible materials in the system due to particle impact;
- Opening the main shut off valve in an oxygen supply pipeline without first equalising the pressure;
- High pressure gas flowing over sharp-edged orifices, rapid expansions, or rapid reductions;
- Poorly located vents that cause an accumulation of oxygen; and
• Using any components and lubricants that have not been approved for use with oxygen at the design conditions.

5.2.4 Incorrect operation and maintenance of oxygen equipment

Incorrect operation and maintenance of oxygen equipment is one of the most frequent causes of fires in oxygen systems.

Examples of incorrect operation include:

• Failing to reset pressure regulators to the closed position when the oxygen cylinder valve has been closed. This results in extremely high oxygen gas velocities when pressurising the regulator the next time it is used;

• Opening valves rapidly, which can result in momentarily high oxygen velocities, sufficient to project any debris present in the system through the system, at sonic velocity causing frictional heat or sparks;

• Opening a valve rapidly against a closed valve (or pressure regulator) downstream in a system can result in high heat being generated through adiabatic compression of the oxygen, causing a fire; and

• Starting an oxygen compressor erroneously with oxygen. This incorrect operation is only relevant to specific cases [5, 6].

Examples of incorrect maintenance include:

• Working on pressurised systems;

• Venting oxygen into restricted, enclosed, or confined spaces;

• Allowing systems to become contaminated. Contamination by particulate matter, dust, sand, oils, greases, or general atmospheric debris creates a potential fire hazard. Portable equipment is particularly susceptible to contamination and precautions shall be taken to prevent ingress of dirt or oil; and

• Failing to completely remove cleaning solvents from components that are to be used in oxygen service. The solvent residues are not compatible with an oxygen-enriched atmosphere.

5.2.5 Use of incorrect materials

The design of oxygen equipment is very complex and the “why and how” is not always obvious. In essence, nearly all materials are combustible in oxygen. Safe equipment for oxygen service is achieved by careful selection of suitable materials or a combination of materials and their use in a particular manner.

Any modifications to a design shall be authorised to prevent incompatible materials being used

Many incidents are reported where the cause was incompatible replacement parts. In many of the incidents, components were used because they looked similar to the original. Substituting materials that merely look similar is extremely dangerous. Examples of this practice include:

• Replacing O-rings and gaskets with similar looking items. There are hundreds of different types of elastomers and most are not compatible with oxygen;

• Replacing a metal alloy with a similar type of alloy. The composition of a particular alloys has a significant effect on their mechanical properties and oxygen compatibility. Bronze, which covers a wide range of alloys, has several varieties that are compatible with oxygen and even more
which are not. For example, tin bronze is used in liquid oxygen pumps while aluminium bronze is considered hazardous;

- Replacing polytetrafluoroethylene (PTFE) tape with a similar white tape. Not all white tape is PTFE and not all brands of PTFE tape are safe for use in oxygen. See EIGA Doc 138, *PTFE Used as a Sealant for Cylinder/Valve Connections* [7];

- Replacing parts/components with non-approved equipment. The geometry of certain components is sometimes critical and approved manufacturer’s parts shall always be used when maintaining oxygen equipment;

- Replacing or the installation of combustible material such as plastics, paper, or adhesives in filters. Filters in oxygen systems are very sensitive to ignition due to presence of particles and complicated flow conditions. Therefore, filters should be made of materials that demand very high ignition energy such as Monel®;

- Using lubricants that have not been approved for use with oxygen at the design conditions; or

- Using incorrect leak detection fluid. See EIGA Doc 78, *Leak Detection Fluids Cylinder Packages* [8].

Using hydrocarbon-based substances such as oils, grease, some soaps, lubricants, degreasers, and organic chemicals are particularly hazardous in oxygen-enriched atmospheres. They can react violently with oxygen causing fire or explosion. In general, hydrocarbon-based oil and grease shall never be used to lubricate equipment that will be in contact with oxygen or oxygen-enriched air. Special lubricants such as approved perfluorocarbon lubricants are available for use in oxygen-enriched atmospheres. Oxygen pressure gauges shall not be tested or calibrated in contact with oil.

5.3 Combustible material

5.3.1 In oxygen-enriched atmospheres

Materials that do not burn in air, including fire-resistant materials, can burn vigorously in oxygen-enriched air or pure oxygen.

In oxygen-enriched atmospheres, a common combustible material that most directly affects the safety of personnel is clothing. All clothing materials will burn fiercely in an oxygen-enriched atmosphere. The same applies to plastics and elastomers.

An example of this increased reactivity is shown in Figure 2, for cotton overall material exposed to fire in atmospheres containing increasing levels of oxygen [5].

![Figure 2 Reactivity for fire exposed cotton in increasing oxygen levels](image)
Similar curves indicating the same type of behaviour could be drawn for other materials, in particular for plastics and elastomers.

5.3.2 In pressurised oxygen systems

In principle, all organic materials will burn in oxygen and so do most metals and metal alloys. Pressure affects the behaviour of materials, for example, by reducing ignition temperatures and increasing combustion rates. It is for these reasons that pressurised oxygen systems are only allowed to be constructed from materials and equipment that have been designed and approved for the relevant operating conditions.

Oil and grease are particularly hazardous in the presence of oxygen as they can ignite extremely easily and burn with explosive violence. In oxygen equipment, oil and grease ignition often causes a chain reaction that finally results in metal burning or melting. In such cases, the molten or burned metal residue is projected away from the equipment and can be followed by an oxygen release. This in turn can lead to fierce and rapidly spreading flames in any adjacent combustible material external to the equipment. Hydrocarbon oil and grease shall never be used to lubricate equipment that will be in contact with oxygen, and any lubricants shall have been approved for the application.

Closed-circuit cooling systems are often filled with water containing up to 50% ethylene glycol or propylene glycol. Both ethylene glycol and propylene glycol are flammable and will concentrate if leaked into an oxygen system and the water evaporates. Although there is good industry experience with closed-circuit cooling systems using 50% glycol when these systems have all low points checked for leakage, incidents have occurred when leakage is undetected in the system.

5.4 Ignition sources

5.4.1 In oxygen-enriched atmospheres

Ignition sources in oxygen-enriched conditions include:

- open fires or open flames (such as cigarettes, welding or other hot work, petrol-fuelled engines, or furnaces);
- electronic cigarettes;
- electrical sparks; and
- grinding or frictional sparks.

5.4.2 In pressurised oxygen systems

In systems containing oxygen under pressure, the potential sources of ignition are not as obvious as open flames and hot surfaces.

The following ignition sources have caused fires in oxygen systems:

- heating by adiabatic compression;
- friction;
- mechanical impact;
- electrical sparks; or
- high gas velocity with presence of particles.
6  Prevention of fires in oxygen systems

6.1 Information/training

Any personnel using oxygen equipment shall be informed of the hazards, properties, and risks of oxygen. These are covered in the safety data sheet for oxygen.

For further information on the hazards of oxygen with materials, the following publications are also recommended:

- EIGA Doc 13, *Oxygen Pipeline and Piping Systems*, or CGA G-4.4, *Oxygen Pipeline and Piping Systems* [10];
- EIGA Doc 27, *Centrifugal Compressors for Oxygen Service* [11];
- EIGA Doc 33, *Cleaning of equipment for oxygen service. Guideline* [12];
- CGA G-4.1, *Cleaning Equipment for Oxygen Service* [13];
- EIGA Doc 42, *Flexible Connections in High Pressure Gas Systems* [14];
- EIGA Doc 136, *Selection of Personal Protective Equipment* [15];
- EIGA Safety Information 15, *Safety principles of high pressure oxygen systems* [17]; and

All maintenance and repair work shall be performed by trained and competent personnel.

All persons who work in areas where oxygen enrichment can occur shall be given instructions as to the risks involved. Emphasis shall be given to the nature of the risks and to the almost immediate consequences. Training shall be given as to how such risks can be minimised, stressing the importance of identifying sources of oxygen enrichment and their isolation.

For many applications in the medical field, oxygen and oxygen-enriched air are used for treatments in equipment such as oxygen tents, incubators, and hyperbaric chambers. This oxygen-enriched air presents a greatly increased fire hazard. Publications addressing this include NFPA 99, *Standard for Health Care Facilities*, EIGA Doc 89, *Medical Oxygen Systems for Homecare Supply* and ISO 15001: *Anaesthetic and respiratory equipment -- Compatibility with oxygen* [19, 20, 21].

6.2 Design

In oxygen systems only equipment that has been specifically designed for oxygen shall be used; for example, nitrogen regulators shall not be used in oxygen service. The design of equipment intended for oxygen service takes into account materials to be used and their configuration, in order to minimise any risk of ignition. The reasons for a particular design and choice of material are not always obvious and expert advice shall be sought before considering a change of materials.

Oxygen equipment shall only be lubricated with lubricants specific to the application and service. Specialist advice shall always be sought, for example from the supplier or test facility.

Oxygen systems shall be designed so that the flow velocity is as low as possible. If the velocity is doubled the energy of a particle in the gas stream will increase four times. See EIGA Doc 13 [10].
Oxygen systems should be positioned in well-ventilated areas away from primary ignition sources such as boilers. Liquid systems should be located away from cable trenches, drains, and ditches.

6.3 Prevention of oxygen enrichment

6.3.1 Leak testing

Newly assembled equipment for oxygen service shall be thoroughly leak checked using air or nitrogen either by a timed gas pressure drop test, a leak detection test with an approved leak spray, or other suitable methods. See EIGA Doc 78 [8].

Periodic retests to check for leaks are recommended.

6.3.2 Operation and practice

When the work period is over, the main oxygen supply valve shall be closed to avoid possible oxygen leakage while the equipment is not being used.

Filters, where fitted, shall not be removed to obtain higher flows. Filters should be inspected at frequent intervals and all debris removed.

Cutting and welding hoses shall be maintained leak-tight and periodically inspected.

Avoid delay in lighting welding or cutting torches after opening the valves, especially in confined spaces. When flame-cutting, five to ten times more oxygen is required for cutting than is required for heating, depending on the thickness of the plate being cut. This amount of oxygen is only partially consumed in burning the metal. It is important to select the correct size nozzle and the correct pressure for the work being performed to minimize the amount of excess oxygen.

6.3.3 Ventilation

Rooms where there is a risk of oxygen enrichment of the atmosphere shall be well ventilated. Examples of such rooms include:

- filling stations;
- rooms in which oxygen vessels or cylinders are stored, handled, or maintained;
- rooms in which oxygen is used or analysed; and
- rooms used for medical treatment with oxygen such as those in hospitals, home care, and other healthcare facilities.

In many cases, natural ventilation can be sufficient such as in halls or rooms provided with ventilation openings. The openings should have a flow area greater than 1/100 of the room’s floor area, be diagonally opposite each other, and shall ensure free air circulation with no obstructions. Where natural ventilation is not possible, a ventilation unit with a capacity of approximately 6 air changes/hour shall be provided. Consideration shall be given to the ventilation of underground rooms, vessels, pits, ducts, and trenches.

There shall be a safety warning to indicate if the ventilation unit fails.

6.3.4 Vessel entry/blanking procedures

Prior to entry into any vessel, which is connected to a gas source, the vessel shall be emptied and isolated from the source. Isolation can be accomplished, for example, by the removal of a section of pipe, by the use of a spectacle plate, by inserting blind flanges, or by double block and bleed valves. The space shall be thoroughly ventilated to maintain an atmosphere of no greater than 23.5% oxygen. Appropriate regulatory confined space entry procedures shall be followed.
6.3.5 Isolation equipment

When an oxygen pipeline enters a building, an isolation valve shall be provided outside the building in an accessible position for operation. This valve and location shall be clearly marked and identified. The purpose is to enable operation of the valve from a safe location, in the event of an oxygen release inside the building.

Disused oxygen lines should either be dismantled or completely severed and blanked off from the supply system.

6.4 Oxygen cleanliness

One of the fundamental safety procedures in preventing oxygen fires is to ensure that all equipment is cleaned before being put into or returned to oxygen service. There are several methods for cleaning oxygen equipment. See EIGA Doc. 33 or CGA G-4.1 for additional information [12, 13].

Oxygen equipment shall be free of solid particles. In order to remove particles, new oxygen equipment shall be purged with oil-free air or nitrogen before start-up.

6.5 Control of hot work

All hot work that has to be performed close to any oxygen equipment or in an area where oxygen enrichment could occur shall be controlled by a work permit. Hot work includes operations such as welding, brazing, drilling, and grinding.

7 Methods of oxygen detection

The method selected for oxygen detection shall offer a high degree of reliability of operation and be sufficiently sensitive to provide warning before a hazardous concentration of oxygen is reached. The usual method is to use an approved atmospheric monitoring instrument to confirm the effectiveness of the isolation and purging procedures before entry into the area and to periodically check during work to confirm that changes have not occurred.

If needed, oxygen measuring instruments should be used as warning devices only and should not be regarded as protection against the risks of oxygen enrichment. They should be seen as an addition to good practice of eliminating the causes of enrichment. Appropriate measuring instruments for the determination of oxygen content indicate an increase as well as a decrease of oxygen concentration in the ambient atmosphere.

Various measuring techniques and methods are used that give visible, audible, and/or tactile (vibration) warning, and they can be used for continuous or intermittent measurement. The manufacturer’s instructions for the use and maintenance of the measuring instruments shall be carefully followed.

8 Protection of personnel

8.1 Clothes

Protective work clothing alone is not sufficient to avoid danger from an oxygen fire. Many textile materials that claim to be non-flammable will burn fiercely in an oxygen-enriched environment.

In areas where flame-resistant clothing (FRC) is required, only flame resistant and natural fibre inner garments or underwear shall be worn. Other synthetic materials, even when worn as inner garments or underwear, can melt and stick to the skin when exposed to a fire (see EIGA Doc 136) [15]. Washing can reduce the effectiveness of some flame-resistant materials; therefore, it is recommended to follow the manufacturer’s guidelines when washing. In areas where FRC is not required, natural fibres are recognized as the best material for work clothes, because they quickly become extinguished when removed from an oxygen-enriched atmosphere to an ambient atmosphere.

Clothing should fit well yet be easy to remove and free from oil and grease.
Persons who have been exposed to an oxygen-enriched atmosphere shall not smoke or go near open flames, hot spots or sparks until they have properly ventilated their clothes in a normal atmosphere. A ventilation period of not less than 15 minutes with movement of the arms and legs and with coats removed is recommended.

8.2 Analysis

Before persons enter a space which can be subject to oxygen enrichment, the atmosphere shall be analysed for oxygen by a reliable and accurate analyser (see Section 7). Entry shall not be allowed if the oxygen concentration is greater than 23.5%. An oxygen concentration greater than 23.5% is potentially dangerous. As a warning against possible variations in concentration, the space should be monitored with a continuous automatic oxygen analyser that sounds an audible, visual, and/or tactile (vibration) alarm when the oxygen concentration in the atmosphere could exceed 23.5% or be less than 19.5%.

8.3 Firefighting equipment

The only effective way of dealing with oxygen-fed fires is to isolate the supply of oxygen. Under oxygen-rich conditions, appropriate firefighting media include water, dry chemical (powder), or carbon dioxide. The selection needs to take into account the nature of the fire, for example, electrical. Burning clothing shall be extinguished by water as covering the clothing with a fire blanket will still allow oxygen-enriched clothing to burn.

Firefighting equipment shall be properly maintained and operating personnel should know where it is located, how to operate it, and which equipment to use for which type of fire.

8.4 Smoking

All personnel shall be informed of the dangers of smoking when working with oxygen or in an area where oxygen enrichment can occur. Many accidental fires and burn injuries have been initiated by the lighting of a cigarette; it is therefore imperative to emphasise the danger of smoking in oxygen-enriched atmospheres or where oxygen enrichment can occur. In such areas, smoking shall be prohibited.

8.5 Emergency response and rescue

The location’s emergency response procedures should contain provisions for entry into potentially oxygen-enriched areas. Victim rescue or entry to shut down the process shall not be attempted until levels of oxygen-enriched gases are determined to be less than 23.5% oxygen and it is safe to enter. Clothing materials including flame-resistant or treated materials can be susceptible to burning in an oxygen-enriched atmosphere. Emergency procedures may include the use of water spray to protect potential victims if it can be done from a safe distance until safe-entry verification can be made.

Effective emergency procedures provide for identifying where oxygen enrichment is a risk, as well as training personnel, conducting drills, and providing readily accessible emergency contact numbers for fire and medical response.

If a major release of liquid or gaseous oxygen-rich gases occurs, all electrical appliances and lighting systems in the affected area are potential sources for a spark and ignition can occur. The source of the oxygen-rich gases shall be shut off as soon as possible. Experience has shown that if liquid oxygen-rich gases are released in an open space, a hazardous oxygen concentration usually exists within the visible fog cloud associated with the spill. Personnel should never enter a visible fog cloud. A hazardous oxygen concentration can exist outside the cloud. A portable oxygen analyser should be used before entering the area near a release.

9 Summary of recommendations

The key points to avoid incidents due to oxygen enrichment are summarised as follows:

- Ensure that people who are expected to work with oxygen are properly trained and informed of the risks caused by an excess of oxygen;
• Ensure that proper equipment is used, that it is leak-tight, and that it is in good operational order;
• Use only materials and equipment approved for use in oxygen service. Never use replacement parts, which have not been specifically approved for oxygen service;
• Use suitable clean clothing, free from oil, grease, and easily combustible contaminants;
• Never use oil or grease to lubricate oxygen equipment;
• Ensure that all existing firefighting equipment is in good condition and ready to be used;
• When working in confined spaces where oxygen is normally used, isolate the equipment, provide good ventilation, and use an oxygen analyser. Entry shall only be allowed by means of a permit issued by a trained, competent person;
• Prohibit smoking where there is any possible risk of oxygen enrichment;
• People catching fire in oxygen-enriched atmospheres cannot be rescued by a person entering the area to pull them out, as the rescuer will almost certainly also catch fire;
• People who have been exposed to oxygen-enriched atmospheres shall not be allowed to approach open flames, burning cigarettes, etc., until after adequate ventilation of their clothing;
• Ensure that all oxygen apparatus and equipment is appropriately identified; and
• Ensure that escape routes are kept clear at all times.

10 References

Unless otherwise specified, the latest edition shall apply.


NOTE—This publication is part of an international program for industry standards. The technical content of each regional document is identical, except for regional regulatory requirements. See the referenced document preface for a list of harmonized regional references.


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11 Additional references

   BCGA TR2, *The probability of fatality in oxygen enriched atmospheres due to spillage of liquid oxygen*, www.bcgaco.uk

   BCGA TR1, *A method for estimating the offsite risks from bulk storage of liquefied oxygen*, www.bcgaco.uk

   EIGA Doc 911, *Odorisation of oxygen in combustion applications*, www.eiga.eu
Properties of oxygen
Oxygen supports combustion

- Oxygen is essential to life. The normal concentration in the atmosphere is approximately 21%.
- It is not flammable but supports combustion. Most materials burn fiercely sometimes explosively in oxygen. As the oxygen concentration in air increases, the potential fire risk increases.
Properties of oxygen
Oxygen gives no warning

- Because oxygen is colourless, odourless and has no taste, oxygen enrichment cannot be detected by the normal human senses.
Properties of oxygen
Oxygen is heavier than air

• Oxygen can accumulate in low lying areas such as pits or underground rooms, especially during or after a liquid spill, as it is heavier than air.
Conditions needed for a fire

In general, for a fire or explosion to occur, 3 elements are required: combustible material, oxygen, and an ignition source.

The fire triangle is the normal way of illustrating these conditions.

When any one of the 3 elements is missing, a fire cannot occur.
Causes of oxygen fires

- Oxygen enrichment of the atmosphere
- Improper use of oxygen
- Incorrect design of oxygen systems
- Incorrect operation and maintenance of oxygen systems
- Use of materials incompatible with oxygen service
Compatibility of materials

• Only certain materials are suitable for use in oxygen service.
• Most materials will burn in pure oxygen, even if they cannot be ignited in air.
• Oils, grease, and materials contaminated with these substances are particularly hazardous in the presence of oxygen, as they can ignite extremely easily and burn with explosive violence.
Never use oil or grease to lubricate oxygen equipment!

- Equipment contaminated with oil and grease shall be cleaned using approved cleaning agents/methods.

- Check with your supervisor that any material/part or substance you intend to use is approved for oxygen service.
Leaking equipment is very dangerous

- It could lead to oxygen enrichment, for example, increased fire hazard.
- Leaking connections, flanges, fittings are hazardous causing the oxygen concentration to increase especially where there is not sufficient ventilation.
- Leak test newly assembled equipment or following
Liquid oxygen spill

- A spill of liquid oxygen creates a dense cloud of oxygen-enriched air as it evaporates.
- The clothing of personnel entering the cloud will become enriched with oxygen.
- When liquid oxygen impregnates ground that contains organic material such as wood or asphalt, there is a danger that the organic material will explode if impacted.
Do not use oxygen for applications for which it is not intended!

Do not use oxygen as a substitute for air, such as when:

- operating pneumatic tools;
- inflating tyres;
- starting diesel engines;
- dusting benches, machinery, or clothing,
In areas where oxygen enrichment can occur, do not smoke and do not use naked flames. If hot work such as welding, flame cutting, soldering, or grinding has to be carried out, ensure that the atmosphere has been checked and confirmed as safe and obtain a work permit.
If you have been in an oxygen-enriched atmosphere, ventilate your clothing in the open air for at least 15 minutes before smoking or going near a source of ignition.
APPENDIX B—Examples of the hazards of oxygen and oxygen-enriched atmospheres

B1 Examples of oxygen enrichment incidents

1. At a factory, a valve on an oxygen feed line which ran into the plant shop was left open. A man’s clothing ignited when contacted by electric welding sparks. He ran out and rolled on the grass but was seriously burnt. Several others who assisted were slightly burnt.

2. A worker attempted to change a blowpipe by nipping the oxygen hose. Escaping oxygen caused a fire that resulted in serious burns to the worker.

3. Men were working on the roof of an oxygen factory near a main oxygen vent which was operating. One man began to smoke, his clothing ignited and he was burned to death.

4. A contractor employee had to grind away a piece of railing on a platform at the air separation column. A work permit had been issued and a pre-job discussion had been held. The ambient temperatures were low and, while waiting for a colleague, the employee leaned over and partially sat down on an oxygen vent warming himself on the escaping relatively warm oxygen leaking through the valve. The moment he started grinding, a spark set his oxygen-saturated clothing alight, causing second and third degree burns on his body, resulting in months of hospital treatment.

5. When using an oxygen lance in a steel foundry, an operator realised that the coupling between the hose and the lance was leaking, but did not stop the leak because it provided some cooling on his stomach. A spark of hot metal was projected towards the operator and ignited the oxygen-saturated clothing at his stomach, resulting in serious burns.

6. Oxygen was vented from a PVSA plant at a customer. The location of the vent outlet caused an oxygen-enriched atmosphere. The work clothing of a maintenance contractor caught fire during a grinding operation, causing burn injuries.

7. At a gas company site in a cryogenic air separation plant production area, a steam pipeline was being welded in a pit. The pit was enriched with oxygen so that the clothing of the fitter caught fire and he subsequently died. The welder sustained burns trying to extinguish the fire. A work permit was in place but not followed and risks were not identified.

8. When internally inspecting an oxygen cylinder, a lamp broke which ignited a flammable gas or material in the cylinder. The operator suffered burn injuries.

9. A patient was smoking a cigarette whilst receiving oxygen therapy through a nasal cannula and oxygen from an oxygen concentrator in his home. The cigarette caused an ignition of the nasal cannula and subsequent burning of the plastic caused small scale scalding of the upper respiratory tract. The patient was seen by a medical practitioner and returned home soon afterwards. Contact with the patient led to an admission that he had been smoking against warnings, instructions, and training.

10. A patient was using an oxygen concentrator at home. Patient’s daughter reported that her mother had lit a cigarette and the cannula and tubing ignited, burning her nose. Cannula had adhered to her nose. Patient taken to hospital via ambulance.

11. A worker in the maintenance shop of a filling station was grinding when his clothing caught fire and he was seriously injured. The worker had brought an oxygen bundle inside to make it possible to check a leak with detection fluid as it was cold outside. After the leak check, he vented the bundle inside the workshop which was against instructions.

12. A local fire officer advised that a patient supplied by an EIGA member company had been victim of a fatality in fire at home. The first elements of investigation suggested that he might have been smoking while having oxygen.
13. A homecare (oxygen concentrator) patient fell asleep with a burning cigarette that ignited the bedding.

14. A driver was driving a homecare liquid and gas oxygen delivery van. He tried to light a cigarette, which was consumed instantly. Incandescent ashes transmitted the fire to the cabin. The driver stopped and tried in vain to extinguish fire which spread quickly to the whole vehicle. A few minutes later, a small aluminium oxygen cylinder exploded and the pin-index valves of two other cylinder valves were ejected.

15. A person who was wearing proper clothing was working in an oxygen-enriched atmosphere. He went to a smoking area and immediately lit a cigarette, whereupon his clothing ignited.

16. Several instances have been reported of deaths in hyperbaric chambers due to smoking or electrostatic sparking under enriched oxygen conditions. In one case, 10 people were killed when a fire broke out caused by the use of a portable hand warmer.

**B2 Examples of improper use of oxygen**

1. An air powered rotary drill was connected by means of an adapter to an oxygen line. After several hours, the air in the working compartment had become so enriched with oxygen that when one of the workers lit a cigarette it flared up and ignited clothing, which resulted in four fatalities and five others being injured.

2. A welder was working in a tank car. After a while, he interrupted his work in order to renew the air in the tank by introducing oxygen. When he resumed welding, a spark ignited his clothing. The worker succumbed to fatal burns.

3. A steelworker attempted to repair his car, which had a blockage in the fuel line. He used oxygen to clear the blockage and the fuel tank exploded killing one person.

**B3 Examples of incorrect design of oxygen system**

1. A temporary filling panel with ball valves, which is against the standard procedure, was used for the filling of oxygen mixtures. The ball valve ignited due to adiabatic compression and the operator was injured.

2. An oxygen pressure regulator burnt out. Only use pressure regulators with a metal membrane designed to a recognized standard.

3. When the oxygen cylinder back-up system at a hospital switched on due to low liquid oxygen (LOX) tank contents, an ignition of a polychlorotrifluoroethylene valve seat occurred and the patients were exposed to the products of the combustion. The valve did not have the correct seat for the oxygen application.

4. A weak design of the lower spindle of an oxygen cylinder valve caused an ignition after the cylinder had been filled to 200 bar.

5. A customer station installation team and some customer employees were severely burned during the commissioning of an oxygen supply installation. The oxygen supply installation was set up to provide an oxygen backup supply during the maintenance shutdown of the customer owned and operated oxygen PSA units. The oxygen supply system was designed, engineered, and constructed by the local merchant customer station installation team without an appropriate engineering design review. During commissioning, there were four employees and six customer's employees standing around the oxygen supply system, as the intention was to carry out the customer training during the commissioning process. The release was caused by particles travelling at high velocity through the piping and impinging onto a stainless-steel mesh in a "Y" type strainer. The resultant fire burned through the piping and control valve downstream of the strainer and, as a result, eight people were severely injured.
6. A defect weld in a LOX pump caused a fatigue crack, LOX leakage, and an ignition of the pump. The pump manufacturer subsequently informed all customers about this pump type and recommended improvements.

7. While making a delivery of liquid oxygen, the driver noticed a glow in the enclosure for the hydraulic pump drive compartment caused by wear and failure of a rubber seal due to misalignment of the pump drive. There was a failure to design a location spigot required to assist alignment.

8. A 50 m³ LOX tank was to be emptied but the connection to the ejector failed. It was incorrectly decided to use the stone pit instead and slowly empty the tank. After 5 tonnes had been emptied, an explosion was heard and a fire was seen close to the pit. A review of the design of new and in-operations stone pits is recommended.

9. A 150-bar cylinder of 1% nitrogen in oxygen connected to an analyser with a stainless-steel needle valve resulted in an oxygen combustion. The laboratory official stance on the valve seat material is unsuitable for extended use in oxygen and should be replaced.

**B4 Examples of incorrect operation and maintenance of oxygen equipment**

1. A worker was welding on the outside of an oxygen pipeline. Before starting the work, the welder isolated the pipeline by closing the valve, purging the pipeline, and checking the atmosphere. Suddenly the welder was engulfed in flames and subsequently died of his burns. The valve was later found to be leaking, which allowed oxygen to enter the isolated pipeline.

2. A mechanical failure of the turbo oxygen compressor caused rubbing and high local temperature, which resulted in a total burn of the oxygen compressor. The compressor was installed in an enclosure that was damaged but prevented damage or injuries outside the enclosure.

3. At a customer site a regulator burned out when an operator opened the valve of a 300-bar bundle filled with 280 bar residual oxygen. Due to the incorrect procedure to not shut the regulator before opening, the sudden oxygen gas stream caused a burn-out of the regulator and of the hose at the low pressure side. One employee suffered minor burns on a hand and his face.

4. A flash fire on the switchboard of a filling ramp occurred when starting to fill oxygen cylinders.

5. In a filling station, the valve of an oxygen cylinder burned out during a pressure equalization procedure. The cause was iron powder inside the valve and cylinder that ignited. The filling connector also burned out. The operator suffered burns at hand and forehand.

6. A person suffered serious burn injuries caused by an oxygen fire, which was caused by a modification done at the regulator by the customer.

7. The connector of a check valve in the high pressure oxygen line caught fire. The Viton O-ring in a radial groove was leaking.

8. Fire on the lubrication system of an oxygen compressor resulted in equipment damage.

9. After the filling of oxygen cylinders was completed and the cylinder valves closed, the operator opened the vent valve. The vent valve ignited, probably due to remaining particles after recent maintenance

10. After completing the filling of oxygen cylinders, the operator closed all but one of the RPV cylinder valves. When opening the vent valve, the adaptor connected to the open cylinder valve ignited.

11. The third stage of an oxygen piston compressor, which was manufactured in 1976, ignited. The compressor cover and emergency shutdown worked very effectively protecting the surroundings.

12. An operator heard a noise at the end of filling 5-liter 200 bar cylinders. When he approached the cylinders, there was a sudden flash fire from the top of one of the cylinders, probably due to a damaged O-ring.
13. A LOX semitrailer turned over. The tank was emptied. When it was connected to the truck an explosion occurred, killing three persons. Some diesel oil had leaked on the road and the safety valve, directed downwards, was venting GOX. When a wire was thrown under the trailer, the oil/oxygen mixture exploded.

14. A liquid oxygen high pressure pump caught fire, probably due to a leakage of cold liquid into the crankcase. The crankcase ruptured and an operator was hit on the finger by a piece of metal.

15. A LOX pump ignited during transfer of LOX due to excessive speed, 7200 rpm instead of the permitted 6800 rpm. Only the pump and transmission sustained damage.

16. An ignition had occurred at some point in the sensor of a LOX flow meter. Possible causes were poor cleaning for oxygen service at commissioning or dry-boiling that lead to the build-up of hydrocarbons over a long period.

17. A LOX tank at a cylinder filling station was going to be emptied for maintenance by applying the usual cylinder filling procedure. Suddenly, the pump ignited due to dry running. The dry running protection system was not correctly designed.

18. A LOX pump caught fire during its normal operation. The pump had been running dry for a period of time without being detected by the safety devices.

19. While supplying liquid oxygen at a customer's premises, the driver noticed smoke in the pump cabinet. Electric arcing inside the power plug of the pump had burned away the insulation of the wires. The extra insulation used in these cases had not been provided for the affected pump.

20. Following a LOX leak when unloading a LOX trailer at a hospital facility, the trailer caught fire. The patients were evacuated.

B5 Examples of use of incorrect materials with oxygen service

1. A safety valve on a gaseous oxygen supply line was greased during repair. When the safety valve was later checked under oxygen pressure, the grease ignited and the operator was badly injured.

2. When checking the pressure of oxygen cylinders, a worker used a pressure gauge filled with glycerine, which not suitable for oxygen service. When opening the valve, the pressure gauge exploded, resulting in nearly total blindness of the worker.

3. A fitter lost the PTFE gasket of his oxygen regulator. Arriving at the place where he had to do a repair, he made a rubber gasket from a car inner tube and connected the regulator to the cylinder valve outlet. When he opened the cylinder, due to the use of a non-compatible gasket, a flash fire occurred that burned his upper arm and shoulder.

4. An ambulance was completely destroyed because of a fire in the regulator of an oxygen cylinder. Probable cause was a non-compatible seal (rubber) in the regulator.

5. When opening the valve of an oxygen cylinder bundle, the connected high pressure flexible hose, which was made from rubber or plastic, ignited and burned.

6. A safety valve in an oxygen filling station burned out when the filling pump was switched on. The cause was an operation fault and perhaps incompatibility of the safety valve with oxygen. The installation and the type of safety valve were changed.