



# CRYO-STORAGE AND TECHNOLOGIES (CST)

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## SafetyAlert-33

### The Hazards of Oxygen and Oxygen-Enriched Mixtures

Most people who use pure oxygen are aware of the hazards of and special precautions for handling this material. Unfortunately, fewer are aware that these hazards extend to oxygen mixtures. This SafetyAlert reviews how to distinguish between the various mixtures of oxygen, the hazards of pure oxygen and oxygen mixtures, and how to safely handle these products. The SafetyAlert concentrates on mixtures above 23% oxygen and pure oxygen because operationally they should be treated with the same precautions and requirements.

#### Oxygen Mixture Classifications

The following information is based upon U.S. Compressed Gas Association (CGA) and ASTM International documentation, but the principles are repeated in other documents from the European Industrial Gas Association (EIGA) and the International Standards Organization (ISO).

The CGA defines oxygen-enriched mixtures or atmospheres as any mixture or atmosphere containing greater than 23% oxygen, since above this concentration, the reactivity of oxygen significantly increases the risk of ignition and fire. Materials that may not burn in normal air may burn vigorously in an oxygen-rich environment. Sparks normally regarded as harmless may cause fires. And materials that burn in normal air may burn with a much hotter flame and propagate at a much greater speed.

The CGA breaks oxygen and its mixtures into four distinct classifications:

- Mixtures containing less than 5% oxygen in an inert: These mixtures are packaged and labeled in the same manner as inert gases like nitrogen and argon. They use the same 580 valve connections and are labeled with a nonflammable gas hazard diamond. These mixtures are considered inert.
- Mixtures in the range 5 to 23% oxygen: These mixtures carry the same nonflammable gas hazard diamond as inerts, but are packaged with a 590 valve connection. This is intended to differentiate these mixtures from the inerts as they will support combustion but not enhance the danger of ignition beyond that of normal air.

- Mixtures containing greater than 23% oxygen: These mixtures must be handled with all the precautions and care of pure oxygen. Mixtures at these levels start to change fire chemistry and enhance combustion similar to oxygen. They carry an oxidizer hazard diamond in addition to the nonflammable gas diamond and are equipped with a 296 valve connection to distinguish them from the less reactive mixtures of oxygen. These mixtures may be ppm level components in otherwise pure oxygen, for example, 8 ppm methane in oxygen.
- Pure oxygen: This material has its own dedicated 540 valve connection and an oxidizer hazard diamond.

These classifications are condensed to three when dealing with materials of extreme purity that are equipped with ultrahigh leak integrity DISS valve connections. Oxygen mixtures using the DISS connections no longer differentiate between oxygen mixes that support combustion and mixes that enhance combustion:

- Concentrations of less than 5% oxygen use the 718 valve connection as used for inerts;
- All mixtures of 5% and greater use the 712 connection; and
- Pure oxygen uses a 714 valve connection.

This classification requires extra vigilance in identifying the hazards of the mixtures.

There are other valve connection standards in use that may or may not distinguish between the various concentrations of oxygen. Therefore, labels must be relied upon to identify these mixtures because they may not be protected from interconnection.

#### Hazards of Oxygen and Mixtures

One of the challenges in educating people about the dangers associated with oxygen is their perception of the product. When most people think about oxygen, medical applications come to mind. Doctors, dentists, nurses, paramedics, and first aid teams administer oxygen to people when they are sick or injured. These professionals would not allow



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us to intentionally inhale a hazardous material. This perception can downplay or at least minimize respect for the hazards of oxygen. But let's look at oxygen from a different perspective.

Oxygen and its mixtures are packaged as compressed gases. They are supplied at pressures up to 4500 psig (300 bar). Pressure is stored energy, and if this pressure is released in an uncontrolled manner, the resulting energy release can cause great damage or injury. This could occur if a cylinder is being handled without a protective valve cap and dropped. If the valve is struck hard enough, it could shear and the escaping pressure could propel the cylinders, like a rocket. For more information on the proper handling of compressed gas cylinders, refer to CST Safety-Alert-10, "Handling, Storage, and Use of Compressed Gas Cylinders." For more information on the consequences of shearing a cylinder valve, refer to CST SafetyAlert-14, "Don't Turn a Cylinder Into a Rocket." All compressed gas cylinders demand proper handling and respect because of the tremendous energy stored within them.

Oxidizers carry additional hazards. To fully understand these hazards, we must first understand some of the terms used.

- **Adiabatic Heat:** A process in which there is no gain of heat to or from the system. With respect to this document, it is the heat picked up by the gaseous oxygen from the rapid pressurization of a system.
- **Autoignition Temperature:** The lowest temperature required to ignite or cause self-sustained combustion in the presence of air and in the absence of a flame or spark.

- **Flammable Range:** The range of concentration in volume percent of flammable gas or vapor between the upper and lower flammability limits.
- **Kindling Chain:** The promotion of ignition from materials of low ignition temperatures to materials of higher ignition temperatures.
- **Limiting Oxygen Concentration:** The minimum oxygen concentration in volume percent (at a given temperature) in a gaseous mixture containing a fuel below, which a flame will not propagate.
- **Lower Flammability Limit:** The minimum fuel mixture in volume percent with air through which a flame will just propagate.
- **Upper Flammability Limit:** The maximum fuel mixture in volume percent with air at which a flame will just propagate.

When oxygen concentrations exceed 23%, oxygen enrichment begins and fire chemistry starts to change. Materials become easier to ignite because their flammable ranges start to expand and their autoignition temperatures begin to drop. This includes the materials of construction used in oxidizer systems, such as metals. This reactivity continues to increase not only with the concentration of oxygen, but also with pressure and/or temperature. In other words, oxygen contacting a material at 2000 psig is more likely to react with the material than at atmospheric pressure. In the case of a contaminant in a system, the contaminant may react and generate enough heat to start another material reacting. This is called the kindling chain. When temperature increases, it can lower the amount of energy required to initiate a reaction.

Let's look at the basic fire triangle. All three legs of the triangle must be present to produce a fire—a fuel, an oxidizer, and an ignition source. If asked to name some fuels, materials like wood, coal, oil, and gas would be mentioned. But would anyone list materials like aluminum, steel, stainless steel? What is the primary

reason we can light a piece of wood with a match but not a steel rod? The ignition temperature of the wood is much lower than that of the steel rod and the heat from the match is sufficient for ignition. Remember what we said about fire chemistry and oxygen—as the oxygen concentration increases, the autoignition temperature decreases. So materials that cannot be ignited in normal air may burn readily in oxygen-enriched atmospheres. With this in mind, it is easy to see that in an oxidizer system we have two legs of the fire triangle present. All that is required for an ignition is an energy source.

Now let's consider ignition sources. Typical sources of ignition would be fire, open flames, sparks, or cigarettes. But that is in the world of normal air, not oxygen-enriched atmospheres. Remember the definition of autoignition temperature—the lowest temperature required to ignite a material in the absence of a flame or spark. Could gas velocity, friction, adiabatic heat, or contamination provide ignition sources? Yes.

In the case of gas velocity, it is not the flow of gas that can cause ignition, but a particle that has been propelled by the gas and impacts the system with sufficient force to ignite. The heat generated may be sufficient to start a fire depending on the material impacted. Friction from a component malfunctioning or operating poorly can generate heat. Friction between two materials generates fine particles, which may ignite from the heat generated.

Adiabatic heat is sometimes confused with the heat of compression. The heat of compression causes the temperature of a system to rise. An example would be a tire pump. The barrel or compression chamber builds heat as the pump compresses air. This process occurs relatively slowly and the system takes on the heat. Adiabatic heat is caused by the rapid pressurization of a system where the gas absorbs the energy and the gas temperature rises. This heating occurs at the point of compression or the point where the flow of gas is stopped, such as at a valve or regulator seat. Depending on the material in use where the hot gas impinges, the heat may be sufficient to ignite the material.

All of these energy sources can be enhanced by the presence of a contaminant. Contaminants are typically easier to ignite than the components of the system. If they react with the oxygen, they may

generate sufficient heat to propagate a reaction to the system. Or as in the case of the pipe in Figure 1, they may react so strongly as to compromise the system.



**Figure 1**

Figure 1 depicts a section of an oxygen pipeline that ruptured. Here's how this happened. The oxygen supply line at an installation needed to be extended an additional 150 feet (45.7 meters). The line was degreased, but shop air was used to clean the line rather than clean, dry nitrogen. Most shop air is compressed with a hydrocarbon compressor and, in this case, the compressor did not have a clean-up system to remove any trapped oil. When the line was purged, a thin film of hydrocarbon oil coated the interior of the pipe. The pipe was put into service and the operation went smoothly until at the end of the shift when a valve at the downstream end was closed. This stopped the flow and the oxygen heated as it compressed against the valve seat. The compression provided enough energy to react with the hydrocarbon oil and a deflagration occurred. The speed of the pressure wave was such that it duplicated the line rupture, as depicted in Figure 1, every 15 feet (4.57 meters). This is a very good example of how materials that burn in normal air can react in oxygen.

It is critical to keep nontypical ignition sources in mind when designing systems for oxygen use. Some applications are very vulnerable to ignition. For

example, the elastomers used in valves and regulator seats have lower ignition energies than metals. Since particle impingement or adiabatic heat can be directed at these valves and regulators, they are particularly susceptible to ignition.

Let's take a look at a carbon steel pipeline used to provide oxygen to a customer. Because most of these pipelines have large diameters, economy and availability make carbon steel the material of choice. Carbon steel is an excellent fuel when used in oxygen service. In fact, due to the operating pressure, the pipelines contain a flammable mixture. To prevent fires in these pipelines, ignition sources must be considered. Since these lines are underground, external sources are usually not a problem. However, carbon steel is prone to rust, which can generate particles. If a particle is picked up in the flow of oxygen, the particle may impinge on part of the system. If the impingement generates sufficient heat, it may provide a source of ignition energy. Carbon steel pipelines in oxygen service must be designed and operated to minimize the potential hazard. This is accomplished by following the gas velocity limitations set forth in CGA Pamphlet G-4.4. By limiting the velocity, the particle impact energy is reduced, which minimizes the chance of an ignition.

The above examples show how contamination can enhance the potential for a reaction. It must be stressed that systems must not only be cleaned to oxidizer service requirements on initial construction but must be maintained in that condition of cleanliness. Contamination of materials like hydrocarbons or contaminants that may be in the form of particles can initiate a system fire.

These are potential problems in oxidizer systems, but what happens when oxygen enters the atmosphere? If oxygen leaks or escapes into the air as part of a normal process, oxygen-enrichment may occur if the ventilation is insufficient. If the surrounding air becomes oxygen-enriched, the same changes in fire chemistry take place.

In other words, materials which become easier to ignite because their autoignition temperatures begin to decrease and their flammability ranges increase. Remember that materials which do not ordinarily burn in air may ignite, and materials that do burn in air will burn hotter and faster. Most areas where enrichment is known to be a possibility are posted with signs warning about smoking or open flames. The real danger is if oxygen enrichment occurs and people carry the hazard with them when leaving the area.

Clothes can trap and hold the oxygen-enriched atmosphere in the countless air spaces within the weave of the fabric. Hair poses the same problem. If someone comes in contact with an enriched atmosphere, it is extremely important to isolate the person from any source of ignition for at least 30 minutes. Get him/her to fresh air, pat the person's clothing, and run fingers through his/her hair. Think about how easily cloth and hair burns in air and then try to imagine how they would burn in an oxygen-enriched environment.



**Figure 2**

Figure 2 shows a normal cotton work shirt stuffed with paper and saturated with oxygen. Inside the shirt is a flash bulb with the glass removed exposing the magnesium wool. This bulb is connected to a battery to provide ignition. The results of the ignition are shown in Figure 3.



**Figure 3**

People must be aware of the hazards of oxygen enrichment, since oxygen is not detectable by human senses. It is colorless, odorless, tasteless, and non-irritating. Likewise, people must be aware where oxygen enrichment is possible, such as at a vent, a leak, or failure of a ventilation system. Sometimes people intentionally saturate themselves with oxygen without recognizing the danger. Think about the person who may use the flow of oxygen from an oxy-acetylene torch to blow off dirt or to cool down.

### Safe Handling of Oxygen and Mixtures

It is important that all personnel handling oxygen and its mixtures be aware of its hazards and trained in the use of proper procedures and personal protective equipment. The MSDS is the primary source of hazard data. All personnel handling a material should be thoroughly familiar with the MSDS, including personal protective equipment recommendations.

As mentioned earlier, oxygen mixtures are classified, labeled, and valved differently. The primary method of product identification is the label. Mixtures with oxidizing potential will have a yellow oxidizer hazard class diamond in addition to the green nonflammable gas diamond. Do not let the

presence of the green nonflammable label lessen the warning of the oxidizer hazard.

The valve connections provided may prevent the possible connection of an incompatible material, but they must not be relied upon for identification of the mix. If the mixture label and valve connection do not comply with the above-mentioned classifications, DO NOT use the cylinder until consulting with the supplier. NEVER use adapters or change connections to accommodate the connection of a cylinder to a system. If a cylinder does not connect easily, do not force. Put the cylinder aside, label as to the problem, and contact the supplier.

From an operating perspective, areas of possible oxygen enrichment must be identified and plans implemented to address these potential hazards. These plans should consider safety systems including but not limited to training, signage, monitoring, and ventilation. Systems using mixtures of oxygen 5% and greater at high pressure (greater than 450 psig/30 bar) should be cleaned for oxygen service. Most compressed air systems use compressors that are hydrocarbon-lubricated. However, the pressures at which they operate do not pose reaction problems and cleaning these systems is not practical because they are self-contaminating from the compressor oil. However, materials of construction and system design requirements for enriched oxygen concentrations must go beyond cleaning.

Plant systems must be designed with the special considerations required for the safe handling of oxygen. There are several documents available to help design systems and equipment for the safe handling of oxygen. They include but are not limited to Compressed Gas Association Pamphlet G-4.4, "Industrial Practices for Gaseous Oxygen Transmission and Distribution Piping Systems," and the ASTM International Standard G-88, "Designing Systems for Oxygen Service." The European Industrial Gas Association and the International Standards Organizations also publish related documents including IGC Doc 13/02/E, "Oxygen Pipeline Systems."

Designing and building these systems requires an intimate knowledge of oxygen and how it reacts with the materials it contacts. Basic design considerations include but are not limited to control and avoidance of unnecessarily high temperatures and pressures, cleanliness, elimination of particles, minimization of heat of compression, avoidance of friction and galling, minimization of resonance with direct flow paths, use of hardware that has a proven history in oxygen service, minimizing available fuel and oxygen through materials selection and system volume, anticipation of indirect oxygen exposure from system failures, and design of systems to manage fires, using techniques such as fire stops and automatic extinguisher systems. The first step in constructing any system for oxygen should be to consult your supplier.

#### Information Sources

- Compressed Gas Association  
1725 Jefferson Davis Highway, Suite 1004  
Arlington, VA 22202-4102  
Phone: 1-703-412-0900
- National Fire Protection Association  
1 Batterymarch Park, P.O. Box 9101  
Quincy, MA 02269-9101  
Phone: 1-800-344-3555

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**USA**

**CHEMTRAC**

1-800-424-9300 (Toll Free in the U.S., Canada, and U.S. Virgin Islands)  
703-527-3887 for calls originating elsewhere (Collect calls are accepted)

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352-323-3500 for calls originating elsewhere (Collect calls are accepted)

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