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Space systems — Oxygen safety —

Part 3:
Selection of non-metallic materials for oxygen systems and components

Systèmes spatiaux — Sécurité des systèmes d'oxygène —

Partie 3: Sélection des matériaux non métalliques pour les systèmes d'oxygène et leurs composants

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 22538-3 was prepared by Technical Committee ISO/TC 20, *Aircraft and space vehicles*, Subcommittee SC 14, *Space systems and operations*.

ISO 22538 consists of the following parts, under the general title *Space systems — Oxygen safety*:

— *Part 1: Design of oxygen systems and components*

— *Part 2: Selection of metallic materials for oxygen systems and components*

— *Part 3: Selection of non-metallic materials for oxygen systems and components*

— *Part 4: Hazards analyses for oxygen systems and components*

The following parts are under preparation:

— *Part 5: Operational and emergency procedures*

— *Part 6: Facility planning and implementation*

Introduction

Polymers, although used extensively, are flammable in oxygen. The ignitability of polymers varies considerably, but the risk associated with the flammability of polymers can be minimized through proper selection combined with proper design. When selecting polymers for high-pressure oxygen systems, the susceptibility to ignition of the polymer and the possible ignition sources in the system are given equal consideration with the structural requirements.

The most common cause of ignition of polymeric materials in high-pressure systems is probably adiabatic compression heating of oxygen in the system by rapid pressurization. For this reason, it is important that oxygen systems containing polymers be pressurized slowly. Mechanical impact is rarely a credible ignition source in high-pressure oxygen systems because the level of mechanical impact to which polymeric materials are now exposed is normally well below the energies required for reaction. However, mechanical valve actuation, which has been largely eliminated from current designs, can cause impact loading of valve seats or other detail parts resulting in failure of the parts or mechanically induced ignition of polymeric materials.

Other mechanisms for ignition of non-metallic materials are considered although test data may not exist. Ignition of polymeric materials by impact of metallic and non-metallic particulate is probably feasible, although no conclusive studies have been conducted. Ignition of polymeric materials by burning contaminants has not been studied experimentally, but the use of incompatible oils and greases (especially hydrocarbon greases) is one of the most common causes of oxygen-system fires. Improper component design or installation can result in extrusion of polymeric materials with insufficient mechanical strength for the pressure application. The fresh, fine, extruded surfaces are far more ignition-susceptible than the undamaged polymer. Polymer extrusion has been blamed for some fires, but no formal ignition studies have been performed.

Space systems — Oxygen safety —

Part 3:
Selection of non-metallic materials for oxygen systems and components

1 Scope

This part of ISO 22538 describes a process for the selection of non-metallic materials for oxygen systems and their components. This part of ISO 22538 applies equally to ground support equipment, launch vehicles and spacecraft.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 4589 (all parts), *Plastics — Determination of burning behaviour by oxygen index*

ISO 11114-3, *Transportable gas cylinders — Compatibility of cylinder and valve materials with gas contents — Part 3: Autogenous ignition test in oxygen atmosphere*

DIN 53508, *Testing of rubber — Accelerated ageing*

ASTM G86, *Standard test method for determining ignition sensitivity of materials to mechanical impact in ambient liquid oxygen and pressurized liquid and gaseous oxygen environments*

3 Terms, definitions and abbreviated terms

3.1 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1.1
auto-ignition temperature
AIT
minimum temperature required to cause a material to ignite spontaneously without the application of a spark or flame in a pressurized oxygen-enriched environment

3.1.2
batch
lot
collection of material that has all been made under the same conditions and at the same time, using the same starting materials

3.1.3
direct oxygen service
service in which materials and components are in direct contact with oxygen during normal operations

3.1.4
oxygen-enriched atmosphere
mixture (gas or liquid) that contains more than 25 volume percent oxygen

3.2 Abbreviated terms

FEP	fluorinated ethylene propylene polymer
GOX	gaseous oxygen
LOX	liquid oxygen
PCTFE	polychlorotrifluoroethylene
PTFE	polytetrafluoroethylene

4 General

4.1 Background

Experience has shown that a safe oxygen system is not necessarily achieved merely by selecting the best materials available. Experienced designers have gained considerable understanding of the effects of geometry on the design of oxygen systems and their components and have developed design features directed at overcoming the physical limitations of materials. Information required for selecting materials includes material composition and configuration, environmental and operational conditions, as well as ignition and combustion behaviour of the materials in the operational conditions. Accelerated oxygen deterioration, degradation and durability tests shall be conducted for overall evaluation of the materials.

Material selection alone cannot preclude ignition but proper choices can markedly reduce the probability of ignition. For example, ignition induced by mechanical impact can be minimized by selecting valve seats that do not shatter under cryogenic conditions. For all types of ignition mechanisms, selecting materials that have relatively small exothermic heats of combustion will reduce not only the probability of ignition, but also the probability of propagation. Materials with high heats of combustion shall be avoided.

Materials used in liquid-oxygen systems shall meet the requirements for gaseous oxygen and have satisfactory physical properties, such as strength and ductility, at low operating temperatures.

4.2 Design considerations

The operational pressure and the structural requirements are given equal attention in the design of the system. While material selection cannot preclude system failures, proper material selection coupled with good design practice can reduce the probability of system failures. Materials evaluation and selection are based on both materials testing for ignition and combustion characteristics and studies of LOX- and GOX-related failures. No single test has been developed that can be applied to all materials to determine either absolute ignition limits or consistent relative ratings. When selecting a material for oxygen systems, its ability to undergo specific cleaning procedures to remove contaminants, particulates and combustible materials without damage shall be considered.

The use of non-metals in oxygen systems is limited and their quantity and exposure to oxygen shall be minimized. Soft goods are necessary in oxygen systems because of their functional properties; however, the limitations involved in their use shall always be considered. A large experience base and material test database for material selection exist for oxygen systems between 1 MPa and 20 MPa; however, only limited experience exists above 20 MPa. When selecting materials where little experience exists, application-specific materials tests are always considered.

Information required to select materials and evaluate system safety includes material compositions and configurations, environmental and operational considerations (temperature, pressure, flow rate or ignition mechanisms) and ignition and combustion behaviour of the materials in the given environmental conditions. Materials used in LOX systems shall have satisfactory physical properties, such as strength and ductility, at operating temperature.

Materials in an oxygen environment below their AIT do not ignite without an ignition source. The rate of energy input shall 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.

Polymers generally ignite at lower temperatures and pressures than metals and may burn at oxygen pressures lower than 7 kPa. The primary concern with polymers in oxygen systems is that, if ignited, they may cause damage to the oxygen system or user. Some damage that might result includes propagation of the fire to metallic components, loss of function arising from system leaks and toxic combustion products entering the oxygen system.

Although not fully understood, the thermal and physical properties of the non-metals play an important part in ignition and combustion. Physical properties play an important role in the kindling chain ignition of metals from burning polymers.

The exposure of a material to stress may result in aging. The stress may be a result of time, pressure, contact with materials or chemicals, temperature, abrasion, light, gaseous or particle impact, tensile or compressive force (either static or cyclic), or other stressors during the service life. Aging may alter the surface, the chemistry and strength of a material and it may affect the ignition properties of a material.

4.3 Materials certification

Materials procured for use in oxygen systems require a material certification from the manufacturer. In addition, it is good practice to confirm the manufacturer-supplied information.

5 Materials control

5.1 General

Materials used in LOX, GOX and oxygen-enriched systems shall be carefully controlled. The materials shall be carefully evaluated and their susceptibility to ignition and the possible ignition sources in the system shall be taken into account. The materials that pass the required tests shall be considered for design.

5.2 Batch/lot testing

5.2.1 Testing

Experience has shown that some materials have such variability in manufacturing that different batches of the same material are not always satisfactory for use. A batch or lot may have a sample drawn from it and be inspected to determine conformance with acceptability criteria. The need for testing shall be determined by the responsible design organization.

Criteria for selection of a preferred non-metallic material for oxygen service are as follows:

a) few reactions when tested by mechanical impact;

b) a high AIT;

c) a low heat of combustion;

d) a high oxygen index;

e) a low flame temperature;

f) a high threshold temperature;

g) a low burn rate.

Materials that do not meet the criteria of the required tests and remain candidates for use shall be verified acceptable in the use configuration by analysis or testing and specifically approved by the responsible design organization. Performing a hazards analysis will provide helpful information when determining if a material can be used safely.

5.2.2 Limitations

When tested by standard mechanical or pneumatic impact tests, many non-metals show a range of reaction pressures when different batches or lots of material from the same source are tested using identical methods. The variability sometimes results from material composition or processing variations and sometimes from the poor statistical base of the tests. If variability results from the changes in material composition or other material performance shortfalls, it is necessary to establish a minimum performance criterion and batch testing procedure. However, when statistical variation limits the sensitivity of an ignition or combustion test to batch variation, other tests can be substituted such as heat of combustion, melting points, density or measurements for evaluating the batch-to-batch consistency of a material. Unfortunately, the current understanding of non-metal ignition and flammability science rarely allows a direct correlation between these physical, thermal and chemical property measurements and the important ignition and combustion characteristics.

6 Ignition mechanisms

6.1 General

In oxygen and oxygen-enriched atmospheres, the ignition of fuel-oxygen mixtures occurs with lower energy inputs and at lower temperatures than in air. For example, the minimum spark energy required for the ignition of hydrogen in air is 0,019 mJ at 1 atmosphere, but the minimum spark energy for the ignition of hydrogen in 1 atmosphere of oxygen is only 0,001 2 mJ.

6.2 Ignition conditions

The usual conditions for ignition are a function of temperature, time and turbulence. The temperature shall be high enough to cause melting, vaporization, significant reactions and/or pyrolysis; the time shall be long enough to allow the heat input to be absorbed by the reactants so that a runaway thermochemical process can occur; and the turbulence shall be high enough to allow good mixing between the fuel and the oxidizer, such that the heat can be transferred from the reacted media to the unreacted media.

6.3 Materials tests

To date, no single test has been developed that can produce either absolute ignition limits or consistent relative ratings for all materials. Materials have been evaluated by testing for their ignition and burning characteristics and by studying oxygen-related failures. An assessment of the causes of accidents and fires suggests that materials and components used in oxygen systems could be vulnerable to ignition that may lead to catastrophic fires.

6.4 Ignition factors

Factors affecting the ignition of solid materials include

- material composition and purity,
- size, shape and condition of the sample,

- characteristics of oxide layers,
- testing apparatus,
- ignition source,
- gas pressure, and
- gas concentration and composition.

The ignition process depends upon the geometry and operating conditions; therefore, caution shall be taken in interpreting the results of any ignition experiment and in generalizing ignition data. Generally, increasing the pressure reduces the ignition temperature for most materials. The data indicate that the selection of polymers for both air and oxygen systems above 20 MPa shall be similar.

Take care in applying ignition temperature data to actual components. Ignition temperatures are not inherent material properties but are dependent upon the items listed previously. When applying ignition temperature data, ensure that the data were obtained in a manner similar to the end-use application. Failure to do this can result in erroneous materials selection decisions.

Should ignition occur, several properties affect the capacity of the material to damage adjacent construction materials. The heat of combustion, mass, flame propagation characteristics, filler content, char formation and shape stability of a polymer affect the propensity to ignite surrounding materials.

6.5 Ignition mechanisms and sources

6.5.1 General

Potential ignition mechanisms and ignition sources to consider are

- particle impact,
- mechanical impact,
- pneumatic impact,
- promoted ignition,
- galling and friction,
- resonance,
- electrical arcing,
- auto-ignition,
- oxygen index, and
- aging.

6.5.2 Particle impact

Heat is generated from the transfer of kinetic, thermal or chemical energy when small particles moving at high velocity strike a component. This heat, which is adequate to ignite the particle, may be caused by the exposure of unoxidized metal surfaces or the release of mechanical strain energy. The heat from the burning particle then ignites the component. For example, high-velocity particles from assembly-generated contaminants striking a valve body just downstream of the control element of the valve can cause particle impact ignition.

6.5.3 Mechanical impact

Heat is generated from the transfer of kinetic energy when an object having a relatively large mass or momentum strikes a component. The heat and mechanical interaction between the object is sufficient to cause ignition on the impacted component. This may be performed in ambient pressure LOX test conditions or in pressurized LOX or GOX test conditions. For example, the poppet of a solenoid-operated valve striking the seat can cause mechanical impact ignition. See ASTM G86 for a detailed test method.

6.5.4 Pneumatic impact

Heat is generated from the conversion of mechanical work when a gas is compressed from a low to high pressure. Pneumatic impact is an effective ignition mechanism with polymers but not metals. For example, high-pressure oxygen released into a dead-end tube or pipe compresses residual oxygen in the tube ahead and causes pneumatic impact.

6.5.5 Promoted ignition

A source of heat input occurs (perhaps caused by a kindling chain) that acts to start the nearby materials burning. For example, contaminants (oil or debris) ignite, releasing heat that ignites adjacent components, thus causing promoted ignition, or a polymer valve seat can ignite and combust, igniting the valve stem.

6.5.6 Galling and friction

Heat is generated by the rubbing together of two parts. The heat and interaction of the two parts, along with the resulting destruction of protective oxide surfaces or coatings, cause the parts to ignite. For example, the rub of a centrifugal compressor rotor against its casing may cause galling and friction.

The resistance to ignition by friction is measured in terms of the Pv product, which is the product of the contact pressure and the surface velocity.

6.5.7 Resonance

Acoustic oscillations within resonance cavities cause a rapid temperature rise. This rise is more rapid and reaches higher values if particles are present or gas velocities are high. For example, a gas flow into a tee and out of a branch port can form a resonant chamber at the remaining closed port.

Results of studies with several types of tee configurations have indicated that temperature increases caused by resonance heating would be sufficient to ignite both aluminium and stainless-steel tubes. Tests with aluminium and stainless-steel particles added to the resonance cavity have indicated that ignition and combustion would occur at lower temperatures. Some of the tests with stainless-steel particles have resulted in ignition, but ignition appears to depend more on system pressures and system design.

6.5.8 Electrical arcing

Electrical arcing can occur from motor brushes, electrical power supplies and lighting. Electrical arcs can be very effective ignition sources for any flammable material. For example, an insulated electrical heater element may experience a short circuit and arc through its sheath to the oxygen gas, causing an ignition.

6.5.9 Auto-ignition

This test measures the minimum sample temperature at which a material will spontaneously ignite when heated in an oxygen or oxygen-enriched atmosphere. These temperatures are much higher than those that normally would occur in actual oxygen systems. The temperature at which a material will spontaneously ignite varies with the system geometry and heating rate.

The test system consists of a reaction pressure vessel, a sample holding assembly and a system whereby this reaction vessel can be charged with oxygen and heated. Thermocouples and/or pressure transducers may be used to determine the temperature at the time ignition occurs. See ISO 11114-3 for a detailed test method.

6.5.10 Oxygen index

This is a determination of the minimum concentration of oxygen in a flowing mixture of oxygen and a diluent, usually nitrogen, that will just support combustion at atmospheric pressure.

The test system consists of a heat-resistant glass cylinder that is attached to a non-combustible base. The base contains a non-combustible material, usually glass beads, to allow the gases to mix and evenly distribute the diluent. The sample is supported from the bottom and is ignited at the top. The diluent is adjusted until the mixed gas barely supports combustion of the test material. See ISO 4589 for a detailed test method.

6.5.11 Aging

Polymeric materials shall be subjected to a systematic evaluation of the effect of oxygen or oxygen-enriched atmospheres before use if the material’s compatibility is unknown. The material is first characterized, subjected to an aging process and then recharacterized after the exposure.

The test system consists of a pressure vessel, a source of oxygen and a heat source. The sample is placed in the pressure vessel; then the vessel is closed, purged and pressurized with an oxygen or oxygen-enriched atmosphere, heated to a predetermined temperature, maintained at that temperature for a predetermined time, removed from the test vessel and evaluated. See DIN 53508 for a detailed test method.

6.5.12 Threshold pressure

The threshold pressure is the minimum gas pressure, at a specified oxygen concentration and temperature, that supports self-sustained combustion of the entire sample. An igniter is placed below the bottom of the test material, which is suspended in a chamber filled with the pressurized test gas. The test conditions are adjusted until self-sustained combustion of the sample does not occur.

7 Material selection

7.1 General

Guidelines on materials compatibility with oxygen can be found in documents such as ASTM Manual Series MNL36 [2].

In general, all polymers are flammable in 100 % oxygen, therefore care shall be taken to minimize or eliminate ignition sources. This clause contains guidelines that shall be considered when selecting non-metals for oxygen systems. Criteria for the selection of a preferred non-metal for oxygen service are as follows:

a) few reactions when tested with mechanical impact;

b) high AIT;

c) a low heat of combustion;

d) a high oxygen index;

e) a low flame temperature;

f) a high threshold pressure;

g) a low burn rate.

7.2 Material types

7.2.1 General

Non-metals used in oxygen service are usually polymers (including elastomers), thermosets, composites and lubricants. Ceramics and glasses are not often used in oxygen systems and are considered inert when used. The selection of non-metals is based upon the results of tests and use experience. The medical industry does not normally use halogenated materials in medical breathing devices due to the toxicity of the gases generated in medical equipment fires.

Although not fully understood, the thermal and physical properties of non-metals play an important role in ignition and combustion. For example, the specific heat of a material determines the amount of heat necessary to bring a polymer to its AIT. For polymers of comparable AITs, the more heat required to reach the AIT, the less likely it is to ignite and burn.

7.2.2 Polymers

The most frequently used polymers are semi-crystalline types such as polytetrafluoroethylene (PTFE) (Teflon™ 1) TFE), fluorinated ethylene propylene (FEP) (Teflon™ FEP), polychlorotrifluoroethylene (PCTFE) (Neoflon™ 2) and Aclar™) 3) and amorphous polymers such a polyimide (Vespel™ 4) SP-21). PTFE is commonly used in oxygen systems because of its resistance to ignition, high AIT, high oxygen index and low heat of combustion. Unfortunately, PTFE has poor creep resistance; therefore, it is frequently replaced by polymers that are less compatible with oxygen. In addition, a very wide selection of PTFE materials which improve the creep characteristics of unfilled PTFE is available, filled with glass fibres, graphite, molybdenum disulfide, various minerals or combinations of fillers.

PTFE is the most compatible soft material in terms of ignition resistance in oxygen-enriched environments. For this reason, it is preferred for a variety of seals and miscellaneous components. PTFE does not have any appreciable resilience, which is a very desirable property for seat materials.

The designer shall ensure that “cold flow” of PTFE can be tolerated for long-term mechanical loading, pressure-induced loading and thermal cycling. Additionally, the designer shall avoid situations where extrusion creates fine PTFE particles that can promote combustion of other components. The designer shall also avoid seal leakage that could create an oxygen-enriched environment around pressurized components and/or high-velocity flow that could create particle impact ignition hazards. PTFE may also be used as a solid lubricant coating on rubbing surfaces, but it will create contamination as the equipment is operated. Designers shall be aware that fillers can adversely affect ignition and combustion of PTFE.

Polypyromellitimide, especially Vespel™ SP-21, is an excellent choice for bearings, bushings, valve seats and seals. This material has good ignition resistance, lubricity, machinability and creep resistance.

PCTFE is a fluorinated material that may sometimes be substituted for PTFE because of its increased rigidity and slight resiliency. However, polypyromellitimide is usually preferred over PCTFE in applications where material strength is important.

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