



# **SAFE PREPARATION OF COMPRESSED OXIDANT-FUEL GAS MIXTURES IN CYLINDERS**

AIGA 058/08

GLOBALLY HARMONISED DOCUMENT

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### **Acknowledgement**

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## **1 Introduction**

Cylinders containing both oxidant and flammable components (oxidant-fuel gas mixtures) are widely used in industry, medical applications, and other fields. Typical applications include calibration of flammable gas detectors, emission monitoring equipment and refinery process analyzers.

Due to the inherent nature of the gases used to manufacture oxidant-fuel gas mixtures there is always the possibility of an explosive mixture being produced. To prevent the inadvertent production of explosive mixtures strict rules and procedures shall be followed during the formulation and manufacturing processes.

Historically the gases industry has experienced accidents and losses resulting from the manufacture and use of these gas mixtures resulting in explosions that have caused injuries and death. These incidents have been caused by mixtures being manufactured that have been within the explosion range.

Compressed oxidant-fuel gas mixtures can be manufactured safely provided the principles contained in this document are followed. This document has been prepared by the European Industrial Gas Association and reviewed and modified by AIGA for use in Asia.

## **2 Scope and purpose**

### **2.1 Scope**

This code of practice documents the minimum recommendations for the safe preparation of compressed oxidant-fuel gas mixtures in cylinders by static methods that is the addition of one component after another into cylinders. The Code of Practice specifically addresses:

- Key principles for compressed oxidant-fuel gas mixture manufacture.
- Manufacturing feasibility studies.
- Gas mixing equipment, filling and analysis.
- The audit of oxidant - fuel gas mixture manufacturing procedures and operations

This Code of Practice specifically describes the manufacture of compressed oxidant - fuel gas mixtures under the conditions of gas temperatures and pressures detailed within this document. The manufacture of liquefied and liquid oxidant – fuel gas mixtures and the manufacture of compressed oxidant –fuel gas mixture by dynamic methods that is the filling into the cylinder by blending the components dynamically at calculated flow-rates) are outside of the scope of this document.

This code of practice shall be used in conjunction with the information and principles contained in IGC Document. 39/07“Guidelines for the safe preparation of gas mixtures in cylinders” ( or refer to AIGA 047/08 ).

### **2.2 Purpose**

The purpose of the code of practice is to describe practices to be used for the safe preparation of compressed oxidant – fuel gas mixtures and to ensure that they are non explosive at the end of the manufacture.

- The safe formulation of compressed oxidant – fuel gas mixture by trained and competent personnel.
- Defined safety considerations which are applied and maintained during the manufacturing process.

- An overall quality system with formally approved documented procedures shall be used for manufacture and these procedures and practices shall be subject to the regular technical review and audit by technical experts independent of the routine production process.

### 3 Definitions

- Combustible gas / flammable gas / fuel: In this document gases which are able to undergo exothermic reaction when mixed with an oxidant and ignited
- Cylinder: For the purposes of this document, a cylinder is defined as a container (of compressed gas) having a water capacity that does not exceed 150 litres.
- Cylinder burst: The bursting or rupture of a cylinder due to the development of internal pressure from a compressed oxidant-fuel gas mixture explosion which exceeds the cylinder burst pressure.
- Cylinder burst pressure: Highest pressure reached in a cylinder during a burst test.
- Cylinder service pressure: Highest pressure permitted to be developed during service.
- Cylinder test pressure: The test pressure of a cylinder is the pressure at which the cylinder is hydraulically or pneumatically tested.
- Expert opinion: Evaluation by a technically competent authority or person in the field of compressed oxidant – fuel gas mixture manufacturing who is not involved in commercial activity in this field and who should not be directly involved in production.
- Explosion pressure: Maximum pressure occurring in a close vessel during the explosion of a gas mixture.
- Explosion (flammable) limits: The concentration limits of the explosion range.
- Explosion (flammable) range: The range of concentrations between the lower and the upper explosion limits (LEL and UEL) where flame propagation could take place.
- HAZOP: A systematic technique to identify and assess potential hazards that might arise during the operation of plant or equipment. A study is normally carried out to assess the potential effects of various malfunctions of the equipment or plant (e.g. reverse flow, excessive temperature or pressure etc.) and human error.
- Inert gas: In this document, a gas that is non combustible and non reactive
- Intermediate analysis: An analysis carried out part-way through the process of filling a gas mixture in a cylinder (or cylinders). Such an analysis is normally carried out to confirm the concentrations (and sometimes the identities) of the components that have already been filled before a subsequent component is added
- Limiting Oxygen Concentration (LOC): Maximum oxygen concentration in any mixtures of a flammable substance, air and inert gas, at atmospheric conditions, in which an explosion would not occur. LOC is usually expressed as mole or volume fraction.
- Lower Explosion (flammable) Limit (LEL): In this document, the lower explosion limit is the fuel lean limit of the explosion range.
- Maximum Explosion Pressure: The maximum possible explosion pressure obtained by varying the concentrations of the components of a mixture (usually nearly stoichiometry).
- Oxidant: In this document, any gaseous material that can react with a fuel (either gas, dust or mist) to produce combustion. Oxygen in air is the most common oxidant.
- Premix: For the purposes of this document, a premix is a gas mixture which is used as one of the supply gases during the filling of a gas mixture. The use of premixes can enable low concentration components to be filled accurately and can also eliminate any potential hazards when filling certain gas mixtures containing potentially incompatible components.
- Safety premix: Mixture of flammable gases in inert gases which cannot react with oxidizing gases whatever their concentrations and vice versa mixture of oxidizing gases in inert gases which cannot react with flammable gases whatever their concentrations
- Shall: The use of the word “shall” in this document implies a very strong concern or instruction.

- Should: The use of the word “should” in this document indicates a recommendation.
- Upper Explosion (flammable) Limit (UEL): In this document, the upper flammable limit is the fuel rich limit of the explosion range.

## **4 Key principles for the manufacture of compressed oxidant-fuel gas mixtures**

### **4.1 Precautions to avoid risks**

- Whenever possible consider if another mixture could be used to substitute an oxidant- fuel mixture in the proposed application since an oxidant –fuel mixture is by its very nature potentially more hazardous to produce. This substitution may require discussion and agreement with the customer.
- If there is insufficient data to enable an evaluation of the explosion limits and safety margins the mixture shall not be manufactured.
- All employees involved in production processes shall be trained and practically competent.
- All computer programmes based on expert systems that are used to evaluate and formulate oxidant-fuel mixtures shall be rigorously tested, validated before use and subject to version control. These programmes shall not be used to evaluate unknown data or to interpolate or extrapolate data.
- All computer programmes shall be password protected to prevent unauthorized changes being made. Any changes to any programme shall only be made by a competent authorized person and a record of these changes shall be retained. All changes shall be validated before the revised programme is used.
- After one technical expert has evaluated the feasibility of safely manufacturing a new oxidant-fuel gas mixture it is strongly recommended that this formulation should be checked by another competent person or by a computer programme in order to detect any potential errors or hazards.
- The production sheet for all oxidant-fuel gas mixtures shall be formally approved following the feasibility study (e.g. indication of feasibility study reference as indicated above, signature of expert).
- The approved formulations of compressed oxidant-fuel gas mixtures shall be protected against unauthorized changes.
- Chemical incompatibility of the component gases shall be considered during the feasibility study.
- Evaluate the critical manufacturing steps which may potentially lead to a dangerous mixture.
- Appropriate safety margins shall be introduced to avoid risks when mixing oxidant and fuel gases.
- The direct simultaneous connection of piped flammable and oxidant gases to the same manifold shall not be allowed.
- Equipment shall be regularly tested and maintained.
- Consider passive safety measures.
- All pipes and raw materials shall be clearly labelled.
- All cylinder connection adaptors shall be controlled (see IGC Document 39/07 or AIGA 0047/08).
- Consider back-flow prevention (raw material source gas pressures greater than the pressure in the receiving cylinder).
- Preparation of compressed oxidant-fuel gas mixtures in small size cylinders (e.g. equal or less to one litre) and in particular in disposable cylinders by static methods is not recommended. Small cylinders and disposable cylinders can be filled only with already prepared compressed oxidant-fuel gas mixtures.



## 4.2 Key steps and checks

- Check that cylinders are at room temperature to avoid condensation of components.
- A complete production sheet shall be prepared before manufacturing the mixture. The instruction shall include as a minimum:
  - ✓ The fill pressure and/or weights of all pure components or mixtures to be added.
  - ✓ The establishment of filling and analytical tolerances (when analysis is conducted) for each component according to the procedure selected.
  - ✓ The final mixture pressure.
  - ✓ The service pressure of the cylinder.
  - ✓ The order of filling of the components.
  - ✓ The selection and control of premixes (homogenization and analytical steps).
  - ✓ Homogenization requirements.
  - ✓ Labelling of the cylinder.
  - ✓ System(s) on which the mixture is to be filled.
- Check the filling steps (vacuum level, pump time, etc.).
- Record the amount of each component introduced (e.g. weight or pressure).
- Record homogenization steps.
- Record final analysis results (when analysis is done).
- Check hazard classification and labelling of final mixture.
- Record cylinder serial numbers.

## 4.3 Organizational requirements

All technical personnel involved in the feasibility, calculation and preparation of instructions for oxidant-fuel gas manufacture shall be independent from the oxidant-fuel gas mixture manufacturing team, and shall be trained, assessed and formally appointed for this activity.

All manufacturing sites filling oxidant-fuel mixtures shall be formally approved by the technically competent company authority for this activity. Approvals shall be based on the:

- Design and use of satisfactory filling equipment.
- Completion of an audit.
- Appointment of technically competent authorized personnel.
- Documented procedures and training records.

Personnel shall be formally authorized for this activity by their management. The company shall define the content of the training and shall define the minimum re-training and assessment periods.

The work instructions shall be version controlled and available at the point of use in the work area.

The organization shall record all of the information necessary to have complete traceability of the preparation and production of such mixtures.

The audit of oxidant-fuel gas mixture formulation and manufacturing should be conducted periodically by a technically competent person. The company shall establish and define this period. An example of a specimen audit check list is included in **Appendix 8**.

**Where serious hazardous conditions are found to exist following an audit a filling plant shall cease filling oxidant – fuel gas mixtures until controls are put in place to remove these hazards.**

## 5 Compressed oxidant-fuel gas mixture manufacturing feasibility study

The purpose of this section is to describe how to evaluate the safe preparation of oxidant-fuel gas mixtures, taking into account:

- Component and cylinder compatibility (section 5.1)
- Formulation of safe compressed oxidant-fuel gas mixtures (section 5.2)
- Mixture manufacturing accuracy (section 5.3)

### 5.1 Component and cylinder compatibility

The compatibility of the mixture components shall be evaluated using literature information or the gas mixture compatibility table given in **Appendix 2**. In general this table supplies information as to whether two components may be:

- Mixed in any concentration.
- In certain restricted concentrations.
- Or mixing is not allowed due to chemical incompatibility.

The compatibility of the components with the cylinder material should also be evaluated using the information contained in ISO standard 11114-1 "Cylinder and cylinder valve material compatibility with gaseous content".

Unstable gases can strongly affect the explosion range. Only oxidant-fuel gas mixtures that are stable under the conditions of temperature and pressure existing during manufacture and use shall be produced. See for example **Appendix 3**, which lists some known unstable gases.

A number of halocarbons have no explosion limit in air under atmospheric conditions but do have at elevated pressure in air or at atmospheric pressure in pure oxygen. See for example the diagram in **Appendix 4**.

### 5.2 Formulation of safe compressed oxidant-fuel gas mixtures

The purpose of this section is to describe how to derive the formulation (final mixture pressure and mixture component introduction order) of safe compressed oxidant-fuel gas mixtures.

The following mixtures shall not be manufactured unless there are experimental data or expert opinion on explosion limits at the filling pressure:

- Oxidants with unknown oxy-potential coefficients with flammable gases.
- Gases with unknown explosion (flammable) limits with oxidant gases.
- Unstable gases (e.g. acetylene, butadiene, ethylene oxide and other gases listed in **Appendix 3**) with oxidant gases.
- Pyrophoric products and other products such as organometallics, silane, disilane, trisilane, chlorosilanes, diborane, arsine, phosphine, germane with oxidant gases.

The formulation of safe compressed oxidant-fuel gas mixtures requires the three following studies:

- To assure non explosive mixtures at the end of manufacture (section 5.2.1).
- To avoid or control explosive mixtures during manufacturing (section 5.2.2).
- To avoid condensation during and after the manufacturing (section 5.2.3).

A “decision tree” diagram for manufacturing safe compressed oxidant-fuel gas mixtures is contained in **Appendix 5**.

### 5.2.1 To assure non-explosive mixtures at the end of manufacture

The uncertainty of mixture production shall be taken into account when assuring that the compressed oxidant-fuel gas mixtures are non-explosive inside the cylinders at the end of their manufacture.

The explosion ranges of gases increase with temperature and in most cases with increasing pressure. Therefore data on explosivity are required not only at atmospheric pressure and standard temperature, but also at manufacturing pressures and up to 65°C (UN/ADR upper temperature).

The study to avoid explosive mixtures shall be based on comprehensive data considering the effect of pressure and temperature on explosion (flammable) limits.

There is little published data available concerning the above. Some gas companies have data available at elevated pressures, but generally covering a limited number of flammable products and mainly in air and/or oxygen.

In the absence of comprehensive data, the following rules shall be applied, taking into account Lower Explosion Limits (LELs) in air at atmospheric pressure (available in ISO 10156), LELs in oxygen at atmospheric pressure and Limiting Oxygen Concentrations (LOCs) of flammable gases with air as the oxidizer and nitrogen as the inert component at atmospheric pressure (available for example in the “Chemsafe” database and see the table in **Appendix 6**).

#### 5.2.1.1 Mixtures containing one flammable gas in air:

Rules to allow the manufacturing of compressed gaseous mixtures of flammable gas in Air below the Lower Explosion Limit (LEL mixtures) when data on explosivity at final filling pressures or expert opinion is not available, when introducing oxygen at the end, are:

- Compressed oxidant-fuel gas mixtures containing one flammable gas in concentrations of less than or equal to 25 % of the lower explosion limit (LEL) in air at atmospheric pressure can be manufactured at a maximum pressure of the cylinder service pressure and at a maximum of 200 bar.
- Compressed oxidant-fuel gas mixtures containing one flammable gas in concentrations greater than 25% and less than or equal to 50 % of the lower explosion limit (LEL) in air at atmospheric pressure can be manufactured at a maximum pressure of the cylinder service pressure and at a maximum of 150 bar.
- Compressed oxidant-fuel gas mixtures containing one flammable gas in concentrations greater than 50 % and less than or equal to 75 % of the lower explosion limit (LEL) in air at atmospheric pressure can be manufactured at a pressure which shall not exceed 1/10 of the cylinder service pressure. The 1/10th of cylinder service pressure is justified by the experimental data (maximum explosion pressures of flammable gas-air mixtures for deflagration) contained in **Appendix 7**.
- Compressed oxidant-fuel gas mixtures containing one flammable gas in concentrations greater than 75% of the lower explosion limit (LEL) in air at atmospheric pressure shall not be manufactured without data on explosivity at final filling pressure.

Note: Special consideration shall be given to halogenated hydrocarbons which are not flammable at atmospheric pressure but may be flammable at elevated pressure (see **Appendix 4**).

Rules to allow the manufacturing of compressed gaseous mixtures of flammable gas in Air above the Upper Explosion Limit (UEL mixtures) when data on explosivity at final filling pressures or expert opinion are not available, when introducing oxygen at the end, are :

- Mixtures containing oxygen in concentrations of less than or equal to 50 % of the Limiting Oxygen Concentration (LOC) in flammable gases at atmospheric pressure can be manufactured at a maximum pressure of the cylinder service pressure.
- Mixtures containing oxygen in concentrations greater than 50 % and less than or equal to 75 % of the Limiting Oxygen Concentration (LOC) in flammable gases at atmospheric pressure can be manufactured at a pressure which shall not exceed 1/20th of the cylinder service pressure. The assumption of 1/20th of cylinder service pressure is based upon the data contained in appendix 6 and additional safety margin necessary because of higher uncertainty on LOC values compared to LEL.

When filling flammable gas at the end, the rules in section 5.2.2 must also be followed.

#### **5.2.1.2 Mixtures containing one flammable gas in oxygen**

Rules to allow the manufacturing of compressed gaseous mixtures of low concentrations of flammable gas in oxygen when data on explosion at final filling pressures or expert opinion is not available, are:

- Compressed oxidant-fuel gas mixtures containing one flammable gas in concentrations of 1000ppm or less in oxygen can be manufactured at the service pressure of the cylinder.
- Compressed oxidant-fuel gas mixtures containing one flammable gas in concentrations greater than 1000 ppm in oxygen can be manufactured only if data on explosion at final filling pressures or expert opinion is available, and following the rules of section 5.2.2. when filling oxygen last.

Rules to allow the manufacturing of compressed gaseous mixtures of high concentrations of flammable gas in oxygen when data on explosion at final filling pressures or expert opinion is not available, are:

- Compressed oxidant-fuel gas mixtures containing oxygen in concentrations of 1000ppm or less in flammable gases can be manufactured at the service pressure of the cylinder.
- Mixtures containing oxygen in concentrations greater than 1000ppm in flammable gases can be manufactured only if data on explosion at final filling pressures or expert opinion is available, and following the rules of section 5.2.2. when filling flammable gases last.

#### **5.2.1.3 Mixtures containing inert gas other than nitrogen**

An equivalent mixture containing the flammable gas in oxygen and nitrogen, shall be defined (using for example ISO 10156 coefficients for the equivalence between inert gases) and then the following rules should apply when data on explosion at final filling pressures or expert opinion is not available:

- When the equivalent mixture has lower oxygen concentration in nitrogen than in air, the same rules as those described in section 5.2.1.1 apply.
- When the equivalent mixture has higher oxygen concentration in nitrogen than in air, the same rules as those described in section 5.2.1.2 apply.

#### **5.2.1.4 Mixtures containing one oxidant other than oxygen**

The manufacturing of compressed oxidant – fuel gas mixtures of either low or high concentration of flammable gas with one oxidant gas other than oxygen with or without inert gas is not allowed except if experimental data or expert opinion is available. In absence of such information the mixtures shall not be manufactured.

### 5.2.1.5 Mixtures containing several flammable / oxidant / inert gases

Mixtures containing one or several flammable gases, and/or several inert gases and oxygen can be manufactured after studying their feasibility taking into account the following rules:

- Several inert gases:
  - An equivalent mixture containing only the “major” inert gas shall be defined using for example, ISO 10156 coefficients to determine the “major” inert gas and to assimilate the other inert gases to the “major” inert gas.
  - Depending upon the type of equivalent mixtures, the rules contained in section 5.2.1.1, 5.2.1.3 or 5.2.1.4 will apply.
- Several flammable gases:
  - An equivalent mixture containing only the “major” flammable gas shall be defined using for example, ISO 10156 coefficients to determine the “major” flammable gas and to assimilate the other flammable gases into the “major” flammable gas.
  - Depending upon the type of equivalent mixture, the rules contained in sections 5.2.1.1, 5.2.1.2, 5.2.1.3 or 5.2.1.4 will apply.

For oxidant gases other than oxygen see section 5.2.1.4

### 5.2.2 Study to avoid or to control explosive mixtures during manufacturing

During the manufacturing of a compressed oxidant-fuel gas mixture an explosive mixture can exist temporarily when passing through the explosion range and before homogenization. This situation should be avoided as much as possible. The following rules shall apply:

#### Non explosive oxidant-fuel gas mixtures inside cylinders during manufacturing:

For compressed oxidant-fuel gas mixtures with a high enough concentration of inert gas, such as for example LEL mixtures in air, the rule is never create an explosive mixture inside cylinders during manufacturing. This can be achieved if:

- Sufficient inert gases are introduced between the flammable gases and the oxidant gases, or
- Oxidant gases or flammable gases are added to a “safety premix”.

#### Controlled explosive oxidant-fuel gas mixtures inside cylinders during manufacturing:

For compressed oxidant-fuel gas mixtures with no or low concentration of inert gases an explosive mixture can be created temporarily by passing through the explosion range during manufacture. This will be the case when all the reactive gases of the same type in minor concentration (according to the stoichiometry) are introduced into the cylinders first.

This temporarily created explosive mixture, inside the cylinder, will then become non explosive when the concentration moves out of the explosion range. This occurs at the end of the introduction of the major concentration reactive gases of the opposite type.

In this situation the requirement is to calculate or have data available on the energy which will be created by a potential explosion. The calculated explosive energy shall result in potential explosion pressures less than the service pressure of the cylinder plus a safety factor taking into account any possible gas detonation.

The potential explosion pressure of the temporarily created explosive mixture at stoichiometry has to be calculated assuming adiabatic conditions. If the oxidant is air or mixtures with an oxygen ratio in nitrogen less than that of air, the data in **Appendix 7** or a factor of 10 should be used to calculate the potential explosion pressures. For oxygen or mixtures with an oxygen ratio in nitrogen greater than air, data or expert opinion is required

This potential explosion pressure shall never be allowed to exceed the service pressure of the cylinder.

### **5.2.3 Study to prevent condensation during or after manufacturing**

An oxidant-fuel gas mixture component introduced as a vapour (liquid or liquefied gas under pressure) may condense due to the exposure of the cylinder to low temperature. This may create a flammable zone inside the cylinder which may remain unless the mixture is re-homogenized at a temperature above the vaporization temperature of the component.

Oxidant-fuel gas mixture pressures shall therefore be calculated to avoid condensation of components at the minimum ambient temperature to which the cylinder will be exposed, particularly during manufacture, transportation, storage and use.

The possibility that some components of the mixture may liquefy in the cylinder during storage or transportation after manufacturing should be noted on the "production sheet" with the indication of the temperature. The possibility that components may liquefy during storage prior to use should be stated with the temperature on the documents sent to the users. The general practice is to use a standard temperature with a "safety margin" to calculate the mixture composition and avoid the condensation of vapours, for example -10°C for some European countries.

### **5.3 Mixture manufacturing accuracy**

Mixtures are usually manufactured by measuring weight or pressure or volume (syringe/ampoules) of the components into the cylinders.

The accuracy of the filling technology used shall be taken into account and incorporated into the safety margins used to calculate the pressure and/or weights of components in oxidant-fuel gas mixtures.

Note: To ensure good precision it is recommended that compressed oxidant-fuel gas mixtures be manufactured in cylinders large enough to allow acceptable mixture accuracy. Therefore these mixtures should not be manufactured in small cylinders, for example with a water capacity equal or less than one litre or in disposable cylinders. Such small size cylinders should be filled only with already prepared compressed oxidant-fuel gas mixtures. Direct manufacture in small cylinders is possible however if safety premixes are used.

## **6 Gas mixing equipment**

Gas mixing systems shall be designed by competent personnel and risk assessed (HAZOP) to ensure that the systems are safe and effective. New cylinder filling manifold designs or modifications shall be reviewed and approved prior to the use of the system. The cylinder filling manifolds should be simple to operate with a logical layout to minimise the potential for operator error.

### **6.1 Considerations in the design of the gas mixing facility**

Gas filling systems and filling areas should be segregated as far as it is practicable to eliminate the risk of the inadvertent mixing of incompatible gases. Flammable and oxidant gases or mixtures should be stored in separate areas or in well identified zones.

Gas filling system components must be compatible with the oxidants (in particular high pressure oxygen) and the flammable gases used.

The design shall take into account the prevention of feed-back of gas from filling systems into supply gas systems.

The equipment shall be designed to prevent simultaneous connection of flammable and oxidant gases to the cylinder being filled.

The interconnection of incompatible supply gases shall not be possible through the various cylinder filling manifolds and mixing systems. Non-return valves and block valves shall not be relied on as the only means of protection against interconnection of incompatible gases.

Adequate provision shall be made to prevent back-feeding of partially filled cylinders into other filling systems or cylinders via supply, vent or vacuum systems. This is particularly important where a common supply feeds different category filling areas.

Where flammable and oxidant gases are being mixed, the provision of a dedicated system combined with strict operational controls is necessary. Mixtures of oxidant and flammable gases shall be filled on systems engineered to minimise the risk of operator errors, which could result in the formation of an explosive mixture. The oxidant and flammable gases shall be filled on separate manifolds, or dedicated manifolds, where there is no possibility of the inadvertent connection of incompatible gases at the same time.

Connections on the cylinder filling manifold system shall be designed to prevent the possibility of the connection of non authorized products. Generally the compressed oxidant-fuel gas mixture cylinder under preparation may require the use of cylinder adaptors during filling. Special procedures shall be put in place to control the issue and use of these adaptors.

Provision should be made for "parking" cylinder filling hoses, so that contamination is prevented when the hoses are not in use. The filling hoses should be dedicated to gases of the same type. Do not use hoses which have been used to fill flammable gases to fill pure oxygen because there is a possibility that the gases can be adsorbed on the internal walls of the hoses.

Where flammable components are to be stored and filled, consideration shall be given to the following:

- The classification of electrical and mechanical equipment and safety devices (voltages, flame proofing etc.).
- The grounding of cylinder filling manifolds and associated equipment.
- The sources of static discharge.
- The building ventilation.
- Flammable gas detection systems and alarms.
- Explosion relief for buildings.

Vent lines from cylinder filling manifolds shall be installed to enable any residual gas be vented in a safe manner. Care shall be taken to ensure that vent lines are installed in a way that avoids any reaction between incompatible products and could lead to explosive mixture formation. The vent lines should be separated with a facility to purge the lines with inert gas.

Precautions should be taken to avoid the suck back of contaminants (oil, scrubber solutions etc.) from vacuum systems into cylinder filling manifolds and cylinders. Vacuum pumps used in oxidant service should use an appropriate oxidant compatible lubricant. (e.g. fluorinated pump oils).

There should be adequate labelling to identify valves and other operating controls and equipment

Pressure gauges, scales and other metering equipment shall be regularly calibrated.

## **6.2 Oxidant and fuel gas sources**

Care shall be taken to prevent the back-flow of an oxidant into a fuel gas system or cylinder or vice versa as this may result in the unintentional formation of an explosive gas mixture.

To avoid such a hazard:

- Always use reactive gas sources at pressures higher than the pressure in the receiving oxidant-fuel gas mixture cylinder.

Ensure that the gas supply systems are designed to prevent back-flow. Care shall be taken to prevent an oxidant fuel gas mixture being produced inside the manifold .To avoid such a hazard:

- Use only one reactive gas source at a time.
- Do not connect flammable and oxidant gas sources to a receiving cylinder at the same time.
- Ensure that reactive gases are effectively removed from the filling system prior to the introduction of an incompatible gas, for example by evacuation or purging with nitrogen.

### **6.3 Inert gas sources**

Inert gas sources should be protected against back-flow by the following:

- Always use inert gas sources at pressures higher than the pressure of the mixture cylinder.
- As a minimum, protect inert gas sources with back-flow protection and/or double block and bleed valves.
- Only one gas source shall be open at a time.
- Create a vacuum inside the entire oxidant -fuel gas mixture manufacturing equipment (up to the receiving cylinder valve) prior to the introduction of inert gas.

## **7 Preparation methods**

### **7.1 Choice of cylinder and valve**

The materials of construction of the cylinder and the valve shall be compatible with all the components of the mixture.

The use of dip-tubes is not recommended because of the potential for a dip tube to become detached and create an ignition source within the cylinder.

The inner surface of the cylinder should be clean (e.g. free of rust or other potentially reactive substances oil, grease etc). New cylinders and re-tested cylinders should be dried in an appropriate way before being used for oxidant-fuel gas mixtures. Before starting the filling procedure the cylinder shall be evacuated.

Consideration shall be given to the potential for customers to contaminate cylinders with materials (liquids gases, solids) that are incompatible with the components of oxidant – fuel mixtures. Preventive actions may include the examination of valve outlet for cleanliness, use of residual pressure / non-return valves.

### **7.2 Filling methods**

In general the two following preparation methods can be used for the manufacture of gas mixtures:



The sequential addition of mixture components, one after the other, into the cylinder and measuring their quantities using the following methods:

- Gravimetric method (component weight measurement).
- Pressure method (component partial pressure and cylinder temperature measurements).
- Volumetric method (syringe, intermediate capacity, etc volume/pressure measurement).

The dynamic blending of oxidant-fuel gas mixtures which is outside the scope of this document.

For the methods of adding mixture components one after the other into the cylinder, it is possible to safely manufacture a compressed oxidant-fuel gas mixture by disconnecting the cylinder containing an intermediate mixture of flammable and inert gases or oxidant and inert gases providing:

- The intermediate mixture is homogenized.
- The mixture composition is measured and identified prior to reconnection to complete mixture filling. Where analysis is not performed a second person must check the filling operation to ensure the correct component quantities are added.

It is also possible to safely manufacture mixtures without disconnecting the cylinder from the manifold when following all the requirements contained in this document.

The filling method shall be selected in order to ensure the final mixture and any intermediate mixtures are within the safety margins detailed in section 5.32.

### **7.3 Rules for safe preparation**

The recipe should define the kind of filling method for each step that has to be used by the operator.

The actual masses and/or pressures of each filling step shall be recorded by the operator to ensure traceable records of the complete filling procedure.

Each step of the filling process has to be conducted in one operation. Therefore the operator shall take care that enough of each component is available prior to starting any filling.

During the filling of mixtures above the UEL, the addition of pure oxygen or comparable oxidants to a mixture should be avoided. It is recommended that premixes of oxygen or oxidant in an inert gas are used instead.

### **7.4 Filling conditions**

The cylinder shall be at or above room temperature (65°C maximum) prior to filling and during the whole production process including homogenization and analysis.

This will avoid condensation of components inside the cylinder.

If the filling process requires going through the explosion range, the flowrate of addition of pure oxygen shall be controlled to avoid adiabatic compression and warming (above 65°C) to avoid possible ignition sources.

Care shall be taken when adding flammable liquids first to make sure that they are totally vaporized inside the cylinder and there is no residual liquid inside the cylinder valve prior to an oxidant being added. This is to prevent possible reaction in the cylinder valve.

### **7.5 Premixes**

In some cases it may be necessary to use premixes to add one or more reactive components to the mixture. The reasons for premix use are:

- To ensure that during the addition of the flammable component the explosion range is not reached in the cylinder at any time.
- To increase the mass or partial pressure of gas added in order to maintain filling accuracy in lower concentration components.

Premix composition shall be analyzed or measured before first use to ensure that the concentrations of all components in the premix are within the desired limits and to positively identify the balance gas.

Premix cylinders shall be identified and a control system implemented to prevent confusion with other cylinders and other premix cylinders.

If premixes are oxidant-fuel mixtures they have to be treated according to the rules defined by this document.

Premixes can be inert, flammable or oxidizing and have to be treated accordingly. They include safety premixes.

Premixes should be protected from back-flow when used.

## **8 Filling**

### **8.1 Production sheet**

The "Production sheet" should specify all of the relevant information necessary to produce the mixture, including safety information. The mixture shall be clearly identified as an oxidant-fuel one.

The production sheet should specify:

- ♦ Cylinder and valve type.
- ♦ Order of component addition.
- ♦ Quantities of gases to be added.
- ♦ Equipment to be used, taking into account the accuracy of weigh scales, manometers and syringes.
- ♦ Classification of the mixture.
- ♦ Labelling requirement.
- ♦ Any homogenization and analysis steps required.
- ♦ Identification of intermediate pre-mix cylinders.

A system shall be put in place to avoid misuse or confusion between production sheets for different compressed oxidant-fuel mixtures.

### **8.2 Safe selection of raw materials**

It is extremely important to ensure that the correct pure gas or mixtures are selected when manufacturing oxidant-fuel gas mixtures as incorrect selection is thought to be one of the main causes of incidents during the manufacturing process.

Pure gases, liquids and premixes used for the manufacturing of oxidant-fuel gas mixtures shall have a defined quality and composition. Impurities should be considered to avoid the possibility of a dangerous mixture being manufactured.

There shall be adequate segregation of oxidant, flammable and inert cylinder supply gases in the production area (i.e. pure products and premixes). These segregated areas shall be clearly identified.

Pure products and premixes shall be clearly identified with all relevant markings and current composition information in the appropriate language for the operator. An identification system (e.g. a bar code or radio frequency device) that can link the cylinder with the content is useful to enable better control.

The cylinders shall be labelled as required by law (that is the pictogram of the danger and the Risk & Safety phrases). Gas mixtures used as premix, shall be labelled with the exact composition of the mixture.

### **8.3 Evacuation of cylinder before filling**

Before filling it is necessary to remove any residual gas from the cylinder by evacuation. Evacuation is necessary to ensure that there are no flammable or oxidant gases present that can create unexpected explosive conditions during filling or change the final mixture composition. The evacuation shall produce a vacuum in the cylinder of at least 1mbar absolute. Alternatively, completing cycles of pressurization and discharge with an inert gas and then evacuation of the cylinder to better than 10 mbar absolute is also permissible.

### **8.4 Single cylinder manufacture**

Oxidant- fuel mixtures can be made by filling one cylinder at a time.

Batches of multiple cylinders can be manufactured only after a risk assessment has been conducted to ensure that the method employed reaches an adequate level of safety. (e.g. Use of safety premix, double independent control of the quantity of gas introduced into each cylinder, etc.).

### **8.5 Topping up adjustment for out of specification mixtures**

The topping up of out of specification mixtures after disconnection from the filling manifold should be avoided unless a risk assessment is made and written approval given by a technically competent person responsible for oxidant-fuel gas mixture formulation.

### **8.6 Gas homogenization requirements**

A mixture shall be homogeneous at the end of the filling process and prior to re-opening the cylinder valve and in some cases during the production process.

The recipe shall take into consideration the need for homogenization and shall be in writing. All homogenization steps shall be documented in the production sheet.

Homogenization can be achieved by rolling the cylinder. Before any method of homogenization is used tests should be made to ensure that the method and equipment used is effective. Special attention should be given to the homogenization process for gases with different molecular weights.

When all the preventive measures contained in this document are taken into account the compressed oxidant – fuel gas mixtures after homogenization are considered safe and can therefore be analyzed or used without the need for protection against explosion of the cylinder.

## 9 Analysis

### 9.1 Principles of Analysis

The composition of all premixes shall be measured and the measures recorded and retained.

Analysis of the final mixture may be required for different reasons such as control of the accuracy of the mixture in particular for quality purpose when it contains low concentrations of reactive gases. The analysis of oxidant-fuel gas mixtures is safe provided that all of the best practices detailed in this document, according to existing knowledge, are followed. It is strongly recommended that all cylinders of oxidant-fuel mixtures be analysed after filling.

### 9.2 Activities of the analyst

Before analysis, the person who conducts the analysis shall check the following:

- All masses and/or pressures are within the allowed limits.
- The homogenization step has been completed.

And:

- All other precautions have been taken prior to the analysis as applicable.

### 9.3 Mixtures out of range

If a mixture is found in the explosive range dispose of it in a safe manner. DANGER: Do not handle the cylinder or close the cylinder valve. Immediately activate emergency plan (See section 11: emergency planning).

## 10 Disposal of residual compressed oxidant-fuel gas mixtures in cylinders

For the general principles and rules relating to the disposal of gas mixtures refer to:

- Disposal of gases IGC Doc 30/07

and to

- Safe preparation of gas mixtures IGC Doc 39/07 or AIGA 047/08

The following specific points shall be included in the design of the disposal facility:

- a) The height of any vent stack shall be sufficient to ensure that the vented product is safely dispersed and will not cause harm to personnel.
- b) The flare stack or scrubber shall be compatible with materials that are to be vented.
- c) The following basic principles of venting cylinders shall be followed:
  - Do not simultaneously vent cylinders with incompatible gases on the same manifold.
  - The preferred option is to vent flammable/oxidant mixtures on a single-point manifold.
  - Where a multi-point manifold is used, a detailed work instruction shall be written which shall include the following:
    - Dedicated valve connections for flammable and oxidant cylinders.

- The manifold vent valve shall be opened before any cylinder valves are opened and shall remain open during the venting operation.
  - Only one cylinder valve shall be open at any time during the venting process.
  - The venting of cylinders containing exactly the same mixture may be completed simultaneously.
  - After the cylinder has been vented and the cylinder valve has been closed the manifold shall be purged using an inert gas.
- Careful consideration shall be given when venting mixtures containing corrosive flammable and oxidant gases, which are treated in the same disposal/scrubbing system, e.g., hydrogen sulfide and chlorine could be treated in the same scrubbing unit and a reaction may occur. Local work instructions shall be put in place to control these disposal operations.

## **11 Emergency planning**

It may happen that a dangerous mixture is identified, for example by:

- Overfilling of one reactive component during the filling procedure.
- Introducing the incorrect type of gas (pure or premix).
- Identification during gas analysis.
- Noticing some reaction during analysis.
- Reviewing the recipe.

The mixture will be potentially dangerous if it is:

- Inside explosion range.
- Not homogenized, with locally limited areas which may be inside explosion range (dangerous until homogenized).
- Over pressurised.
- Contains incompatible materials.

In these cases the following actions should be taken:

- Identify the cylinder as potentially dangerous and inform all people responsible.
- Do not touch the cylinder.
- Evacuate people from the direct area and neighbourhood.
- Establish how many dangerous cylinders may exist and what their condition is.
- Contact the local competent authority in explosives for special advice.

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## Appendix 2: List of gas compatibility

### **LEGEND:**

- ✕ - Can be mixed at any concentration, dangerous reactions are not possible
- - Can be mixed in certain concentrations, but dangerous reactions are possible
- - Not allowed to mix (exceptions are possible, if an expert opinion is available)
- - Information is not available (empty field)

### **FTSC-CODE:**

<sup>1)</sup> FTSC-Code according to ISO 5145 (1990), including a number of revised fire potential codes (F = Fire potential; T = Toxicity; S = Gas state in the cylinder, C = Corrosiveness)

#### **Fire potential**

- F0** inert gas
- F1** supports combustion having an oxipotential equal or less than air
- F2** flammable gas having explosion limits in air
- F3** spontaneously flammable
- F4** highly oxidizing having an oxipotential greater than that of air
- F5** flammable and subject for decomposition or polymerisation

#### **Toxicity**

- T1** non-toxic (over 500 ppm in air permitted for an 8h exposure)
- T2** toxic (50 ppm to 500 ppm in air permitted for an 8h exposure)
- T3** very toxic (less than 50 ppm in air permitted for an 8h exposure)

#### **State of the gas in the cylinder at 15°C**

- S0** liquefied at 35 bar or less
- S1** liquefied over 35 bar
- S2** liquid withdrawal – liquefied gas (optional)
- S3** dissolved gas
- S4** gas phases withdrawal at 35 bar or less
- S5** permanent gas between 35 bar and 300 bar
- S6** permanent gas between 35 bar and 200 bar
- S7** permanent gas above 200 bar or 300 bar

#### **Corrosiveness**

- C0** non-corrosive
- C1** non-halogen acid forming
- C2** basic
- C3** halogen acid forming

### **VAPOUR PRESSURE:**

<sup>2)</sup> Vapour pressures at + 5°C according to the German TRG 102, annex 2, recognizing that other temperatures may be used (e.g. : - 10°C) as mentioned in the text.



Gas	FTSC Code <sup>1)</sup>	Vapour pressure <sup>2)</sup>	Acetylene	Air	Ammonia	Argon	Arsine		Boron trichloride	Boron trifluoride	Butadiene	n-Butane	Butene-1	Butene-2 (cis)	Butene-2 (trans)		Carbon dioxide	Carbon monoxide	Carbonyl dichloride	Carbonyl fluoride	Chlorine	Cyanogen	Cyanogen chloride	Cyclopropane	Deuterium
Acetylene	5130	31,2		■	■	■	■		■	■	■	■	■	■	■		■	■	■	■	■	■	■	■	■
Air	1150	-	■		O	X	■				■	O	O	O	O		X	O			X	■	■	■	O
Ammonia	0202	5,3	■	O		X			■	■	■	X	X	X	X		■	■	■	■	■	■	■	X	X
Argon	0150	-	■	X	X		X		X	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X
Arsine	2300		■	■		X											■				■				X
Boron trichloride	0203	0,8	■		■	X					■		■	■	■									■	■
Boron trifluoride	0253	-	■		■	X					■		■	■	■									■	■
Butadiene	5100	1,5	■	■	■	X			■	■		X	X	X	X		X	X	■	■	■		■	X	X
n-Butane	2100	1,3	■	O	X	X					X		X	X	X		X	X	■	■	■	X	■	X	X
Butene-1	2100	1,6	■	O	X	X			■	■	X	X		X	X		X	X	■	■	■	X	■	X	X
Butene-2 (cis)	2100	1,1	■	O	X	X			■	■	X	X	X		X		X	X	■	■	■	X	■	X	X
Butene-2 (trans)	2100	1,2	■	O	X	X			■	■	X	X	X	X			X	X	■	■	■	X	■	X	X
Carbon dioxide	0110	40,4	■	X	■	X	■				X	X	X	X	X			X	X	X				X	X
Carbon monoxide	2250	-	■	O	■	X					X	X	X	X	X		X				■			X	X
Carbonyl dichloride	0303	0,9	■		■	X					■	■	■	■	■		X				X			■	
Carbonyl fluoride	0213		■		■	X					■	■	■	■	■		X				X			■	
Chlorine	4203	4,4	■	X	■	X	■				■	■	■	■	■			■	X	X		■		■	■
Cyanogen	2300		■	■	■	X						X	X	X	X						■			X	X
Cyanogen chloride	0303	0,8	■		■	X					■	■	■	■	■									■	
Cyclopropane		4,2	■	■	X	X					X	X	X	X	X		X	X	■	■	■	X	■		X
Deuterium	2150	-	■	O	X	X	X				X	X	X	X	X		X	X			■	X		X	
Diborane	5350		■	■	■	X	■				■	■	■	■	■		■	■	■	■	■	■	■	■	■
Dimethylamine	2202	1,0	■	O	X	X			■	■	■	X	X	X	X		■	■	■	■	■	■		X	X
Dimethyl ether	2100	3,2	■	O	X	X					X	X	X	X	X		X	X			■			X	X
Dimethylsilane	2300	2,5	■	■		X						X	X	X	X				■	■	■			X	X
Ethane	2110	27,4	■	O	X	X					X	X	X	X	X		X	X	■	■	■	X	■	X	X
Ethylamine	2202	0,6	■	O	X	X			■	■	■	X	X	X	X		■	■	■	■	■	■	■	X	X
Ethylene	2150	46,7	■	■	X	X			■	■	X	X	X	X	X		X	X	■	■	■	X	■	X	X
Ethylene oxide	5200	0,8	■	■	■	X			■	■	■	X	X	X	X		X		■	■	■		■	X	
Fluorine	4343	-	■	■	■	■	■		■	■	■	■	■	■	■		■	■	■	■	■	■	■	■	■
Germane	2300		■	■	■	■	■		■	■	■	■	■	■	■		■	■	■	■	■	■	■	■	■
Helium	0150	-	■	X	X	X	X		X	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X
Hydrogen	2150	-	■	O	X	X	X				X	X	X	X	X		X	X			■	X		X	X
Hydrogen bromide	0203	14,6	■	■	■	X					■	X	■	■	■		X				■			■	X
Hydrogen chloride	0213	30,5	■	■	■	X					■	X	■	■	■		X				X			■	X
Hydrogen cyanide	5301	0,4	■	■	■	X						X	X	X	X						■			X	X
Hydrogen sulfide	2301	12,4	■	O	■	X						X	X	X	X		X				■			X	X
Isobutane	2100	1,9	■	O	X	X					X	X	X	X	X		X	X	■	■	■	X	■	X	X
Isobutene	2100	1,6	■	O	X	X					X	X	X	X	X		X	X	■	■	■	X	■	X	X
Krypton	0150	-	■	X	X	X	X		X	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X
Mercaptomethane	2201	1,0	■	O	■	X						X	X	X	X		X		■	■	■			X	X
Methane	2150	-	■	O	X	X					X	X	X	X	X		X	X	■	■	■	X	■	X	X

Gas	Diborane	Dimethylamine	Dimethyl ether	Dimethylsilane		Ethane	Ethylamine	Ethylene	Ethylene oxide		Fluorine		Germane		Helium	Hydrogen	Hydrogen bromide	Hydrogen chloride	Hydrogen cyanide	Hydrogen sulfide		Isobutane	Isobutene		Krypton		Mercaptomethane	Methane	Methylamine
Acetylene	■	■	■	■		■	■	■	■	■	■		■		■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Air	■	○	○	■		○	○	■	■		■		■		×	○	■	■	■	○		○	○		×		○	○	○
Ammonia	■	×	×			×	×	×	■		■		■		×	×	■	■	■	■		×	×		×		■	×	×
Argon	■	×	×	×		×	×	×	×		■		■		×	×	×	×	×	×		×	×		×		×	×	×
Arsine	■												■		×	×									×				
											■																		
Boron trichloride	■	■					■	■	■		■		■		×										×				■
Boron trifluoride	■	■					■	■	■		■		■		×										×				■
Butadiene	■	■	×			×	■	×	■		■		■		×	×	■	■				×	×	×			×	×	■
n-Butane	■	×	×	×		×	×	×	×		■		■		×	×	×	×	×	×	×	×	×	×	×	×	×	×	×
Butene-1	■	×	×	×		×	×	×	×		■		■		×	×	■	■	×	×	×	×	×	×	×	×	×	×	×
Butene-2 (cis)	■	×	×	×		×	×	×	×		■		■		×	×	■	■	×	×	×	×	×	×	×	×	×	×	×
Butene-2 (trans)	■	×	×	×		×	×	×	×		■		■		×	×	■	■	×	×	×	×	×	×	×	×	×	×	×
Carbon dioxide	■	■	×			×	■	×	×		■		■		×	×	×	×		×		×	×	×	×	×	×	×	■
Carbon monoxide	■	■	×			×	■	×			■		■		×	×						×	×	×	×		×	×	■
Carbonyl dichloride	■	■		■		■	■	■	■				■		×							■	■	×			■	■	■
Carbonyl fluoride	■	■		■		■	■	■	■				■		×							■	■	×			■	■	■
Chlorine	■	■	■	■		■	■	■	■		■		■		×	■	■	×	■	■	■	■	■	■	×		■	■	■
Cyanogen	■					×		×			■		■		×	×						×	×	×	×		×		■
Cyanogen chloride	■					■	■	■	■		■		■		×							■	■	×			■	■	■
Cyclopropane	■	×	×	×		×	×	×	×		■		■		×	×	■	■	×	×		×	×	×	×	×	×	×	×
Deuterium	■	×	×	×		×	×	×			■		■		×	×	×	×	×	×	×	×	×	×	×	×	×	×	×
Diborane		■	■	■		■	■	■	■		■		■		■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Dimethylamine	■		×			×	×	×	■		■		■		×	×	■	■		■		×	×	×	×		■	×	×
Dimethyl ether	■	×				×	×	×			■		■		×	×	■	■				×	×	×	×			×	×
Dimethylsilane	■					×		×			■		■		×							×	×	×	×			×	
Ethane	■	×	×	×			×	×	×		■		■		×	×	×	×	×	×	×	×	×		×	×	×	×	×
Ethylamine	■	×	×			×		×	■		■		■		×	×	■	■		■		×	×	×	×		■	×	×
Ethylene	■	×	×	×		×	×		×		■		■		×	×	■	■	×	×		×	×	×	×	×	×	×	×
Ethylene oxide	■	■				×	■	×			■		■		×		■	■		■		×	×	×	×		■	×	■
Fluorine	■	■	■	■		■	■	■	■			■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Germane	■	■	■	■		■	■	■	■		■				■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Helium	■	×	×	×		×	×	×	×		■		■			×	×	×	×	×	×		×	×	×	×	×	×	×
Hydrogen	■	×	×			×	×	×			■		■		×		×	×	×	×	×		×	×	×	×	×	×	×
Hydrogen bromide	■	■	■			×	■	■	■		■		■		×	×		×				×	■	×			×	×	■
Hydrogen chloride	■	■	■			×	■	■	■		■		■		×	×	×					×	■	×			×	×	■
Hydrogen cyanide	■					×		×			■		■		×	×						×	×	×	×		×	×	■
Hydrogen sulfide	■	■				×	■	×	■		■		■		×	×						×	×	×	×		×	×	■
Isobutane	■	×	×	×		×	×	×	×		■		■		×	×	×	×	×	×	×		×		×		×	×	×
Isobutene	■	×	×	×		×	×	×	×		■		■		×	×	■	■	×	×	×	×		×		×	×	×	×
Krypton	■	×	×	×		×	×	×	×		■		■		×	×	×	×	×	×	×		×	×			×	×	×
Mercaptomethane	■	■				×	■	×	■		■		■		×	×						×	×	×	×			×	■
Methane	■	×	×	×		×	×	×	×		■		■		×	×	×	×	×	×	×	×	×	×	×	×	×	×	×

Gas	Methylsilane	Monosilane	Neon	Nitric oxide	Nitrogen	Nitrogen dioxide	Nitrous oxide	Nitrogen trifluoride	Oxygen	Ozone	Phosphine	Propane	Propylene	R12	R12B1	R13	R13B1	R14	R21	R22	R23	R40	R40B1	R114	R115
Acetylene	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Air	■	■	X	■	X	X	X	X	X	■	■	O	O	X	X	X	X	X	■	■	■	■	■	X	X
Ammonia			X	■	X	■	■	■	O	■	■	X	X												
Argon	X	X	X	X	X	X	X	X	X	■	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Arsine			X	■	X	■	■	■	■	■															
Boron trichloride			X		X					■															
Boron trifluoride			X		X					■															
Butadiene			X	■	X	■	■	■	■	■	■	X	X												
n-Butane	X	X	X	■	X	■	■	■	O	■	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Butene-1			X	■	X	■	■	■	O	■		X	X	X	X	X	X	X	X	X	X	X	X	X	X
Butene-2 (cis)			X	■	X	■	■	■	O	■		X	X	X	X	X	X	X	X	X	X	X	X	X	X
Butene-2 (trans)			X	■	X	■	■	■	O	■		X	X	X	X	X	X	X	X	X	X	X	X	X	X
Carbon dioxide			X	X	X	X	X	X	X	■		X	X	X	X	X	X	X	X	X	X	X	X	X	X
Carbon monoxide			X	■	X	■	■	■	O	■		X	X												
Carbonyl dichloride	■	■	X		X					■		■	■												
Carbonyl fluoride	■	■	X		X					■		■	■												
Chlorine	■	■	X		X					■		■	■					■	■	■	■	■			
Cyanogen			X	■	X	■	■	■	■	■		X	X												
Cyanogen chloride	■	■	X		X					■		■	■												
Cyclopropane			X	■	X	■	■	■	■	■		X	X	X	X	X	X	X	X	X	X	X	X	X	X
Deuterium	X	X	X	■	X	■	■	■	O	■	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Diborane	■	■		■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Dimethylamine		■	X	■	X	■	■	■	O	■	■	X	X												
Dimethyl ether			X	■	X	■	■	■	O	■		X	X	X	X	X	X	X	X	X	X	X	X	X	X
Dimethylsilane	X	X	X	■	X	■	■	■	■	■	X	X	X												
Ethane	X	X	X	■	X	■	■	■	O	■	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Ethylamine			X	■	X	■	■	■	O	■	■	X	X												
Ethylene			X	■	X	■	■	■	■	■		X	X	X	X	X	X	X	X	X	X	X	X	X	X
Ethylene oxide	■	■	X	■	X	■	■	■	■	■	■	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Fluorine	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Germane	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Helium	X	X	X	X	X	X	X	X	X	■	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Hydrogen	X	X	X	■	X	■	■	■	O	■	X	X	X												
Hydrogen bromide	■	■	X	■	X	■	■	■	■	■	■	X	■	X	X	X	X	X	X	X	X	X	X	X	X
Hydrogen chloride	■	■	X	■	X	■	■	■	■	■	■	X	■	X	X	X	X	X	X	X	X	X	X	X	X
Hydrogen cyanide			X	■	X	■	■	■	■	■		X	X												
Hydrogen sulfide			X	■	X	■	■	■	O	■		X	X												
Isobutane	X	X	X	■	X	■	■	■	O	■	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Isobutene			X	■	X	■	■	■	O	■		X	X	X	X	X	X	X	X	X	X	X	X	X	X
Krypton	X	X	X	X	X	X	X	X	X	■	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Mercaptomethane			X	■	X	■	■	■	O	■		X	X												
Methane	X	X	X	■	X	■	■	■	O	■	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X

Gas	R116	R125	R133a	R134a	R142b	R143a	R152a	R160	R1113	R1132a	R1140B1	R1141	R218	R227		Sulfur dioxide	Sulfur hexafluoride		Trimethylamin	Trimethylsilane		Vinyl chloride	Xenon								
Acetylene	■	■	■	■	■	■	■	■	■	■	■	■	■	■		■	■		■	■		■	■								
Air	X	■	■	■	■	■	■	■	■	■	■	■	X	■		X	X		O	■		■	X								
Ammonia																■			X				X								
Argon	X	X	X	X	X	X	X	X	X	X	X	X	X	X		X	X		X	X		X	X								
Arsine																							X								
Boron trichloride																			■			■	X								
Boron trifluoride																			■			■	X								
Butadiene									■	■	■	■				■			■			■	X								
n-Butane	X	X	X	X	X	X	X	X					X	X		X			X	X		X	X								
Butene-1	X	X	X	X	X	X	X	X					X	X					X			X	X								
Butene-2 (cis)	X	X	X	X	X	X	X	X					X	X					X			X	X								
Butene-2 (trans)	X	X	X	X	X	X	X	X					X	X					X			X	X								
Carbon dioxide	X	X	X	X	X	X	X	X					X	X		X	X		■				X								
Carbon monoxide																			■				X								
Carbonyl dichloride																			■	■			X								
Carbonyl fluoride																			■	■			X								
Chlorine		■	■	■	■	■	■	■	■	■	■	■		■		■			■	■		■	X								
Cyanogen																							X								
Cyanogen chloride																							X								
Cyclopropane	X	X	X	X	X	X	X	X					X	X					X				X								
Deuterium	X	X	X	X	X	X	X	X					X	X					X	X			X								
Diborane	■	■	■	■	■	■	■	■	■	■	■	■	■	■		■	■		■	■		■	■								
Dimethylamine																■			X			■	X								
Dimethyl ether	X	X	X	X	X	X	X	X					X	X					X				X								

Gas	FTSC Code <sup>1)</sup>	P <sub>vap</sub> ,+5°C <sup>2)</sup> in bar(a)	Acetylene	Air	Ammonia	Argon	Arsine		Boron trichloride	Boron trifluoride	Butadiene	n-Butane	Butene-1	Butene-2 (cis)	Butene-2 (trans)		Carbon dioxide	Carbon monoxide	Carbonyl dichloride	Carbonyl fluoride	Chlorine	Cyanogen	Cyanogen chloride	Cyclopropane		Deuterium
Methylamine	2202	1,7	■	○	X	X			■	■	■	X	X	X	X		■	■	■	■	■		■	X		X
Methylsilane	2300	9,2	■	■		X						X							■	■	■		■			X
Monosilane	3150	-	■	■		X						X							■	■	■		■			X
Neon	0150	-	■	X	X	X	X		X	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X
Nitric oxide	4351	-	■	■	■	X	■				■	■	■	■	■		X	■				■	■			■
Nitrogen	0150	-	■	X	X	X	X		X	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X
Nitrogen dioxide	4301	0,5	■	X	■	X	■				■	■	■	■	■		X	■				■	■			■
Nitrous oxide	4110	35,9	■	X	■	X	■				■	■	■	■	■		X	■				■	■			■
Nitrogen trifluoride	4XXX		■	X	■	X	■				■	■	■	■	■			■				■	■			■
Oxygen	4150	-	■	X	○	X	■				■	○	○	○	○		X	○				■		■		○
Ozone	4330		■	■	■	■	■		■	■	■	■	■	■	■		■	■	■	■	■	■	■	■	■	■
Phosphine	3310	25,2	■	■	■	X					■	X									■					X
Propane	2100	5,6	■	○	X	X					X	X	X	X	X		X	X	■	■	■	X	■	X		X
Propylene	2100	6,9	■	○	X	X					X	X	X	X	X		X	X	■	■	■	X	■	X		X
R12	0100	3,7	■	X		X						X	X	X	X		X							X		X
R12B1	0100	1,6	■	X		X						X	X	X	X		X							X		X
R13	0100	22,7	■	X		X						X	X	X	X		X							X		X
R13B1	0100	10,0	■	X		X						X	X	X	X		X							X		X
R14	0150		■	X		X						X	X	X	X		X							X		X
R21	0100	0,9	■	■		X						X	X	X	X		X				■			X		X
R22	0100	6,0	■	■		X						X	X	X	X		X				■			X		X
R23	0100	29,3	■	■		X						X	X	X	X		X				■			X		X
R40	2200	3,1	■	■		X						X	X	X	X		X				■			X		X
R40B1	2300	1,1	■	■		X						X	X	X	X		X				■			X		X
R114	0100	1,1	■	X		X						X	X	X	X		X							X		X
R115	0100	5,3	■	X		X						X	X	X	X		X							X		X
R116	0100		■	X		X						X	X	X	X		X							X		X
R125	0100		■	■		X						X	X	X	X		X				■			X		X
R133a	0100	1,1	■	■		X						X	X	X	X		X				■			X		X
R134a	0100		■	■		X						X	X	X	X		X				■			X		X
R142b	2100	1,8	■	■		X						X	X	X	X		X				■			X		X
R143a	2100	7,4	■	■		X						X	X	X	X		X				■			X		X
R152a	2100	3,3	■	■		X						X	X	X	X		X				■			X		X
R160	2100	0,8	■	■		X						X	X	X	X		X				■			X		X
R1113	5200	3,6	■	■		X					■										■					
R1132a	5100	26,0	■	■		X					■										■					
R1140B1	5200	0,7	■	■		X					■										■					
R1141	5100	16,8	■	■		X					■										■					
R218	0100		■	X		X						X	X	X	X		X							X		X
R227	0100		■	■		X						X	X	X	X		X				■			X		X
Sulfur dioxide	0201	1,9	■	X	■	X					■	X					X				■					
Sulfur hexafluoride	0100	14,6	■	X		X											X									
Triméthylamine	2202	1,1	■	○	X	X			■	■	■	X	X	X	X		■	■	■	■	■			X		X
Trimethylsilane	2300	0,8	■	■		X						X	X	X	X				■	■	■					X
Vinyl chloride	5200	2,1	■	■	■	X					■	X									■					
Xenon	0150	46,9	■	X	X	X	X		X	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X

Gas	Diborane	Dimethylamine	Dimethyl ether	Dimethylsilane		Ethane	Ethylamine	Ethylene	Ethylene oxide		Fluorine	Germane		Helium	Hydrogen	Hydrogen bromide	Hydrogen chloride	Hydrogen cyanide	Hydrogen sulfide		Isobutane	Isobutene		Krypton		Mercaptomethane	Methane	Methylamine
Methylamine	■	X	X			X	X	X	■		■	■		X	X	■	■		■		X	X		X		■	X	
Methylsilane	■			X		X			■		■	■		X	X	■	■				X			X			X	
Monosilane	■	■		X		X			■		■	■		X	X	■	■				X			X			X	■
Neon	■	X	X	X		X	X	X	X		■	■		X	X	X	X	X	X	X		X	X		X		X	X
Nitric oxide	■	■	■	■		■	■	■	■		■	■		X	■	■	■	■	■	■		■	■		X		■	■
Nitrogen	■	X	X	X		X	X	X	X		■	■		X	X	X	X	X	X	X		X	X		X		X	X
Nitrogen dioxide	■	■	■	■		■	■	■	■		■	■		X	■	■	■	■	■	■		■	■		X		■	■
Nitrous oxide	■	■	■	■		■	■	■	■		■	■		X	■	■	■	■	■	■		■	■		X		■	■
Nitrogen trifluoride	■	■	■	■		■	■	■	■		■	■		X	■	■	■	■	■	■		■	■		X		■	■
Oxygen	■	O	O	■		O	O	■	■		■	■		X	O	■	■	■	O		O	O		X		O	O	O
Ozone	■	■	■	■		■	■	■	■		■	■		■	■	■	■	■	■	■		■	■		■		■	■
Phosphine	■	■		X		X	■		■		■	■		X	X	■	■				X			X			X	■
Propane	■	X	X	X		X	X	X	X		■	■		X	X	X	X	X	X	X		X	X		X		X	X
Propylene	■	X	X	X		X	X	X	X		■	■		X	X	■	■	X	X		X	X		X		X	X	X
R12	■		X			X		X	X		■	■		X		X	X				X	X		X			X	
R12B1	■		X			X		X	X		■	■		X		X	X				X	X		X			X	
R13	■		X			X		X	X		■	■		X		X	X				X	X		X			X	
R13B1	■		X			X		X	X		■	■		X		X	X				X	X		X			X	
R14	■		X			X		X	X		■	■		X		X	X				X	X		X			X	
R21	■		X			X		X	X		■	■		X		X	X				X	X		X			X	
R22	■		X			X		X	X		■	■		X		X	X				X	X		X			X	
R23	■		X			X		X	X		■	■		X		X	X				X	X		X			X	
R40	■		X			X		X	X		■	■		X		X	X				X	X		X			X	
R40B1	■		X			X		X	X		■	■		X		X	X				X	X		X			X	
R114	■		X			X		X	X		■	■		X		X	X				X	X		X			X	
R115	■		X			X		X	X		■	■		X		X	X				X	X		X			X	
R116	■		X			X		X	X		■	■		X		X	X				X	X		X			X	
R125	■		X			X		X	X		■	■		X		X	X				X	X		X			X	
R133a	■		X			X		X	X		■	■		X		X	X				X	X		X			X	
R134a	■		X			X		X	X		■	■		X		X	X				X	X		X			X	
R142b	■		X			X		X	X		■	■		X		X	X				X	X		X			X	
R143a	■		X			X		X	X		■	■		X		X	X				X	X		X			X	
R152a	■		X			X		X	X		■	■		X		X	X				X	X		X			X	
R160	■		X			X		X	X		■	■		X		X	X				X	X		X			X	
R1113	■										■	■		X		■	■	■						X				
R1132a	■										■	■		X		■	■	■						X				
R1140B1	■										■	■		X		■	■	■						X				
R1141	■										■	■		X		■	■	■						X				
R218	■		X			X		X	X		■	■		X		X	X				X	X		X			X	
R227	■		X			X		X	X		■	■		X		X	X				X	X		X			X	
Sulfur dioxide	■	■				X	■		■		■	■		X					■		X			X			X	■
Sulfur hexafluoride	■					X					■	■		X										X				
Triméthylamine	■	X	X			X	X	X	■		■	■		X	X	■	■		■		X	X		X		■	X	X
Trimethylsilane	■			X		X			■		■	■		X	X	■	■				X	X		X			X	
Vinyl chloride	■	■				X	■		■		■	■		X		■	■	■			X			X			X	■
Xenon	■	X	X	X		X	X	X	X		■	■		X	X	X	X	X	X	X		X	X		X		X	X

Gas	Methylsilane	Monosilane	Neon	Nitric oxide	Nitrogen	Nitrogen dioxide	Nitrous oxide	Nitrogen trifluoride	Oxygen	Ozone	Phosphine	Propane	Propylene	R12	R12B1	R13	R13B1	R14	R21	R22	R23	R40	R40B1	R114	R115
Methylsilane		X	X	■	X	■	■	■	■	■	X	X													
Monosilane	X		X	■	X	■	■	■	■	■	X	X													
Neon	X	X		X	X	X	X	X	X	■	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Nitric oxide	■	■	X		X	X	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Nitrogen	X	X	X	X	X	X	X	X	X	■	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Nitrogen dioxide	■	■	X	X	X		■		X	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Nitrous oxide	■	■	X	X	X		■		X	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Nitrogen trifluoride	■	■	X	■	X		■			■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Oxygen	■	■	X	■	X	X	X			■	■	O	O	■	■	■	■	X	■	■	■	■	■	■	■
Ozone	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Phosphine	X	X	X	■	X	■	■	■	■	■		X													
Propane	X	X	X	■	X	■	■	■	O	■		X	X	X	X	X	X	X	X	X	X	X	X	X	X
Propylene			X	■	X	■	■	■	O	■		X		X	X	X	X	X	X	X	X	X	X	X	X
R12			X	■	X	■	■	■	■	■		X	X		X	X	X	X	X	X	X	X	X	X	X
R12B1			X	■	X	■	■	■	■	■		X	X	X	X	X	X	X	X	X	X	X	X	X	X
R13			X	■	X	■	■	■	■	■		X	X	X	X	X	X	X	X	X	X	X	X	X	X
R13B1			X	■	X	■	■	■	■	■		X	X	X	X	X	X	X	X	X	X	X	X	X	X
R14			X	■	X	■	■	■	X	■		X	X	X	X	X	X		X	X	X	X	X	X	X
R21			X	■	X	■	■	■	■	■		X	X	X	X	X	X	X		X	X	X	X	X	X
R22			X	■	X	■	■	■	■	■		X	X	X	X	X	X	X	X		X	X	X	X	X
R23			X	■	X	■	■	■	■	■		X	X	X	X	X	X	X	X	X		X	X	X	X
R40			X	■	X	■	■	■	■	■		X	X	X	X	X	X	X	X	X	X		X	X	X
R40B1			X	■	X	■	■	■	■	■		X	X	X	X	X	X	X	X	X	X	X		X	X
R114			X	■	X	■	■	■	■	■		X	X	X	X	X	X	X	X	X	X	X	X		X
R115			X	■	X	■	■	■	■	■		X	X	X	X	X	X	X	X	X	X	X	X	X	
R116			X	■	X	■	■	■	■	■		X	X	X	X	X	X	X	X	X	X	X	X	X	X
R125			X	■	X	■	■	■	■	■		X	X	X	X	X	X	X	X	X	X	X	X	X	X
R133a			X	■	X	■	■	■	■	■		X	X	X	X	X	X	X	X	X	X	X	X	X	X
R134a			X	■	X	■	■	■	■	■		X	X	X	X	X	X	X	X	X	X	X	X	X	X
R142b			X	■	X	■	■	■	■	■		X	X	X	X	X	X	X	X	X	X	X	X	X	X
R143a			X	■	X	■	■	■	■	■		X	X	X	X	X	X	X	X	X	X	X	X	X	X
R152a			X	■	X	■	■	■	■	■		X	X	X	X	X	X	X	X	X	X	X	X	X	X
R160			X	■	X	■	■	■	■	■		X	X	X	X	X	X	X	X	X	X	X	X	X	X
R1113			X	■	X	■	■	■	■	■		X													
R1132a			X	■	X	■	■	■	■	■		X													
R1140B1			X	■	X	■	■	■	■	■		X													
R1141			X	■	X	■	■	■	■	■		X													
R218			X	■	X	■	■	■	■	■		X	X	X	X	X	X	X	X	X	X	X	X	X	X
R227			X	■	X	■	■	■	■	■		X	X	X	X	X	X	X	X	X	X	X	X	X	X
Sulfur dioxide			X	■	X	■	■	■		■															
Sulfur hexafluoride			X		X					■															
Triméthylamine		■	X	■	X	■	■	■	O	■	■	X	X												
Trimethylsilane	X	X	X	■	X	■	■	■	■	■		X	X												
Vinyl chloride			X	■	X	■	■	■	■	■															
Xenon	X	X	X	X	X	X	X	X	X	■	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X





### Appendix 3: List of unstable gases

List of unstable (decomposable) gases according to "Unfallverhütungsvorschrift BGV B6 „Gase“, Carl Heymanns Verlag, Koeln, Ausgabe 1999b"

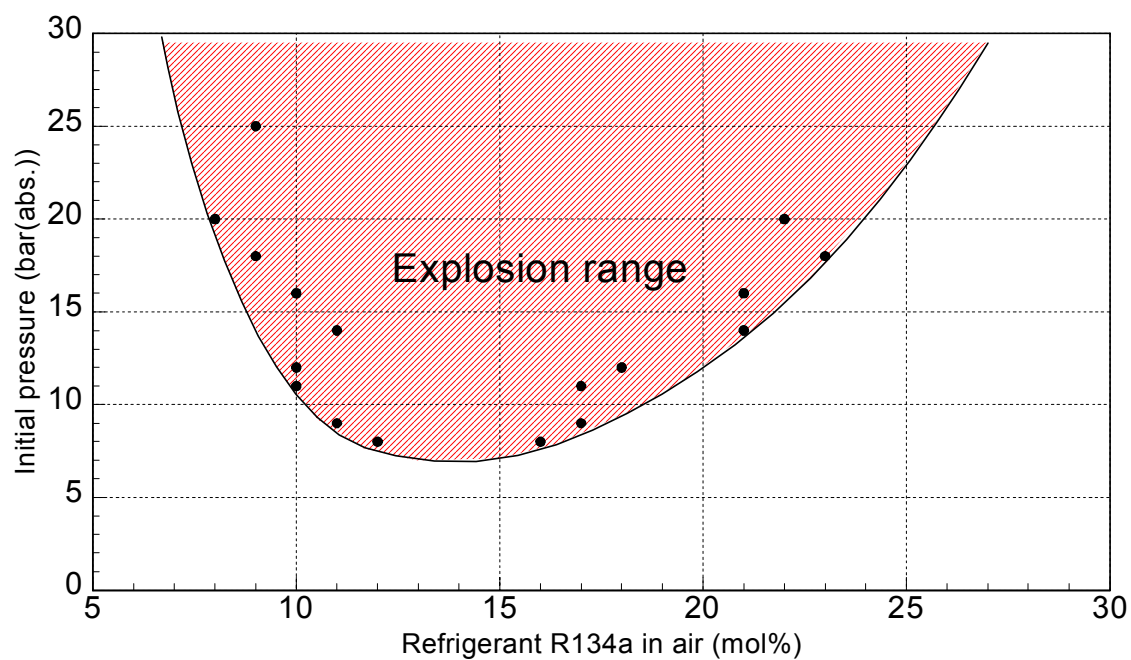
No.	Gas name	Formula	CAS-No.	$\Delta G_f$ (25 °C; 1,013 bar) in J mol <sup>-1</sup>
01	Acetylene	HC≡CH	74-86-2	2,093 E+5
02	Bromo trifluoroethylene(1)	BrFC=CF <sub>2</sub>	598-73-2	
03	Butadiene-1,2 (1)	H <sub>2</sub> C=C=CH-CH <sub>3</sub>	590-19-2	1,986 E+5
04	Butadiene-1,3 (1)	H <sub>2</sub> C=CH-CH=CH <sub>3</sub>	106-99-0	1,508 E+5
05	Ethyl acetylene (1)	H <sub>3</sub> C-CH <sub>2</sub> -C≡CH	107-00-6	2,022 E+5
06	Chloro cyanide (1)	N≡CCl	506-77-4	
07	Chloro trifluoroethylene (1)	ClFC=CF <sub>2</sub>	79-38-9	
08	Hydrogen cyanide (1)	HC≡N	74-90-8	1,202 E+5
09	Diborane (1)	H <sub>2</sub> B:H <sub>2</sub> :BH <sub>2</sub>	19287-45-7	
10	Cyanogen (1)	N≡C-C≡N	460-19-5	2,974 E+5
11	1,1-Difluoro ethylene (1)	F <sub>2</sub> C=CH <sub>2</sub>	75-38-7	-3,217 E+5
12	Nitrous oxide (2)	N <sub>2</sub> O	10204-97-2	1,037 E+5
13	Ethylene (1)	H <sub>2</sub> C=CH <sub>2</sub>	74-85-1	6,816 E+4
14	Ethylene oxide	H <sub>2</sub> C-O-CH <sub>2</sub>	75-21-8	-1,310 E+4
15	Hydrogen iodide (1)	HI	10034-85-2	1,59 E+3
16	Methyl nitrite	H <sub>3</sub> C-ON:O	624-91-9	
17	Methyl vinyl ether (1)	H <sub>3</sub> C-O-HC=CH <sub>2</sub>	107-25-5	
18	Ozone	O <sub>3</sub>	10028-15-6	1,629 E+5
19	Propadiene (1)	H <sub>2</sub> C=C=CH <sub>2</sub>	463-49-0	2,02 E+5
20	Propylene (1)	HC≡C-CH <sub>3</sub>	74-99-7	1,94 E+5
21	Stibine	SbH <sub>3</sub>	7803-52-3	
22	Nitric oxide (1)	NO	10102-43-9	8,675 E+4
23	Tetrafluoro ethylene (1)	F <sub>2</sub> C=CF <sub>2</sub>	116-14-3	-6,241 E+5
24	Tetrafluoro hydrazine (1)	F <sub>2</sub> N-NF <sub>2</sub>	10036-47-2	7,988 E+4
25	Vinyl bromide (1)	BrHC=CH <sub>2</sub>	593-60-2	
26	Vinyl chloride (1)	ClHC=CH <sub>2</sub>	75-01-4	5,154 E+4
27	Vinyl fluoride (1)	FHC=CH <sub>2</sub>	75-02-5	

(1) unstable at elevated conditions;

(2) difficult to ignite unstable gas;

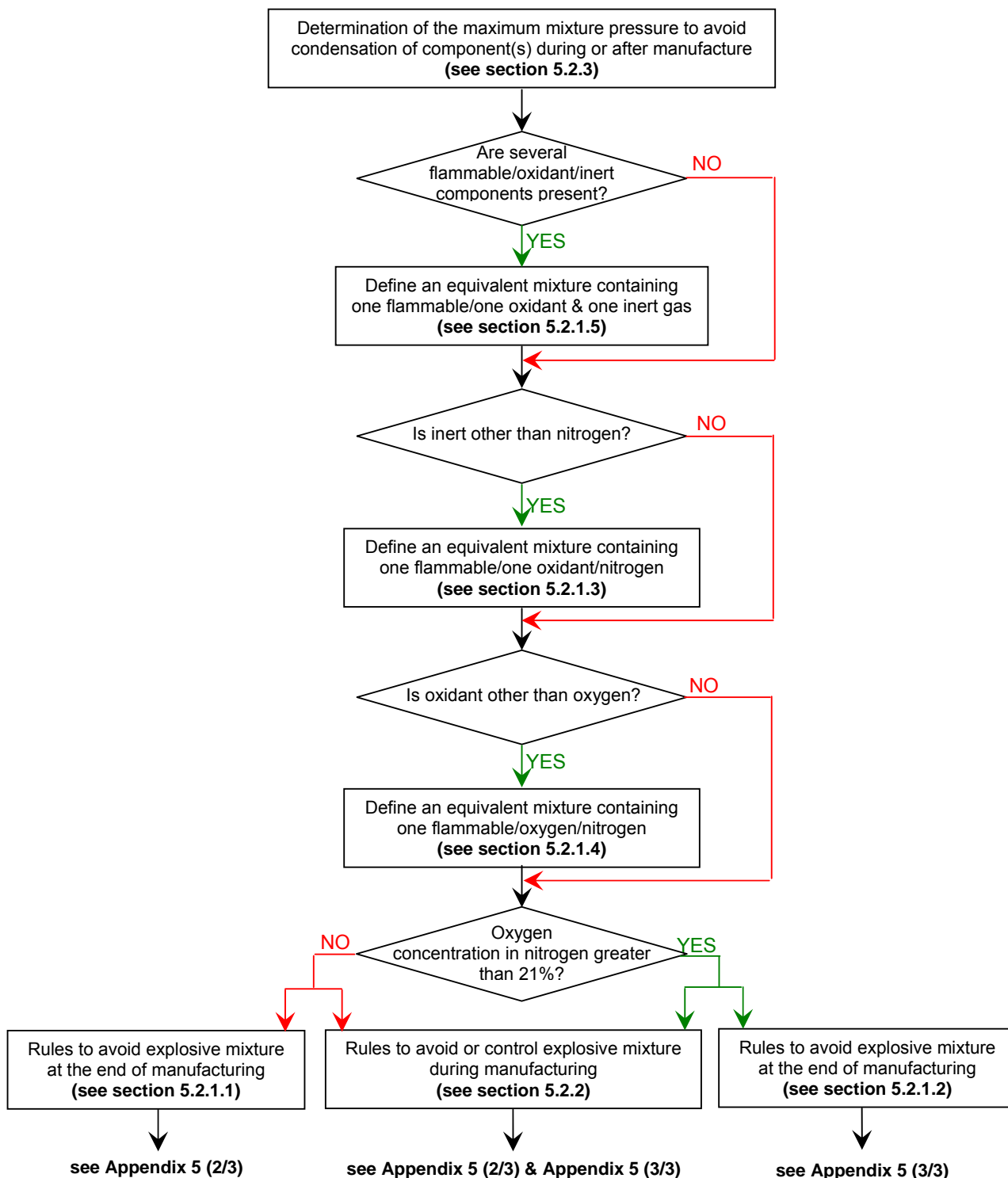
$\Delta G_f$  free enthalpy of formation from R. C. Reid, J. M. Prausnitz, B. E. Poling: "The Properties of Gases and Liquids", 4th edition., McGraw-Hill; New York; 1989

#### Appendix 4: Pressure dependence of explosion range



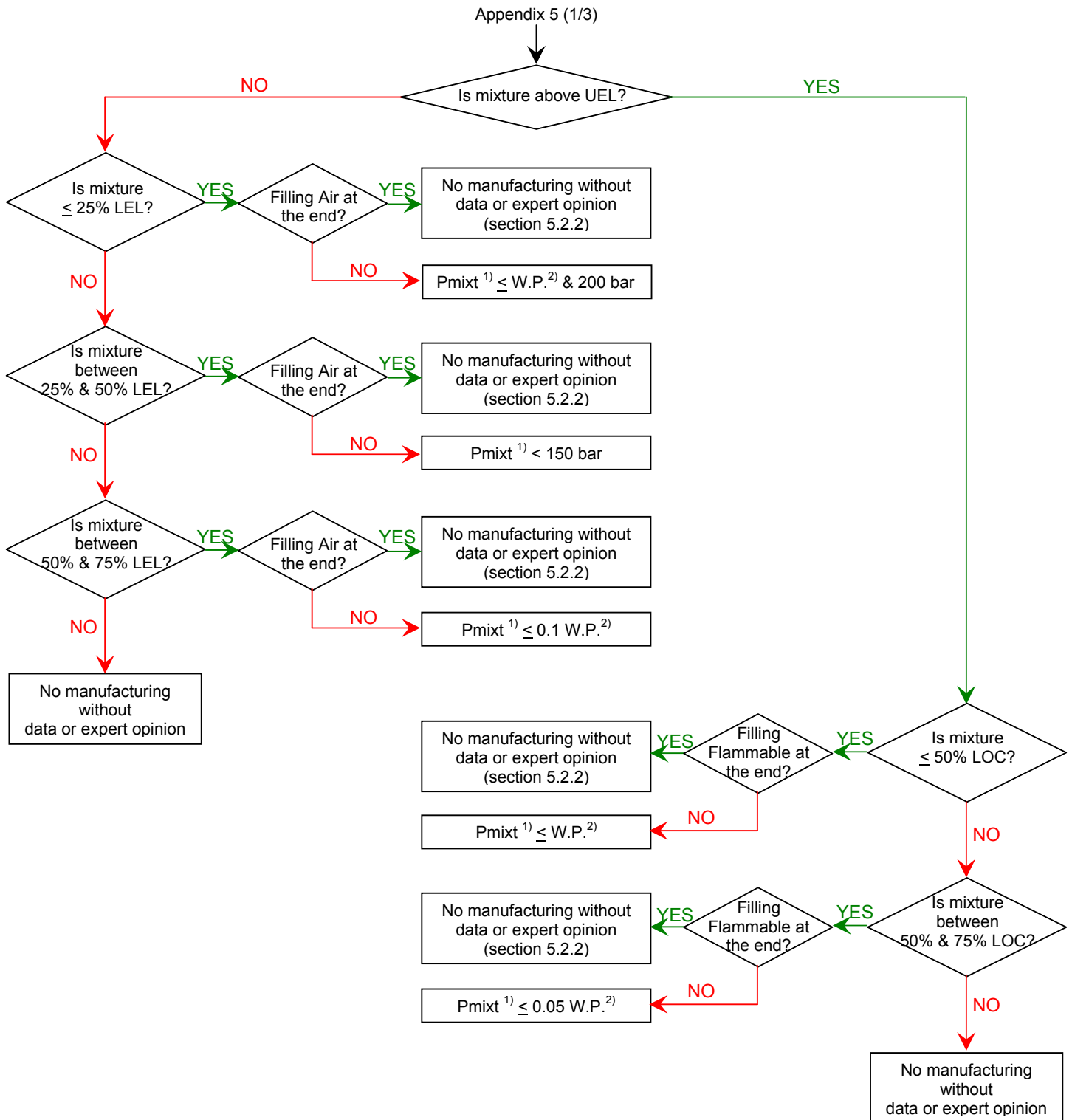
## Appendix 5 (1/3)

« Decision tree » diagram for the safe manufacturing of compressed oxidant-fuel gas mixtures



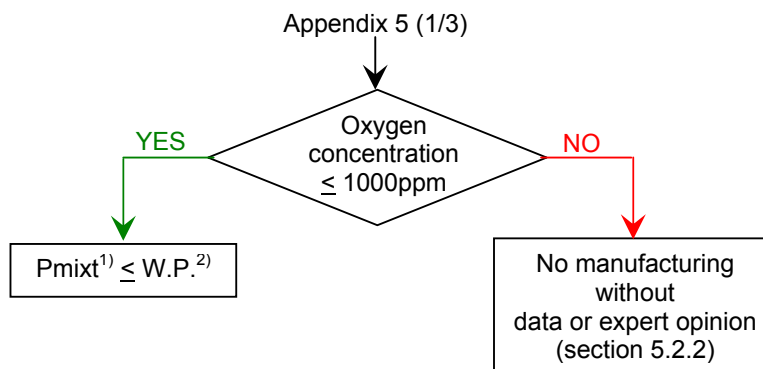
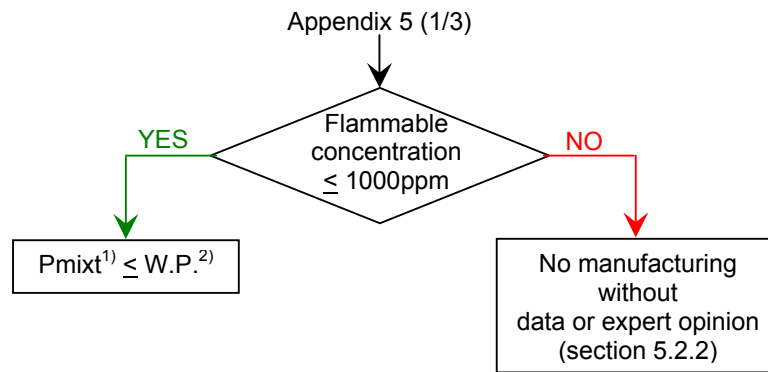
## Appendix 5 (2/3)

“Decision tree” diagram for sections 5.2.1.1 and 5.2.2



## Appendix 5 (3/3)

“Decision tree” diagram for section 5.2.1.2 and 5.2.2



- 1)  $P_{\text{mixt}}$  = Maximum mixture pressure  
2) W.P. = Cylinder Working Pressure

## Appendix 6: LOC values

Limiting oxygen concentrations (LOC) of some flammable gases from CHEMSAFE, Database of evaluated safety characteristics, Update 2004, DECHEMA, BAM und PTB, Frankfurt/M., Germany.

LOC corresponds to the Limiting Oxygen Concentration for non explosive gas mixture consisting of a flammable gas, Air and Nitrogen as inert gas at atmospheric pressure and ambient temperature.

Flammable substances	LOC in Vol.-% O <sub>2</sub>
Ammonia	12,2
Benzene	8,5
n-Butane	9,6
Butene-1	9,7
Carbon monoxide	4,7*)
Carbon sulfide	4,6
Dimethyl ether	8,5
Ethane	8,8
Ethanol	8,5
Ethylene	7,6
n-Hexane	9,1
Hydrogen	4,3
Hydrogen sulfide	9,1
Isobutane	10,3
Isobutylene	10,6
Methane	11,0
Methanol	8,1
n-Pentane	9,3
Propane	9,8
Propanol-1	9,3
Propanol-2	8,7
Propylene	9,3
Propylene oxide	7,7

\*) Data for contaminated CO with moisture or hydrocarbons which is the worst case. The combustion of very pure carbon monoxide is kinetically inhibited.

## Appendix 7: Maximum explosion pressures of flammable gas - air mixtures

Flammable substances	$p_{\max}^{1)}$ (in bar abs.)
Acetic acid	6,3
Ammonia	5,0
Acetaldehyde	8,2
Acetone	9,7
Acetylene	11,1
Benzene	9,8
n-Butane	9,4
Carbon monoxide	8,2
Cyclohexane	9,4
Dichloroethane	7,3
Dichloromethane	5,9
Diethyl ether	10,0
Dimethyl ether	9,8
1,4-dioxane	9,1
Ethanol	8,4
Ethyl acetate	9,5
Ethylene	9,7
Ethylene oxide	10,7
Heptane	9,4
Hexane	9,5
Hydrogen	8,3
Hydrogen cyanide	10,2
Hydrogen sulfide	5,9
Methane	8,1
Methanol	8,5
Methyl acetate	9,6
2-Methylbutane	9,1
Methoxyethane	9,3
n-Pentane	9,5
Propane	9,4
Propylene	9,4
Propylene oxide	9,1
Vinyl chloride	7,7

- 1)  $p_{\max}$  are the maximum experimental explosion pressures of stoichiometric flammable substance mixtures in air, initially at room temperature and atmospheric pressure, from CHEMSAFE data base. These explosion pressures correspond to deflagration and not detonation.

## Appendix 8: Audit guideline

It is recommended that facilities manufacturing compressed oxidant-fuel gas mixtures undergo periodic audits to assess their compliance with this code and with other recognised safe working practices. The nature and detail of such audits will be determined by its level of involvement with manufacturing compressed oxidant-fuel gas mixtures and compliance with local regulations.

The following checklist of items to audit is unlikely to be exhaustive, however they may provide a helpful starting point. The "Ref" column gives, where appropriate, the section of this document where more information on the checklist item may be found.

<b>1</b>	<b>Compressed oxidant-fuel gas mixtures manufacturing feasibility study</b>	<b>Ref.</b>
1a	Are there people designated as having responsibility for the formulation, review and approval of recipes?	4.1, 4.3
1b	Is there a system for approval of new recipes?	4.1, 4.3
1c	Formulation of compressed oxidant-fuel gas mixtures shall be approved by at least 1 authorized person other than the creator of the formulation (checker)	4.1, 4.3
1d	Are approved formulations of compressed oxidant-fuel gas mixtures protected against unauthorized changes?	4.1
1e	Are data sources relevant to the oxidant-fuel formulation available to personnel creators and checkers of the formulation ?	5.2. & appendices 1 to 7
1f	Do the rules applied for creating complex oxidant-fuel gas mixtures taking into account the rules as required for: <ul style="list-style-type: none"> <li>- Unstable gases</li> <li>- Pressure influence on the flammability of certain halocarbons</li> <li>- Oxidant other than oxygen and air</li> <li>- More than one flammable gas and/or more than one inert gas</li> </ul>	5.2 & appendix 4
1g	Has a study to avoid explosive mixtures or cylinder bursting during manufacturing been conducted for each formulation?	5.2.2
1h	Has a study to prevent condensation after manufacturing been conducted for each formulation?	5.2.3
1i	Does the mixture composition conform to the specified safety margins during filling?	5.2
1j	Does the mixture composition conform to the safety margins with respect to the mixture accuracy?	5.3

<b>2</b>	<b>Compressed Oxidant-Fuel gas mixtures manufacturing equipment</b>	<b>Ref.</b>
2a	Is the manufacturing site approved for the manufacture of compressed oxidant-fuel gas mixtures by the technically company competent authority?	6
2b	Has a HAZOP been conducted on the complete gas mixing equipment considering as example systems to prevent back feed? <ul style="list-style-type: none"> <li>- Between flammables and oxidants</li> <li>- Between inert and reactive gases</li> </ul>	6
2c	Has the equipment been designed to prevent simultaneous connection of flammable and oxidant gases to the cylinder being filled?	6.1, 6.2 & 6.3
2d	Are gas supplies clearly labelled to avoid operator confusion?	6.1
2e	Is a manifold purge and/or vacuum available?	6.2, 6.3 & 8.3
2f	Does the filling equipment prevent back-feed of gases into the supply gases? Is the system being checked on a regular basis	6.2 & 6.3
2g	Are appropriate adaptor control systems in use? Strict controls shall be in use for adaptors (such as RH to LH valve) enabling filling oxidizers into flammable cylinders.	4.1, 6.1
2i	Are the gas filling system components compatible with the oxidants (in particular high pressure oxygen) and to the flammable gases used?	6.1



<b>3</b>	<b>Compressed Oxidant-Fuel gas mixtures manufacturing procedures</b>	<b>Ref.</b>
3a	Are current (and relevant) work instructions available in the work area?	4.3
3b	Are the mixtures filled to approved formulation and all associated instructions? Are the instructions followed exactly?	5.2
3c	Do the filling instructions in the production sheet identify the mixture as an oxidant-fuel one?	8.1
3d	Is the production sheet in accordance with section 8.1?	8.1
3e	Has each step of filling been defined with filling amount of each component, intermediate composition confirmation if required, the method of mixing?	8.1
3f	Are critical elements of cylinder preparation and valve type specified?	7.1
3g	Are premixes clearly identified on the production sheet?	7.5 & 8.1
3h	Is the storage area for premixes clearly identified?	7.5
3i	Are premix cylinders analyzed and approved prior to use?	7.5
3j	Does the production sheet indicate the filling methods and the equipment to use?	8.1
3k	Are the pressure gauges, scales, other metering equipment regularly calibrated?	6.1
3l	Are analysis records easily retrieved and retained?	4.2
3m	Is the adjustment of non-conforming mixtures controlled?	8.5
3n	Is there a procedure for the selection of the raw materials	8.2
<b>4</b>	<b>Compressed oxidant-fuel gas mixtures manufacturing personnel qualification</b>	<b>Ref.</b>
4a	Are personnel involved in the formulation and in the preparation of oxidant-fuel mixtures suitably qualified, experienced and trained?	4.3
4b	Have the operators been signed off as competent in the filling, hazards and safety aspects of oxidant-fuel filling?	4.3
<b>5</b>	<b>Compressed oxidant-fuel gas mixtures manufacturing quality system</b>	<b>Ref.</b>
5a	Is a quality system in place	2.2
5b	Does the quality system include a documentation system	4.2, 4.3 & 8.1