



CGA P-58—2022 SAFE PREPARATION OF COMPRESSED OXIDANT-FUEL GAS MIXTURES IN CYLINDERS

THIRD EDITION

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PREFACE:

As part of a program of harmonization of industry standards, the Compressed Gas Association (CGA) has issued CGA P-58, *Safe Preparation of Compressed Oxidant-Fuel Gas Mixtures in Cylinders*, jointly produced by members of the International Harmonization Council and originally published by the European Industrial Gases Association (EIGA) as EIGA Doc 139, *Safe Preparation of Compressed Oxidant-Fuel Gas Mixtures in Cylinders*.

This publication is intended as an international harmonized standard for the worldwide use and application of all members of the Asia Industrial Gases Association (AIGA), Compressed Gas Association (CGA), European Industrial Gases Association (EIGA), and Japan Industrial and Medical Gases Association (JIMGA). Each association's technical content is identical, except for regional regulatory requirements and minor changes in formatting and spelling.

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NOTE—Technical changes from the previous edition are underlined.

NOTE—Appendices A, B, and C (Informative) are for information only.

NOTE—Appendix D (Normative) is a requirement.

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

Compressed oxidant-fuel gas mixtures can be manufactured safely provided the principles contained in this publication are followed.

2 Scope and purpose

2.1 Scope

This publication documents the minimum requirements for the safe preparation of compressed oxidant-fuel gas mixtures in cylinders by static methods (addition of one component after another in cylinders). The publication specifically addresses:

- key principles for compressed oxidant-fuel gas mixture manufacture;
- manufacturing feasibility studies;
- gas mixing equipment, filling, and analysis; and
- the audit of oxidant-fuel gas mixture manufacturing procedures and operations.

This publication specifically describes the manufacture of compressed oxidant-fuel gas mixtures under the conditions of gas temperatures and pressures detailed within this publication. The manufacture of liquefied and liquid oxidant-fuel gas mixtures is outside of the scope of this publication.

This publication shall be used in conjunction with the information and principles contained in CGA P-36, *The Safe Preparation of Gas Mixtures* [1].¹

2.2 Purpose

The purpose of the publication 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.

- 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; and
- 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.

¹ References are shown by bracketed numbers and are listed in order of appearance in the reference section.

3 Definitions

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

3.1 Publication terminology

3.1.1 Shall

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

3.1.2 Should

Indicates that a procedure is recommended.

3.1.3 May

Indicates that the procedure is optional.

3.1.4 Will

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

3.1.5 Can

Indicates a possibility or ability.

3.2 Technical definitions

3.2.1 Combustible gas/flammable gas/fuel

Gas able to undergo exothermic reaction with an oxidant when ignited.

3.2.2 Cylinder

Transportable receptacle that can be filled with gas under pressure, excluding small disposable cylinders.

3.2.3 Cylinder burst

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.

3.2.4 Cylinder burst pressure

Highest pressure reached in a cylinder during a burst test.

3.2.5 Cylinder working pressure

Highest pressure permitted to be developed during service (59° F [15° C] as defined by ADR) [2].

NOTE—In other jurisdictions, the referenced temperature may be defined slightly differently.

3.2.6 Cylinder test pressure

Required pressure applied during a pressure test for qualification or requalification.

3.2.7 Expert opinion

Opinion of a technically competent authority or person in the field of compressed oxidant-fuel gas mixture manufacturing who is not directly involved in commercial activity in this field or involved in oxidant-fuel mixture production.

3.2.8 Explosive pressure

Maximum pressure occurring in a closed vessel during the explosion of a gas mixture.

3.2.9 Explosive (flammable) limits

Concentration limits of the explosive range.

3.2.10 Explosive (flammable) range

Range of concentrations between the lower and the upper explosive limits where flame propagation can take place.

3.2.11 Hazard and operability study (HAZOP)

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 (for example, reverse flow, excessive temperature or pressure, etc.) and human error.

3.2.12 Inert gas

A gas that is non-flammable and non-oxidizing.

3.2.13 Intermediate analysis

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.

3.2.14 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.

NOTE—LOC is usually expressed as mole or volume fraction.

3.2.15 Lower explosive (flammable) limit (LEL)

Fuel lean limit of the explosive range.

3.2.16 Maximum explosive pressure

Maximum possible explosive pressure obtained by varying the concentrations of the components of a mixture (usually nearly stoichiometry).

3.2.17 Oxidant

Any gaseous material that can react with a fuel (gas, dust, or mist) to produce combustion. Oxygen in air is the most common oxidant.

3.2.18 Premix

Gas mixture that 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.

3.2.19 Safety premix

Mixture of flammable gases in inert gases where the flammable gas fraction cannot react with oxidizing gases whatever their concentrations and/or mixture of oxidizing gases in inert gases where the oxidizing gas fraction cannot react with flammable gases whatever their concentrations.

3.2.20 Upper explosive (flammable) limit (UEL)

Fuel-rich limit of the explosive range.

3.2.21 Oxy-potential coefficients

Oxidizing power related to oxygen as determined by a method specified in ISO 10156, *Gases and gas mixtures—Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets* [3].

3.2.22 Unstable gas

Gases which, under the storage and operating conditions, can be brought to an exothermic reaction by the action of energy or by the catalytic action of foreign substances, even if oxygen is excluded.

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

4.1 Precautions to avoid risks

The following precautions should be taken 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. It is advised that this substitution is discussed with the customer;
- If there is insufficient data to enable an evaluation of the explosive limits and safety margins, the mixture shall not be manufactured;
- All employees involved in production processes shall be trained and tested for proficiency;
- All computer programs 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 programs shall not be used to evaluate unknown data or to interpolate or extrapolate data;
- All computer programs shall be password protected to prevent unauthorized changes being made. Any changes to any program 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 program 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 program in order to detect any potential errors or hazards;
- Production sheet for all oxidant-fuel gas mixtures shall be formally approved following the feasibility study (for example, indication of feasibility study reference as indicated previously, signature of expert);
- 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 that can lead to a dangerous mixture;
- Safety margins shall be introduced to avoid risks when mixing oxidant and fuel gases;
- 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 (e.g., a protection wall);
- All pipes and raw materials shall be clearly labelled;
- All cylinder connection adaptors shall be controlled (see CGA P-36) [1];
- Consider backflow prevention (raw material source gas pressures greater than the pressure in the receiving cylinder); and
- Preparation of compressed oxidant-fuel gas mixtures in small size cylinders (for example, equal to or less than one liter) 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; and
- Prepare a complete production sheet before manufacturing the mixture (see 8.1 for requirements).

4.3 Organizational requirements

The manufacturing of a fuel/oxidizer mixture shall not be executed by the person who grants final approval of the feasibility, calculation, and preparation of instructions for the production of the mixture.

Persons involved in the feasibility, calculations, and preparation of instructions shall be trained, assessed, and formally appointed for these activities.

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; and
- 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 retraining 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 A.

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 (5.1);
- formulation of safe compressed oxidant-fuel gas mixtures (5.2); and
- mixture manufacturing accuracy (5.3).

5.1 Component and cylinder compatibility

The compatibility of the mixture components shall be evaluated using literature information (e.g., TRGS 407 Tätigkeiten mit Gasen - Gefährdungsbeurteilung or NOAA Expanded Chemical Reactivity Worksheet (CRW4) for determining chemical compatibility, past, present, and future) [4, 5].

The compatibility of the components with the cylinder material should also be evaluated using the information contained in ISO 11114-1, *Gas cylinders—Compatibility of cylinder and valve materials with gas contents—Part 1: Metallic materials* [6].

Unstable gases can strongly affect the explosive 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 CGA P-36, which lists some known unstable gases [1].

A number of halocarbons have no explosive limit in air under atmospheric conditions but do have at elevated pressure in air (see Appendix B) or at atmospheric pressure in pure oxygen.

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 an expert opinion on explosive limits at the filling pressure:

- oxidants with unknown oxy-potential coefficients with flammable gases;
- gases with unknown explosive (flammable) limits with oxidant gases;
- unstable flammable gases (for example, acetylene, butadiene, ethylene oxide) with oxidant gases; and
- pyrophoric products and other products such as organometallics, silane, disilane, trisilane, chlorosilanes, diborane, arsine, phosphine, and germane with oxidant gases.

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

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

Appendix C presents an evaluation method which is used in the gas industry and applied in the absence of sufficient knowledge about the combustion behavior of a specific oxy-fuel mixture under elevated pressure conditions. The principle of the evaluation method is to limit the total combustion enthalpy of an oxy-fuel mixture, so there is not enough energy present to burst a high-pressure cylinder in case of an unintentional combustion reaction.

5.2.1 To ensure non-explosive mixtures at the end of manufacture

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

The explosive 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 pressure and temperature.

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

In the absence of comprehensive data, the following rules shall be applied, taking into account:

- Lower explosive limits (LELs) in air at atmospheric pressure (see ISO 10156) [3];
- 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. For example, see ISO 10156 [3].