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Gas cylinders — Compatibility of cylinder and valve materials with gas contents —

Part 1:
Metallic materials

Bouteilles à gaz — Compatibilité des matériaux des bouteilles et des robinets avec les contenus gazeux —

Partie 1: Matériaux métalliques

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Foreword

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

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 58, *Gas cylinders*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 23, *Transportable gas cylinders*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This third edition cancels and replaces the second edition (ISO 11114-1:2012), which has been technically revised. It also incorporates the Amendment ISO 11114-1:2012/Amd.1:2017. The main changes compared to the previous edition are as follows:

— inclusion of all changes in ISO 11114-1:2012/Amd.1:2017;

— clarification of the definition of dry;

— addition of notes in Table 1.

A list of all parts in the ISO 11114 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Industrial, medical and special gases (e.g. high-purity gases, calibration gases) can be transported or stored in gas cylinders. An essential requirement of the material from which such gas cylinders and their valves are manufactured is compatibility with the gas content.

Compatibility of cylinder materials with gas content has been established over many years by practical application and experience. Existing national and international regulations and standards do not fully cover this aspect.

This document is based on current international experience and knowledge.

This document has been written so that it is suitable to be referenced in the UN Model Regulations[1].

Gas cylinders — Compatibility of cylinder and valve materials with gas contents —

Part 1: Metallic materials

1 Scope

This document provides requirements for the selection of safe combinations of metallic cylinder and valve materials and cylinder gas content.

The compatibility data given is related to single gases and to gas mixtures.

Seamless metallic, welded metallic and composite gas cylinders and their valves, used to contain compressed, liquefied and dissolved gases are considered.

NOTE In this document the term "cylinder" refers to transportable pressure receptacles, which also include tubes and pressure drums.

Aspects such as the quality of delivered gas product are not considered.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 10156, *Gas cylinders — Gases and gas mixtures — Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets*

ISO 10286, *Gas cylinders — Terminology*

ISO 10297, *Gas cylinders — Cylinder valves — Specification and type testing*

ISO 11114-2, *Gas cylinders — Compatibility of cylinder and valve materials with gas contents — Part 2: Non-metallic materials*

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

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 10286 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
competent person
person who has the necessary technical knowledge, experience and authority to assess and approve materials for use with gases and to define any special conditions of use that are necessary

3.2
acceptable
A
material/gas combination that is safe under normal conditions of use, provided that any indicated non-compatibility risks are taken into account

Note 1 to entry: Low levels of impurities can affect the acceptability of some single gases or gas mixtures.

3.3
not acceptable
N
material/single gas combination that is not safe under all normal conditions of use

Note 1 to entry: For gas mixtures special conditions may apply (see 6.2 and Table 1).

3.4
dry
state in which there is no free water in a cylinder under any service conditions, including at the highest expected operating pressure and at the lowest expected operating temperature

Note 1 to entry: For compressed gases at, for example, 200 bar and −20 °C, the maximum moisture content is not to exceed 5 ppmV, to avoid condensation of free water. For other temperatures and pressures, the maximum moisture content needed to avoid condensation of water will be different. Another source of moisture to be considered is the cylinder itself which implies appropriate drying procedures such as purging and vacuuming.

3.5
wet
state in which the conditions as defined for *dry* (3.4) are not met

3.6
gas mixture
combination of different single gases deliberately mixed in specified proportions

3.7
single gas
gas which does not contain deliberately added content of another gas or gases

4 Materials

4.1 General

The compatibility of most materials used to manufacture gas cylinders and valves is identified in this document.

Other materials whose compatibility is not identified in this document may be used if all compatibility aspects have been considered and validated by a competent person.

4.2 Cylinder materials

The most commonly used metallic materials for cylinders are (among others) carbon manganese steel, chromium molybdenum steel, chromium molybdenum nickel steel, stainless steel and aluminium alloys, as specified in the following documents:

— aluminium and aluminium alloys: ISO 6361-2, ISO 7866 and ISO 11118;

— steel: ISO 4706, ISO 9328-5, ISO 9809-1, ISO 9809-2, ISO 9809-3, ISO 11118 and ISO 11120;

— stainless steel: ISO 9809-4 and ISO 15510.

4.3 Valve materials

4.3.1 General

The most commonly used metallic materials for valve bodies and internal gas wetted parts are brass and other similar copper-based alloys, carbon steel, stainless steel, refined nickel and nickel alloys, Cu–Be (2 %) and aluminium alloys.

4.3.2 Particular considerations

4.3.2.1 In special cases, non-compatible materials may be used for non-oxidizing gases if suitably plated, protected or coated. This may only be done if all compatibility aspects have been considered and validated by a competent person for the entire life of the valve.

4.3.2.2 Special precautions, in accordance with ISO 11114-3 (which addresses testing, not precautions per se), shall be taken for oxidizing gases as specified in ISO 10156. In this case, non-compatible materials are *not acceptable* (see 3.3) for use in valves, even if plated, protected or coated.

4.3.2.3 For cylinder valves, compatibility in wet conditions shall be considered because of the high risk of contamination by atmospheric moisture and an airborne contaminant.

NOTE Reference is made in this document to stainless steels by their commonly used AISI identification numbers, i.e. 304. For example, the equivalent grades according to EN 10088-1 are as follows:

304	1.4301
304L	1.4306 and 1.4307
316	1.4401
316L	1.4404
316Ti	1.4571
321	1.4541
904L	1.4539

5 Compatibility criteria

5.1 General

Compatibility between a gas and the cylinder/valve material is affected by chemical reactions and physical influences, which can be classified into five categories:

— corrosion;

— stress corrosion cracking;

— hydrogen embrittlement;

— generation of dangerous products through chemical reaction;

— violent reactions, such as ignition.

Non-metallic components (valve sealing, gland packing, O-ring, etc.) shall be in accordance with ISO 11114-2.

Sealing or lubricating materials (when used) at the valve stem shall be compatible with the gas content.

NOTE Annex A gives the gas/materials NQSAB compatibility codes, for information.

5.2 Corrosion

5.2.1 General

Many types of corrosion mechanisms can occur due to the presence of the gas, as outlined in 5.2.2 to 5.2.4.

5.2.2 Corrosion in dry conditions

This corrosion is affected by chemical attack by a dry gas on the cylinder material. The result is a reduction of the cylinder wall thickness. This type of corrosion is not very common, because the rate of dry corrosion is very low at ambient temperature.

5.2.3 Corrosion in wet conditions

This is the most common type of corrosion, which only occurs in a gas cylinder due to the presence of free water or aqueous solutions. However, with some hygroscopic gases (e.g. HCl, Cl_2) corrosion would occur even if the water content were less than the saturation value. Therefore, some gas/material combinations are not recommended, even if inert in the theoretical dry conditions. It is thus very important to prevent any water ingress into gas cylinders. The most common sources of or reasons for water ingress are:

a) the customer, by retro-diffusion/backfilling or when the cylinder is empty, by air entry, if the valve is not closed,

b) ineffective drying following hydraulic testing, and

c) during filling.

In some cases, it is very difficult to completely prevent water ingress – particularly when the gas is hygroscopic (e.g. HCl, Cl_2). In cases where the filler cannot guarantee the dryness of gas and cylinder, a cylinder material which is compatible with the wet gas shall be used, even if the dry gas is not corrosive.

There are several different types of “wet corrosion” in alloys:

1) general corrosion leading to the reduction of the wall thickness, e.g. by acid gases (CO_2, SO_2) or oxidizing gases (O_2, Cl_2);

2) localized corrosion, e.g. pitting corrosion or grain boundary attack.

Additionally, some gases, even inert ones, when hydrolysed could lead to the production of corrosive products.

5.2.4 Corrosion by impurities

Gases which themselves are inert (non-corrosive) can cause corrosion due to the presence of impurities. Contamination of gases can occur, during filling, during use or if the initial product is not properly purified.

The most common pollutants are:

a) atmospheric air, in which case the harmful impurities can be moisture (see also 5.2.3) and oxygen (e.g. in liquefied ammonia);

b) aggressive products contained in some gases, e.g. H_2S in natural gas;

c) aggressive traces (acid, mercury, etc.) remaining from the manufacturing process of some gases.

The materials compatible with the impurities shall be used if the presence of these impurities cannot be prevented and if the corresponding corrosion rate is unacceptable for the intended application.

5.3 Hydrogen embrittlement phenomenon

Embrittlement caused by hydrogen can occur at ambient temperature in the case of certain gases and under service conditions which stress the cylinder or valve material.

This type of stress cracking phenomenon can, under certain conditions, lead to the failure of gas cylinders and/or valve components containing hydrogen, mixtures of hydrogen and other gases.

5.4 Generation of dangerous products

In some cases, reactions of a gas with a metallic material can lead to the generation of dangerous products. Examples are the possible reactions of C_2H_2 with copper alloys containing more than 65 % copper and of CH_3Cl in aluminium alloy cylinders.

5.5 Violent reactions (e.g. ignition)

In principle, violent reactions of gas/metallic material are not very common at ambient temperatures, because high activation energies are necessary to initiate such reactions. In the case where a combination of non-metallic and metallic materials is used, e.g. for valves, this type of reaction can occur with some gases (e.g. O_2, Cl_2).

5.6 Stress corrosion cracking

Stress corrosion cracking can occur in many metallic materials subjected to stress, moisture and a contaminant at the same time. Stress corrosion cracking can, under certain conditions, lead to the failure of the gas cylinder or valve and/or its components (e.g. ammonia in contact with copper alloy valves or carbon monoxide/carbon dioxide mixtures in steel cylinders).

6 Material compatibility

6.1 Table of compatibility for single gases

Before any gas/cylinder/valve combination is chosen a careful study of all the *key compatibility characteristics* given in Table 1 shall be made. Particular attention shall be paid to any restrictions, which shall be applied to acceptable materials.

NOTE The gases are generally listed in the table in English alphabetical order.

6.2 Compatibility for gas mixtures

Any gas mixtures containing single gases that are all compatible with a given material shall be considered as being compatible with this material.

For gas mixtures containing gases causing embrittlement (see 5.3, and Clause A.4, groups 2 and 11) the risk of hydrogen embrittlement only occurs if the partial pressure of the gas is greater than 5 MPa (50 bar) and the stress level of the cylinder material is high enough. In a gas mixture, the partial pressure for hydrogen sulphide and methyl mercaptan shall be less than 0,25 MPa (2,5 bar) at a maximum UTS (ultimate tensile strength) of 950 MPa. If the stress level of the cylinder material is high, see Table 1, row 63.

Some International Standards, such as ISO 11114-4, specify test methods for selecting appropriate steels with a maximum UTS greater than 950 MPa.

For the halogenated gases that are not compatible with aluminium alloy cylinders, the maximum acceptable concentration in gas mixtures shall be limited to 0,1 % as indicated in Table 1 unless higher concentrations have been validated after conducting specific tests (examples of such tests are given in EIGA document 161/16[14]). The moisture content (dryness) in these mixtures shall be limited to a maximum of 10 ppmV.

For non-compatibility of some halogenated gases with aluminium alloys, the maximum acceptable content is given in Table 1. The level of moisture can affect the acceptability of such mixtures.

6.3 Using Table 1

6.3.1 Conventions and numbers

In Table 1, **bold face** type indicates that the material is commonly used under normal service conditions:

— A = acceptable (see 3.2);

— N = not acceptable (see 3.3).

If there is no UN number listed for a gas (or liquid), the gas has no official UN number but may be shipped using a generic NOS (not otherwise specified) number.

EXAMPLE UN 1954, Compressed gas, flammable, N.O.S.

6.3.2 Abbreviations for materials

CS carbon steels used for the manufacture of cylinder valve bodies

NS carbon steels heat treated by normalization that are used for the manufacture of seamless and welded cylinders

QTS alloy steels that are treated by quenching and tempering and that are used for the manufacture of seamless steel cylinders

SS austenitic type stainless steels used for the manufacture of seamless and welded cylinders and some valve bodies and valve components

AA aluminium alloys specified in ISO 7866 when used for the manufacture of seamless cylinders; for aluminium valve bodies, alloys not specified in ISO 7866 may also be used

B brass and other copper alloys used for the manufacture of cylinder valves

Ni nickel alloys used for the manufacture of cylinders, valves and valve components

Cu copper

ASB aluminium silicon bronze

Table 1 — Gas/material compatibility

No.	Gas number UN number	Name	Formula	Key compatibility characteristics	Material			
					Cylinder		Valve (body and components)	
					A	N	A	N
1	(UN 1001) (UN 3374)	ACETYLENE	C_2H_2	Ability to form explosive acetylides with certain metals, including copper and copper alloys. Use <65 % Cu and copper alloy. This also applies to mixtures of more than 1 % C_2H_2. The acceptable limit of the silver content of alloys should preferably be 43 % (by mass) but in no case exceeding 50 %. There is no known incompatibility between the solvents used and any metallic materials, this is more relevant for ISO 11114-2.	**NS** QTS AA SS Ni		**B** CS AA SS Ni	B (Cu >65 %) Cu-Be (2 %)
2	(UN 1005)	AMMONIA	NH_3	Risk of stress corrosion cracking with brass (and other copper alloys) valves due to atmospheric contaminant. This applies to all gases and mixtures containing even traces of NH_3.	**NS** QTS AA SS Ni		**CS** SS AA Ni	B
3	(UN 1006)	ARGON	Ar	No reaction with any common materials in dry or wet conditions.	**NS** **QTS** **AA** SS		**B** CS SS AA	

[a] Brass is only acceptable as a valve body but not as a general valve component material.

[b] For mixtures containing up to 1 000 ppm of dry NO, brass valves can be used.

Table 1 *(continued)*

No.	Gas number UN number	Name	Formula	Key compatibility characteristics	Material			
					Cylinder		Valve (body and components)	
					A	N	A	N
4	(UN 2188)	ARSINE	AsH_3	Because of risk of hydrogen embrittlement: — QTS are limited to a maximum ultimate tensile strength of 950 MPa; — SS may be used for valve diaphragms and springs when there is operating experience that shows the design is suitable and safe. Alternatively, use is also authorized if failure of the SS springs or SS diaphragms does not result in an unsafe condition. NOTE Some SS alloys can be sensitive to hydrogen embrittlement. See special conditions for mixtures given in 6.2.	**NS** **QTS** **AA** SS		**B** CS **SS** AA Ni	
5	(UN 1741)	BORON TRICHLORIDE	BCl_3	Hydrolyses to hydrogen chloride in contact with moisture. In wet conditions, see specific risk of hydrogen chloride compatibility, i.e. severe corrosion of most of the materials and risk of hydrogen embrittlement. Mixtures of dry gas not exceeding 0,1 % of this gas may be filled into AA cylinders.	**NS** **QTS** SS Ni	AA	CS SS **Ni**	AA B
6	(UN 1008)	BORON TRIFLUORIDE	BF_3	Hydrolyses to hydrogen fluoride in contact with moisture. In wet conditions, see specific risk of hydrogen fluoride compatibility, i.e. severe corrosion of most of the materials and risk of hydrogen embrittlement. Mixtures containing less than 0,1 % BF_3 may be filled into AA cylinders.	**NS** **QTS** SS Ni	AA	CS SS **Ni**	AA B

[a] Brass is only acceptable as a valve body but not as a general valve component material.

[b] For mixtures containing up to 1 000 ppm of dry NO, brass valves can be used.

Table 1 *(continued)*

No.	Gas number UN number	Name	Formula	Key compatibility characteristics	Material			
					Cylinder		Valve (body and components)	
					A	N	A	N
7	(UN 1974)	BROMOCHLORODIFLUORO-METHANE	$CBrClF_2$ (R12B1)	No reaction with any common materials when dry but in the presence of free water, corrosion can occur.	NS QTS AA SS		B CS SS AA	
8	(UN 1009)	BROMOTRIFLUOROMETHANE	$CBrF_3$ (R13B1)	No reaction with any common materials when dry but in the presence of free water, corrosion can occur.	**NS** **QTS** AA SS		**B** CS SS AA	
9	(UN 2419)	BROMOTRIFLUOROETHYLENE	C_2BrF_3	No reaction with any common materials when dry but in the presence of free water, corrosion can occur.	**NS** **QTS** AA SS		**B** CS SS AA	
10	(UN 1010)	BUTADIENE-1,3	$H_2C:CHCH:CH_2$	No reaction with any common materials. See 5.2.4 for the effect of impurities in wet conditions.	**NS** QTS AA SS		**B** CS SS AA	
11	(UN 1010)	BUTADIENE-1,2	$H_2C:C:CHCH_3$	No reaction with any common materials. See 5.2.4 for the effect of impurities in wet conditions.	**NS** QTS AA SS		**B** CS SS AA	
12	(UN 1011)	BUTANE	C_4H_{10}	No reaction with any common materials. See 5.2.4 for the effect of impurities in wet conditions.	**NS** QTS AA SS		**B** CS SS AA	

[a] Brass is only acceptable as a valve body but not as a general valve component material.

[b] For mixtures containing up to 1 000 ppm of dry NO, brass valves can be used.