INTERNATIONAL STANDARD

ISO 11114-1

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

Part 1:
Metallic materials

Bouteilles à gaz transportables — Compatibilité des matériaux des bouteilles et des robinets avec les contenus gazeux —
Partie 1: Matériaux métalliques

Reference number
ISO 11114-1:1997(E)

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.

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

International Standard ISO 11114-1 was prepared by the European Committee for Standardization (CEN) in collaboration with ISO Technical Committee TC 58, *Gas cylinders*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

ISO 11114 consists of the following parts, under the general title *Transportable gas cylinders — Compatibility of cylinder and valve materials with gas contents*:

— *Part 1: Metallic materials*

— *Part 2: Non-metallic materials*

— *Part 3: Autogenous ignition test in oxygen atmosphere*

Annex A forms an integral part of this part of ISO 11114. Annex ZZ is for information only.

Annex ZZ provides a list of corresponding International and European Standards for which equivalents are not given in the text.

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Foreword

The text of EN ISO 11114-1:1997 has been prepared by Technical Committee CEN/TC 23 "Transportable gas cylinders" the secretariat of which is held by BSI in collaboration with Technical Committee ISO/TC 58 "Gas cylinders".

The text of the draft standard was submitted to the Formal Vote and was approved by CEN as EN ISO 11114-1 on 97-09-18.

This European Standard has been submitted for reference into the RID and/or in the technical annexes of the ADR. Therefore in this context the standards listed in the normative references and covering basic requirements of the RID/ADR not addressed within the present standard are normative only when the standards themselves are referred to in the RID and/or the technical annexes of the ADR.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by April 1998, and conflicting national standards shall be withdrawn at the latest by April 1998**.**

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

Introduction

This Standard is one part of a three-part standard concerning compatibility of gases and gas mixtures with materials :

- Part 1 : Metallic materials ;
- Part 2 : Non metallic materials ;
- Part 3 : Autogenous ignition test in oxygen atmosphere.

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 contents.

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 Standard is based on current international experience and knowledge.

1 Scope

This standard gives guidance in the selection and evaluation of compatibility between metallic gas cylinder and valve materials, and the gas content.

The compatibility data given is related to single component gases.

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

> NOTE: In this Standard the term “cylinder” refers to transportable pressure receptacles, which also include tubes and pressure drums.

Aspects such as quality of delivered product are not considered.

2 Normative references

This Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

EN 485-2	Wrought aluminium and aluminium alloys - Sheets, strips and plates - Part 2 : Mechanical properties.
EN 586-2	Aluminium and aluminium alloys forgings - Part 2 : Mechanical and additional properties.
EN 720-2:1996	Transportable gas cylinders - Gases and gas mixtures - Part 2: Determination of flammability and oxidizing ability of gases and gas mixtures
EN 849:1996	Transportable gas cylinders - Cylinder valves - Specification and type testing
prEN 1964-1:1995	Transportable gas cylinders - Specification for the design and construction of refillable transportable seamless steel gas cylinders of capacity from 0,5 litre up to and including 150 litres - Part 1 : Seamless steel with a maximum R_m value of 1100 N/mm^2
prEN 1975:1996	Transportable gas cylinders - Specification for the design and construction of refillable transportable seamless aluminium alloy gas cylinders of capacity from 0,5 litre up to 150 litre
EN 10088-1	Stainless steels - Part 1: List of stainless steels
prEN ISO 11114-2:1997	Transportable gas cylinders - Compatibility of cylinder and valve materials with gas contents - Part 2 : Non metallic materials

EN ISO 11114-3:1997	Transportable gas cylinders - Compatibility of cylinder and valve materials with gas contents - Part 3 : Autogenous ignition test in oxygen atmosphere
ISO/DIS 7866	Refillable transportable seamless aluminium alloy gas cylinders for worldwide usage - Design, construction and testing
ISO 9328-5	Steel plates and strips for pressure purposes - Technical delivery conditions - Part 5 : Austenitic steels
ISO/DIS 9809-1	Transportable seamless steel gas cylinders - Design, construction and testing - Part 1 : Quenched and tempered steel cylinders with tensile strength below 1100 MPa
ISO 10156:1996	Gases and gas mixtures - Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets

3 Definitions

For the purposes of this Standard the following definitions apply :

3.1 Competent person

A 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. Such a person will also normally be formally qualified in an appropriate technical discipline.

3.2 Acceptable

A material/gas combination that is satisfactory under normal conditions of use, provided the key compatibility features, given in Table 1, are taken into account.

3.3 Not recommended

A material/gas combination that may not be safe. Such combinations can be used where they have been assessed and authorized by a competent person who specifies the conditions of use.

4 Materials

4.1 Cylinder material

The metallic materials most commonly used in the manufacture of gas cylinders are specified in the following standards :

Aluminium :

EN 485-2
EN 586-2
prEN 1975
ISO/DIS 7866

Steel :

ISO 9328-5
prEN 1964-1
ISO/DIS 9809-1

4.2 Valve materials

The most commonly used materials for valve bodies for gas cylinders are brass and other copper based alloys, carbon steel, stainless steel and aluminium alloys.

In some special applications nickel or nickel plated alloys are used.

Some carbon steels, stainless steels and aluminium alloys for valve bodies are specified in the same standard as those for gas cylinders (see 4.1).

4.3 Particular considerations

4.3.1 In particular cases non-compatible materials may be used if suitably plated or protected. This can only be done, if all compatibility aspects have been considered and validated by a competent person.

4.3.2 Non-metallic components, e.g. valve sealing, gland packing, O-ring etc... shall be in accordance with prEN ISO 11114-2. Sealing or lubricating materials, when used, at the valve stem shall be compatible with the gas content.

Special precautions (see EN ISO 11114-3) shall be taken for oxidizing gases (see ISO 10156 or the technically equivalent EN 720-2).

4.3.3 For cylinder valves, compatibility in wet condition shall be considered because of the high risk of contamination by atmospheric moisture.

4.3.4 Reference is made in this Standard to stainless steels by their commonly used AISI identification numbers, eg 304. The equivalent grades in EN 10088-1 are as follows:

304	1.4301
304L	1.4306 - 1.4307
316	1.4401
316L	1.4404

5 Compatibility criteria

5.1 General

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

- corrosion (probably the most frequent type of reaction which could be expected) ;

- hydrogen embrittlement ;

- generation of dangerous products through chemical reaction ;

- violent reactions (like ignition) ;

- embrittlement at low temperature.

5.2 Corrosion

Many types of corrosion mechanisms can occur due to the presence of the gas.

5.2.1 Dry corrosion

Is the 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.

5.2.2 Wet corrosion

Is the most common type of corrosion which only occurs in a gas cylinder due to the presence of free water. However with some hygroscopic gases (e.g. HCl, Cl_2) corrosion would occur even if the water content is less than the saturation. Therefore some gas/material combinations are not recommended, even if inert in the theoretical dry conditions. It is therefore very important to prevent any water ingress in gas cylinders.

The most common sources of water ingress are :

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

- during hydraulic testing ;

- during filling.

In some cases it is very difficult to prevent any water ingress - particularly when the gas is hygroscopic (e.g. Cl_2, HCl). 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 different types of "wet corrosion" in alloys :

- general corrosion: e.g. by acid gases (CO_2, SO_2) or oxidizing gases (O_2, Cl_2). Additionally some gases, even inert ones, when hydrolysed could lead to the production of corrosive products (e.g. SiH_2Cl_2) ;

- localised corrosion: e.g. pitting corrosion by wet HCl in aluminium alloys or stress corrosion cracking of highly stressed steels by wet CO/CO_2 mixtures.

5.2.3 Corrosion by impurities

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

The most common pollutants are :

- atmospheric air, in this case the harmful impurities can be moisture (see also 5.2.2) and oxygen (e.g. in liquefied ammonia) ;

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

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

When the effects of these types of corrosion are expected to be dangerous and the presence of these impurities cannot be prevented, then cylinder materials compatible with the impurities shall be used.

5.3 Hydrogen embrittlement

Embrittlement by dry gas can occur at ambient temperature in the case of certain gases and under service conditions which stresses the cylinder material. The best known example is embrittlement caused by hydrogen.

This type of stress cracking phenomenon can, under certain conditions, lead to the failure of gas cylinders containing hydrogen, hydrogen mixtures and hydrogen bearing compounds including hydrides. The risk of hydrogen embrittlement only occurs if the partial pressure of the gas and the stress level of the cylinder material is high enough.

NOTE : For 34 Cr Mo 4 Q and T steels and equivalent hydrogen partial pressures above 5 MPa (50 bar), the maximum ultimate tensile strength (UTS) of the steel should be 950 MPa. Some standards specify testing methods to select appropriate steels with appropriate maximum UTS for hydrogen cylinders. Equivavent partial pressure for hydrogen sulphide and methyl mercaptan is reduced to 0,25 MPa (2,5 bar) at a maximum UTS of 950 MPa.

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 reaction of C_2H_2 with copper alloys containing more than 70 % copper and of CH_3Cl in aluminium cylinders.

5.5 Violent reactions (e.g. ignition)

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

5.6 Embrittlement at low temperature

In some cases, for toxic gases when pumps or compressors are not recommended, the gas cylinders are filled by cooling the gas cylinder using a cryogenic product (e.g. liquid nitrogen). In such cases materials having good impact behaviour at low temperature (aluminium alloys, stainless steels) shall be used and carbon or low alloyed steels shall be rejected. In some other cases cylinders are regularly filled at low temperature e.g. with CO_2. Materials used shall have adequate impact behaviour at the minimum temperature in service.

6 Material compatibility

6.1 Table of compatibility

Before any gas/cylinder/valve combination is chosen a careful study of all "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 English alphabetic order.

6.2 Conventions and symbols used in table 1

Bold type face indicates that the material is commonly used ;

"A" means that the material is acceptable (see 3.2) ;

"NR" means that the material is not recommended (see 3.3) ;

"Dry" means no free water in the cylinders under any service conditions including at the highest expected operating pressure and at the lowest expected operating temperature ;

"Wet" means that the conditions as defined above for "dry" are not met.

6.3 Abbreviations for materials

NS = Normalized steels and carbon steels ;

QTS = Quenched and tempered steels ;

AA = Aluminium alloys ;

SS = Stainless steels ;

B = Brass and copper alloys ;

CS = Carbon steels.

Table 1 : Gas/material compatibility

Gas number Name Formula	Key compatibility characteristics	Materials			
		Cylinder		Valve	
		A	NR	A	NR
1 ACETYLENE C_2H_2	Ability to form explosive acetylides with certain metals including pure copper. Use < 70 % Cu copper alloy.	**NS** QTS AA SS		**B** CS AA SS	B (Cu >70%)
2 AMMONIA NH_3	Risk of stress corrosion with brass (and copper alloys) valves due to atmospheric moisture.	**NS** QTS AA SS		**CS** SS AA	B
3 ARGON Ar	No reaction with any common materials in dry or wet conditions.	**NS** **QTS** **AA** SS		**B** CS SS AA	
4 ARSINE AsH_3	Because of risk of hydrogen embrittlement special QTS and NS with a limitation on the maximum strength shall be used. (see 5.3). Some SS alloys (e.g. AISI 304) can be sensitive to hydrogen embrittlement. Risk of corrosion by impurities in wet conditions has to be considered.	**NS** **QTS** **AA** SS		**B** CS **SS** AA	
5 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.	**NS** **QTS** SS	AA	CS **SS**	AA **B**

(continued)

Table 1 *(continued)*

Gas number Name Formula	Key compatibility characteristics	Materials			
		Cylinder		Valve	
		A	NR	A	NR
6 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.	**NS** **QTS** SS AA		CS **SS**	AA B
7 BROMOCHLORODIFLUOROMETHANE C $BrClF_2$ (R12B1)	No reaction with any common materials when dry. In the presence of water, slight risk of corrosion.	NS **QTS** AA SS		**B** CS SS AA	
8 BROMOTRIFLUORO-METHANE $CBrF_3$ (R13B1)	No reaction with any common materials when dry. In the presence of water slight risk of corrosion.	**NS** **QTS** AA SS		**B** CS SS AA	
9 BROMOTRIFLUORO-ETHYLENE C_2BrF_3	No reaction with any common materials when dry. In the presence of water slight risk of corrosion.	**NS** **QTS** AA SS		**B** CS SS AA	
10 BUTADIENE - 1,3 $H_2C:CHCH:CH_2$	No reaction with any common materials : however in wet conditions risk of corrosion from impurities has to be considered.	**NS** QTS AA SS		**B** CS SS AA	
11 BUTADIENE - 1,2 $H_2C:C:CHCH_3$	No reaction with any common materials ; however in wet conditions risk of corrosion from impurities has to be considered.	**NS** QTS AA SS		**B** CS SS AA	
12 BUTANE C_4H_{10}	No reaction with any common materials ; however in wet conditions risk of corrosion from impurities has to be considered.	**NS** QTS AA SS		**B** CS SS AA	

(continued)

Table 1 *(continued)*

Gas number Name Formula	Key compatibility characteristics	Materials			
		Cylinder		Valve	
		A	NR	A	NR
13 BUTENE - 1 $CH_3CH_2CH:CH_2$	No reaction with any common materials ; however in wet conditions risk of corrosion from impurities has to be considered.	**NS** QTS AA SS		**B** CS SS AA	
14 BUTENE - 2 (CIS) $CH_3CHCHCH_3$	No reaction with any common materials ; however in wet conditions risk of corrosion from impurities has to be considered.	**NS** QTS AA SS		**B** CS SS AA	
15 BUTENE - 2 (TRANS) $CH_3CHCHCH_3$	No reaction with any common materials ; however in wet conditions risk of corrosion from impurities has to be considered.	**NS** QTS AA SS		**B** CS SS AA	
16 CARBON DIOXIDE CO_2	No reaction with common materials when dry. Forms slightly acidic carbonic acid in the presence of water ; corrosive for NS, QTS and CS. For NS and CS, risk of low temperature embrittlement. Risk of stress corrosion in presence of CO (see carbon monoxide) and water.	**NS** **QTS** **AA** SS		**B** CS SS AA	
17 CARBON MONOXIDE CO	Risk of formation of toxic metal carbonyls. Highly sensitive to any traces of moisture [> 5 ppmV at 20 MPa (200 bar)], in the presence of CO_2 (> 5 ppmV). Industrial grades of monoxide normally contain traces of CO_2 This can result in risk of stress corrosion, in the case of QTS, CS and NS cylinders if used at the normal service stress levels.	**NS** QTS **AA** SS		**B** CS SS AA	
18 CARBON TETRAFLUORIDE CF_4	No reaction with any common materials when dry. In the presence of water, slight risk of corrosion.	**NS** **QTS** AA SS		**B** CS SS AA	

(continued)