GAS COMPATIBILITY WITH ALUMINIUM ALLOY CYLINDERS

Document 161/16

Revision of Doc 161/10

EUROPEAN INDUSTRIAL GASES ASSOCIATION AISBL

AVENUE DES ARTS 3-5 • B – 1210 BRUSSELS
Tel: +32 2 217 70 98 • Fax: +32 2 219 85 14
E-mail: info@eiga.eu • Internet: www.eiga.eu

Doc 161/16

GAS COMPATIBILITY WITH ALUMINIUM ALLOY CYLINDERS

Prepared by WG-4 Specialty Gases

Disclaimer

EUROPEAN INDUSTRIAL GASES ASSOCIATION AISBL
Avenue des Arts 3-5 B 1210 Brussels Tel +32 2 217 70 98 Fax +32 2 219 85 14
E-mail: info@eiga.eu Internet: www.eiga.eu

Table of Contents

All technical changes to Doc 161/10 are shown underlined.

1 Introduction

Information on gas material compatibility is given in ISO 11114-1: 2012 *Transportable gas cylinders - Compatibility of cylinder and valve materials with gas contents - Part 1: Metallic materials* [1][1].

ISO 11114-1 covers the compatibility between pure gases and some common metals and gives some guidance for the compatibility of mixtures with these metals. For mixtures containing halogenated gases, the standard gives an overall limit of 0.1% (Vol) to be compatible with aluminium alloys. The current experience from the special gases industry is that the limit of 0.1% may be exceeded provided that the dryness of the gas and of the cylinder is strictly controlled.

2 Scope and purpose

2.1 Scope

This publication details the criteria necessary to establish the compatibility of reactive gas mixtures, used in the Special Gases industry with the aluminium alloy cylinders. The scope of the publication includes fully vaporised liquid components present in gaseous mixtures but excludes liquid mixtures.

The publication does not cover issues relating to the compatibility of valves, valve seat materials or cylinder materials other than aluminium alloy.

2.2 Purpose

The purpose of the publication is to establish rules and criteria to ensure the safe production and use of gas mixtures containing halogen and halogenated components (mainly at ppm concentrations) that are listed in ISO 11114-1: 2012 as incompatible with aluminium cylinders.

3 Definitions

3.1 Publications 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.

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

3.2 Technical definitions

3.2.1 Cylinder

Transportable receptacle that can be filled with gas under pressure. It excludes small disposable cylinders.

3.2.2 Expert opinion

Opinion of a technically competent authority or person with experience of cylinder manufacturing technology and in the formulation/specification of special gases mixtures. They should not be involved directly in commercial or production activities.

3.2.3 Inert gas

Gas that has no other hazard classification than being under pressure.

3.2.4 Internal treatment

Treatment performed on the internal surface of the cylinder.

3.2.5 Reactive gas

Gas that can react with the aluminum alloy.

4 Organization principles

All technical personnel involved in feasibility studies and the calculation and preparation of incompatible halogenated components in aluminum alloy cylinders shall be trained, assessed and formally appointed for this activity.

All manufacturing sites filling halogenated components into aluminum cylinders shall be formally qualified by the technically competent company authority for this activity. Qualification shall be based on:

- internal audit programmes;
- the appointment of technically competent qualified personnel; and
- documented procedures and training records.

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 the preparation and production processes involved in the manufacture of mixtures containing halogenated components in aluminum cylinders should be conducted periodically by a technically competent person. The company shall establish and define this period. For an example of a specimen audit check list see Section 19.

5 Composition of different aluminium alloys and specification

This publication covers any aluminium alloy included in ISO 7866:2012, *'Gas cylinders – Refillable seamless aluminium alloy gas cylinders – Design, construction and testing* [2]. Before considering the

use of aluminium alloy cylinders in reactive gas service check internal gas company rules and EIGA safety alerts.

6 Feasibility

The feasibility of producing a mixture containing reactive gases in an aluminium alloy cylinder should be based on experimental tests, literature studies or other controls, such as establishing the dryness of the gaseous components and the absence of dangerous contaminants in the cylinders.

It should be noted that the compatibility between gases and aluminium cylinders can be modified if impurities are present on the aluminium surface. Special care shall be taken to establish if the presence of impurities change the cylinder compatibility and mechanical properties.

It is recommended that gas companies have specifications for the cylinders suppliers to meet and procedures to control the internal cleanliness of the cylinders received from the manufacturers.

These evaluations shall include an appraisal of safety over the service life of the cylinder, which is the period between cylinder testing.

Before beginning mixture preparation, establish:

- if the procedures permit the inclusion of the component at the required concentration;
- the preparation procedures and any particular precautions required, for example, drying, evacuation, cylinder passivation;
- the specification of the gases, with special regard to the impurities than can impact on the compatibility of the mixtures with the cylinder aluminium alloy; and
- the general cylinder checks shall also include the usual controls such as cylinder integrity, valve compatibility etc.

It is recommended that cylinders are dedicated to service with a particular component, or at the least chemically similar reactive components at concentrations consistent with experimental tests.

The specific mixture formulation includes:

- cylinder type and size;
- valve type;
- cylinder preparation instructions (including evacuation, passivation etc.);
- components, their concentrations and the procedure for filling into the cylinder; and
- analysis/certification requirements.

These requirements shall be checked and approved by an authorized person independent of the formulation or production process.

The potential for the condensation of any of the components at the temperature of use shall be considered and taken into account in any calculations. Condensation shall be avoided.

7 Destructive or non-destructive testing

The feasibility of producing the gas mixture in an aluminium alloy cylinder shall be evaluated by conducting mixture composition analysis over time and establishing stability. Destructive tests followed by metallurgical examination are useful to support the decisions made on the basis of stability trials and confirm the compatibility between the aluminium alloy and the reactive gas.

In some cases a possible reaction producing hydrogen can be analysed and quantified. For low halogenated gas concentrations this phenomena is not a safety issue but can be used to establish mixture reactivity and stability.

8 Guidelines to perform the tests

The acceptance criteria for mixture feasibility are based on time and on the structural integrity of the cylinder. Tests shallt be completed for both binary and multi-component reactive gas mixtures. The tests are valid for the aluminium alloy tested and shall be performed again at least if another alloy is used.

8.1 Current experience

Collect cylinder tests and stability data from previous mixtures manufactured. Evaluate the results using a statistical approach, say a minimum of 10 cylinders, and base the results on the retesting of the cylinders containing the mixture to be approved.

8.2 Tests for new and higher concentration mixtures

Test mixtures shall be evaluated under controlled conditions for a minimum of 6 months. A validation procedure shall be undertaken for each new gas or mixture. It is recommended that tests should:

- include cylinders filled above the maximum concentration required by the customer (for safety) and at the minimum concentration (for quality);
- be performed at the temperature, at which the cylinder will be exposed; and
- be performed at the maximum pressure required for the mixture.

For new gases and higher concentration mixtures, it is recommended to plan tests to avoid safety risks (for example, increasing the test concentrations slowly in order to understand whether a reaction occurs).

Following these tests, considering the chemical analysis of the components introduced, or formed by reaction in the cylinders, some analyses shall be considered to improve knowledge about compatibility.

If a reaction between the gas, or mixture, and the cylinder occurs, a final cylinder burst test (at the test pressure of the cylinder) and a metallurgical examination shall be completed to establish the structural integrity of the cylinder and its safety for use. The burst test and metallurgical analysis shall be undertaken if the chemical analysis of the mixture has shown a significant decrease of the halogenated gas concentration before the mixture reaches a stable concentration.

As a minimum, the feasibility study shall report on:

- aluminium alloy used;
- internal treatment of the cylinder under test;
- name and the concentration of the component tested;
- filling pressure of the test mixture;
- procedure used to prepare the mixture; and
- results of the tests (analysis data, internal cylinder inspection, metallurgical data, etc.).

Any other information required to enable the test to be repeated shall be documented in the report.

The objective of the test is to establish that there are no dangerous reactions between the internal cylinder walls and the reactive gas mixture and the filled cylinder is safe for use.

Visual inspection, hydraulic test, ultrasonic test, or other tests shall prove the acceptability of the result.

The preparation procedure for the mixtures in aluminium alloy cylinders shall be approved by an expert.

9 Gas and concentration

Pure reactive gases that are not compatible with aluminium alloys according to ISO 11114-1: 2012 [1] are listed in Appendix A.

Other gases or vapours of liquids not included in the list that can react with aluminium alloy cylinders in presence of water or other impurities include, for example, ammonia and sulphur dioxide.

It is recommended that feasibility studies are performed for these gases as well.

The current experience from the special gases industry is that, provided the cylinder preparation is conducted under strictly controlled conditions and the moisture content is controlled to confirm the cylinder is dry(Note), the use of aluminium alloys is compatible with mixtures containing gases listed in Annex A.

Note: for a definition of “dry” see section 3.4 in ISO 11114-1: 2012.

10 Cylinder selection

Control the pressure test and the material compatibility of the cylinder with respect to the mixture to be filled. Control the previous filling of the cylinders to establish the gas compatibility with the new gas to be filled.

The coating of the internal cylinder walls with special liners can be considered.

11 Cylinder preparation

The cylinder shall be dried by suitable heating and by evacuation or other equivalent methods. The moisture in the cylinder shall be minimised and the concentration established by analysis or other means.

This can be achieved by:

- introducing an inert dry gas into the cylinder at approximately 10 barg;
- leaving the gas to equilibrate with the cylinder over several hours;
- measuring the concentration of moisture present; and
- repeating the process until the required level of dryness is achieved.

The final moisture concentration shall be compatible with the mixture to be produced and shall be equal or less than 10 ppm.

A residual pressure valve (RPV) - non return valve (NRV) cylinder valve should be fitted in order to avoid back flow and exposure of the internal cylinder walls to air during the use of the mixture.

12 Mixtures components purity and compatibility

The purity of all components shall be established to make sure that the mixture is compatible with the aluminium alloy internal cylinder surface according to the principles detailed in this procedure. Moisture is a key impurity which shall be minimised within the cylinder and all raw materials including the balance gases used. Any other impurities in the balance gas that can react with components in the mixture shall be considered.

13 Cylinder preparation before filling

Before filling the aluminium alloy cylinder with the reactive gases, a particular preparation of the internal walls to passivate them may be required. This preparation may be done in different ways, for example:

- filling the cylinder with the same gas mixture that will ultimately be filled into the cylinder but at a lower filling pressure (for example, 3 bar) followed by evacuation; or
- treating the internal walls with some specific chemicals to passivate them.

The preparation shall be completed based on the procedure approved and feasibility tests performed.

14 Results of the analysis

Analysis to validate the preparation should be done on all the cylinders. If the analysis shows that the concentration of the reactive component has decreased by an unacceptable value, an investigation shall be completed to explain the results. The mixture can be prepared again in the same cylinder repeating all of the preparation cycle.

If the mixture is still not stable, the cylinder shall be withdrawn from reactive gas service and retested.

15 Traceability

Records to maintain the traceability of the cylinder containing reactive mixtures is strongly recommended. This enables an assessment of the cylinder and components on return from the customer and allows the supplier to keep the cylinder in a similar service.

As a minimum the records shall show the type of components and their concentration for the previous mixture filled in the cylinder.

If traceability is not possible the cylinders should be dedicated to the service with the reactive gas mixtures and hard stamped with mixture and concentration contained.

16 Control and reuse of returned cylinders

If the cylinder is returned with residual pressure, it may be reused after evacuation.

If the cylinder is returned without residual pressure, internal procedures shall be in place to determine whether the cylinder may be returned to service and what level of testing and examination is required before it can be returned to service. The procedures should include the internal inspection of the cylinder.

The cylinder can be reused in other service (a risk assessment shall be done to establish safety before changing the cylinder service).

A visual examination of the cylinder valve is recommended. If there is no pressure in the cylinder a leak check should be performed.

17 Residual mixture evacuation before the hydraulic retesting

Before performing a hydraulic re-test special care shall be taken to ensure that all residual gas is removed from the cylinder including any gas adsorbed on the cylinder walls (for example, washing the cylinder internally). Furthermore, particular care should be taken to ensure that the cylinder is dried quickly following hydraulic testing to avoid damage to the internal walls. An ultrasonic test may be performed instead of a hydraulic test.

After testing/re-testing of a cylinder which is to be used in reactive gas service the internal treatment/preparation shall be repeated to ensure that the cylinder surface has not been compromised by prior service and by the re-test procedure. Tests and procedures need to be in place to document and to provide verification of these activities.

18 Customer information to avoid contamination

Information should be provided to customers requesting that they leave residual pressure in the cylinder and avoid contamination (for example, using a cylinder label).

19 Audit guideline

It is recommended that facilities manufacturing halogenated gas mixtures in aluminium alloy cylinders undergo periodic audits to assess their compliance with this publication and with other recognised safe working practices. The nature and detail of such audits will be determined by the facilities level of involvement with reactive gas mixtures and compliance with local regulations.

The following checklist of items to audit (see Table 1) is unlikely to be exhaustive; however they may provide a helpful starting point. The *Reference section* column gives, where appropriate, the section of this publication where more information on the checklist item may be found.

Table 1 - Gas compatibility with aluminium alloy cylinders

Serial No.	Gas compatibility with aluminium alloy cylinders	Reference section
1	Is the manufacturing site approved for the manufacture of compressed halogenated gas mixtures by the technically competent company authority?	4
2	Is there a person designated as having overall responsibility for the formulation, review and approval of recipes?	4
3	Is there a system for the approval of new recipes?	6
4	Formulation of compressed halogenated gas mixtures shall be approved by at least one authorized person other than the creator of the formulation (checker)	6
5	Are data sources relevant to the compressed halogenated gas mixtures formulation available to the creators and checkers of the formulation?	6
6	Has a study to prevent condensation after manufacturing been conducted for each formulation?	6
7	There is a clear production procedure for the authorized halogenated mixture?	6
8	There is a procedure detailing all of the steps to be followed for the mixture preparation?	6
9	The feasibility approval based on current experience has been done on at least 10 cylinders?	8
10	The tests for a new preparation have been done above the maximum concentration required?	8
11	The feasibility study for a new preparation contains the information suggested in section 8?	8
12	Has a study to control the stability of the mixture been conducted for each reactive gas?	8
13	The cylinder preparation is done according to the procedures established during the feasibility test?	11
14	Are the impurities in the balance gas checked?	12
15	The results of the analysis are evaluated by a competent person to check if the mixture is acceptable?	14
16	The re-preparation is authorized by a competent person?	14
17	There is a cylinder traceability system in place?	15
18	There are controls on returned cylinders?	16
19	Before the hydraulic re-test the mixture is removed?	17
20	After the hydraulic re-test the cylinder is dried quickly?	17
21	The user is asked to leave residual pressure in the cylinder?	18

20 References

Unless otherwise specified, the latest edition shall apply.

[1] ISO 11114-1: 2012 *Transportable gas cylinders - Compatibility of cylinder and valve materials with gas contents - Part 1: Metallic materials* www.iso.org

[2] ISO 7866:2012, *'Gas cylinders – Refillable seamless aluminium alloy gas cylinders – Design, construction and testing* www.iso.org

Appendix A - Gases not compatible with aluminium according to ISO 1114-1: 2012 Note

(Informative)

Serial No.	Gas name	Remarks
5	Boron trichloride	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
6	Boron trifluoride	Mixtures containing less than 0.1% BF3 may be filled into AA cylinders
20	Chlorine	Mixtures containing less than 0.1% of this gas may be filled into AA cylinders
22	Chloromethane	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
35	Dichlorosilane	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
46	Ethyl chloride	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
49	Fluorine	Mixtures containing less than 0.1% of this gas may be filled into AA cylinders
58	Hydrogen bromide	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
59	Hydrogen chloride	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
61	Hydrogen fluoride	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
62	Hydrogen iodide	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
69	Methyl bromide	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
83	Phosgene	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
90	Silicon tetrachloride	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
91	Silicon tetrafluoride	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
94	Sulphur tetrafluoride	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
96	Trichlorosilane	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
100	Tungsten hexafluoride	Mixtures containing less than 0.1% of this gas may be filled into AA cylinders
101	Vinyl bromide	Mixtures containing less than 0.1% of this gas may be filled into AA cylinders
102	Vinyl chloride	Mixtures containing less than 0.1% of this gas may be filled into AA cylinders
103	Vinyl fluoride	Mixtures containing less than 0.1% of this gas may be filled into AA cylinders

Note The standard is currently being amended and at the FDIS stage for final approval at the date of publication of this document..