



**WORKING PAPER**

**DANGEROUS GOODS PANEL (DGP)  
MEETING OF THE WORKING GROUP OF THE WHOLE**

**The Hague, 3 to 7 November 2008**

**Agenda Item 2: Development of recommendations for amendments to the *Technical Instructions for the Safe Transport of Dangerous Goods by Air* (Doc 9284) for incorporation in the 2011/2012 Edition**

**2.4: Part 4 — Packing Instructions**

**ETHYL CHLORIDE AND SIMILAR GASES**

(Presented by G. A. Leach)

**SUMMARY**

This paper seeks to place additional safeguards on the transport of ethyl chloride and similar gases in aluminium alloy cylinders.

Action by the DGP-WG is in paragraph 2.

**1. INTRODUCTION**

1.1 Following the explosion of an aluminium alloy cylinder at a cargo warehouse in Dubai, an emergency ad-hoc meeting of the Working Group of the Whole met in Montreal from 8 to 10 April 2008 to decide what the appropriate action of ICAO should be. A working paper detailing all the issues is in the appendix to this working paper.

1.2 Following the ad-hoc meeting, an addendum to the Technical Instructions was produced on 13 June 2008. Amongst other things, this banned the carriage of pure ethyl chloride in aluminium alloy cylinders. However, defining requirements for mixtures containing ethyl chloride was difficult, and it was suggested mixtures should similarly be banned in aluminium alloy cylinders (it was a mixture which was involved in the Dubai incident). However, a representative from the gas industry advised that mixtures containing much lower concentrations than that involved in the incident had been carried in aluminium alloy cylinders for many years without incident. They believed that provision should exist for low concentrations to continue to be transported. However, it was not possible to specify the maximum safe concentration. The gas industry representative also advised that requiring the use of steel cylinders could cause different problems, although at the time of the ad-hoc working group meeting they were unable to specify these, and undertook to provide details. Consequently the ad-hoc group agreed not to forbid mixtures of ethyl chloride (irrespective of concentration) in aluminium alloy cylinders, but instead to require their carriage with the approval of the appropriate national authority of the State of Origin.

1.3 To date, no details have been received concerning compatibility issues surrounding ethyl chloride and steel. This panel member has also not been able to learn of any despite searches of the internet. In fact, the only information which was found (including ISO 11114-1) suggested that ethyl chloride and steel were an acceptable combination.

1.4 Whilst the actions taken by the ad-hoc working group have improved the situation, there still exists the possibility for an ethyl chloride mixture of the same concentration as that involved in the incident to be shipped in an aluminium alloy cylinder (on a passenger aircraft if an A1 approval is granted) if approved by an appropriate national authority of a State of Origin. However, as stated in DGP-WG/08-WP/12, analysis of results from the ICAO Universal Safety Oversight Audit Programme (USOAP) show that 50% of Contracting States have not addressed the issue of the transport of dangerous goods by air, yet the Technical Instructions would still provide for these States to authorize the carriage of ethyl chloride in an aluminum alloy cylinder.

## 2. ACTION BY THE DGP-WG

2.1 The DGP-WG is invited to forbid the use of aluminium alloy cylinders for the transport of mixtures containing ethyl chloride and other gases with similar properties identified in Packing Instruction 200, given the potential for a catastrophic situation to occur on an aircraft. This could be achieved by the following amendment to Packing Instruction 200 5) as follows:

200	PACKING INSTRUCTION 200	200
	<p>For cylinders, the general packing requirements of 1.1 and 4.1.1 must be met.</p> <p>...</p> <p>5) Gas mixtures containing any of the following gases must not be offered for transport in aluminium alloy cylinders <del>unless approved by the appropriate national authority of the State of Origin:</del></p> <p>UN 1037 <b>Ethyl chloride</b>  UN 1063 <b>Methyl chloride</b>  UN 1063 <b>Refrigerant gas R 40</b>  UN 1085 <b>Vinyl bromide, stabilized</b>  UN 1086 <b>Vinyl chloride, stabilized</b>  UN 1860 <b>Vinyl fluoride, stabilized</b>  UN 1912 <b>Methyl chloride and methylene chloride mixture</b></p> <p>...</p>	

2.2 If this change is agreed it is suggested that in the interests of safety it should be promulgated in an addendum to the 2009-2010 Edition of the Technical Instructions.

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## APPENDIX



International Civil Aviation Organization

DGP-AH-WG/08-WP/xxxx  
1/4/08

### DISCUSSION PAPER

## DANGEROUS GOODS PANEL (DGP)

### AD HOC MEETING

Montréal, 8 to 10 April 2008

**Agenda Item 2: Development of recommendations for amendments to the *Technical Instructions for the Safe Transport of Dangerous Goods by Air* (Doc 9284) for incorporation in the 2009/2010 Edition**

#### **2.7: Part 7 — Operator's Responsibilities**

### **EXPLOSION OF A CYLINDER CONTAINING ETHYL CHLORIDE**

(Presented by G A Leach)

#### **SUMMARY**

This paper describes a serious incident involving a cylinder containing ethyl chloride. It is suggested the incident has highlighted significant deficiencies in the wording of the Technical Instructions which are in need of urgent amendment

## **1. INTRODUCTION**

1.1 On 3 December 2007, in a cargo warehouse at Dubai Airport, a cylinder containing ethyl chloride exploded, fortunately causing only minor injuries. The cylinder had been shipped from the UK and was carried from Manchester to Dubai on a B747 freighter aircraft. Had the explosion occurred on the aircraft, the consequences may well have been catastrophic.

1.2 The cylinder in question was made of aluminium alloy and was manufactured in October 2007. On 19 November 2007, the cylinder was filled with 99.995% ethyl chloride, 20 ppm 1,1,1 Trichloroethane and 30 ppm Trichloroethylene, and an overpressure of 20 bar of helium. The substance was classified as "Liquefied gas, flammable, n.o.s. (Trichloroethylene, Ethyl Chloride mixture)", UN3161, division 2.1. The cylinder was marked, labelled and documented as required by the Technical

Instructions. On 27 November 2007, the cylinder was carried by air to Dubai and on 3 December the explosion occurred.

1.3 The remnants of the cylinder were returned to the UK where they underwent metallurgical examination. This revealed that the interior of the cylinder had been subjected to a severe corrosion attack. It is believed that a probable sequence of events was that a chemical reaction between the cylinder contents and the aluminium cylinder generated corrosion an increase in the internal pressure. As the corrosion process continued with time, the cylinder wall would have become weaker and the pressure greater, until the explosion occurred.

## 2. THE ISSUES

2.1 It is suggested there are 3 issues which this incident has raised, assignment of an n.o.s. proper shipping name (this is the subject of a further discussion paper); compatibility and reference to an ISO standard; and the continued application of Special Provision A1 for substances of the type involved in this incident.

### 2.2. *Compatibility and reference to an ISO standard*

2.2.1 As stated above, the issues surrounding the choice of proper shipping name is the subject of another discussion paper. However, irrespective of whether a substance is classified as UN1037 Ethyl chloride or UN3161 Liquefied gas, flammable, n.o.s., the Technical Instructions contains text relating to compatibility, but a close study of this text has revealed some significant anomalies.

2.2.2 For Ethyl chloride, Packing Instruction 200, Special packing provision “a” applies, which states:

“Aluminium alloy cylinders are not authorized”

This is presumably intended to place a prohibition on the use of aluminium alloy cylinders with ethyl chloride, but this is not clear; Packing Instruction 200 refers to ISO 11114-1:1997 and this says only that aluminium alloy is “not recommended” but can be used if assessed and *authorised* by a “competent person”. It is suggested that if the intention was to forbid the use of aluminium alloy cylinders, text similar to that in special packing provision “b” (copper valves *must not be used*) or the word “forbidden” should have been used.

2.2.3 The ISO Standard defines a “Competent Person” as:

“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.”

In the incident in question, the “competent person” was a chemistry graduate with 10 years experience or manufacturing gas mixtures.

2.2.4 Although ISO 11114-1 does not recommend the use of an aluminium alloy cylinder, it does not explicitly forbid its use, nor does it give any specific warning about the apparent dangers. The "key compatibility characteristics" of ethyl chloride are quoted as:

"No reaction with any common materials when dry. In the presence of water, slight risk of corrosion"

This is the same comment as is made for many other gases where compatibility with aluminium alloy is not an issue e.g. fluoroethane, fluoromethane. This is in stark contrasts to the key compatibility characteristics for Methyl bromide which states:

"RISK OF VIOLENT REACTIONS WITH AA (aluminium alloy)"

2.2.5 The shipper also referred to the "Matheson Gas Data Book", an apparently widely used journal in the gas industry. This also gives no warning on the use of aluminium alloy cylinders with ethyl chloride. It is understood this is because when this publication was first produced (it is updated periodically), aluminium was not used as a material of construction for cylinders and this has not been revised as the use of aluminium became common.

2.2.6 It has been suggested that the explosion is proof that the shipper did not ensure compatibility of his product with the cylinder. But he referred to the ISO standard (as the Technical Instructions required him to do) which does not forbid its use, nor adequately indicate the dangers, and also the Matheson Gas Data book which was similarly silent on the matter. The shipper also stated an evaluation is made of known reactions between materials when making cylinder selection decisions and he has been unable to identify any work in the public domain which shows any evidence of a reaction between ethyl chloride and aluminium alloy. If the actions the shipper took to ensure compatibility were inadequate, this raises questions about what exactly, short of actual testing, is expected of a shipper in this area.

2.2.7 For liquefied gas, flammable, n.o.s., Special packing provision "z" applies which is a general requirement for compatibility and so the comments above would be equally relevant. It is not clear why "z" does not appear against all gases or instead as a stand alone general requirement. It has been suggested that certain percentages of ethyl chloride may be contained in aluminium alloy cylinders, but at what level is it safe? In the absence of this knowledge, restriction to steel cylinders of any concentration of ethyl chloride (and any other substance with Special packing provision a) against it) may be an option.

2.2.8 Part 6;5.2.2 contains the following text:

"In addition to the material requirements specified in the cylinder and closed receptacle design and construction standards, and any restriction specified in the applicable Packing Instruction for the gas(es) to be transported (e.g. Packing Instruction 200 or Packing Instruction 202), the following standards apply to material compatibility:

(ISO 11114-1:1997 and ISO 11114-2:2000)"

It is not clear what "cylinder and closed receptacle design and construction standards" are referred to; this may be Part 6;5 but this text does not align with the Chapter 5 heading. Also, "the following standards

apply” effectively require compliance with the ISO standards, but the ISO Standard, in paragraph 1 states “This standard gives *guidance*...” and the status, intended or otherwise of an ISO Standard is queried.

2.2.9 The ISO Standard is 48 pages long but apart from 6.1 which requires a study of Table 1, the problems with which have been highlighted above, only 4 paragraphs contain mandatory requirements i.e. 4.3.2, 4.3.3, 5.2.3 and 5.6. It would therefore appear possible to specify these paragraphs in the Technical Instructions and add a note simply referring to the ISO Standard as guidance material e.g. as one source of information concerning compatibility.

2.2.10 Whilst preparing this paper, other anomalies were noted.

2.2.10.1 Special packing provision d) states:

“When steel cylinders are used, only those bearing the “H” mark must be authorized”

This could be interpreted as meaning steel cylinders not bearing the “H” mark do not require to be authorized and it is suggested the text should read:

~~“When Only steel cylinders are used, only those bearing the “H” mark must be authorized may be used”~~

2.2.10.2 In ISO 11114-1:1997 brass valves are “Not recommended” for a number of substances, but there is no reference in the UN Model Regulations P200 or the Technical Instructions Packing Instruction 200 to any restriction on brass valves for these substances, which are:

UN Number	Proper Shipping Name	Comment
UN 1005	Ammonia	Div 2.3 F/F
UN 1026	Cyanogen	Div 2.3 F/F
UN 1032	Dimethylamine	Div 2.1 F/PI 200
UN 1036	Ethylamine	Div 2.1 F/PI 200
UN 1061	Methylamine	Div 2.1 F/PI 200
UN 1660	Nitric oxide	Div 2.3 (5.1, 8) F/F
UN 1067	Nitrogen dioxide	Div 2.3 (5.1, 8) F/F
UN 1083	Trimethylamine	Div 2.1 F/PI 200

2.2.11 It has also been noted that, for example, for oxidising substances in aluminium alloy cylinders, the ISO Standard appears to potentially require 7 additional standards to be referred to referred to:

*para 4.1 – cylinder material*

EN 485-2

EN586-2

PrEN 1975

ISO/DIS 7866

*Para 4.3.2 – non-metallic components e.g. valve sealing*

PrEN ISO 11114-2

*Para 4.3.2 – special precautions for oxidizing gases*

EN ISO 11114-3

ISO 10156/ EN 720-2

The ad-hoc working group may wish to discuss whether it is appropriate for the Technical Instructions to effectively cross refer to 8 documents which are not under the control of ICAO. Indeed, the DGP may wish to request the UN COE to conduct a review of all ISO Standards (and any other standards) which are cross referred to.

### *2.3 Carriage on a passenger aircraft under Special provision A1*

2.3.1 Ethyl chloride is currently allowed for carriage on a passenger aircraft under Special Provision A1. It is suggested the ad-hoc working group discuss whether this should remain, if the use of aluminium alloy cylinders continues to be permitted.

## **3. SUMMARY**

3.1 It is suggested that to minimise the likelihood of a recurrence, which might prove catastrophic, it is suggested the applicable wording of the Technical Instructions is subjected to close scrutiny by the ad-hoc working group and amended as necessary.

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