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Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals

Sub-Committee of Experts on the Transport of Dangerous Goods

Forty-fifth session
Geneva, 23 June – 02 July 2014
Item 4 (c) of the provisional agenda
Listing, classification and packing: miscellaneous

Subsidiary risks for uranium hexafluoride

Transmitted by the expert from Austria[1]

Introduction

1. A proposal for a new UN number was approved by the IAEA Transport Safety Standards Committee at its twenty-second session (TRANSSC 22, June 2011). It was recommended to establish a fifth UN number for "Radioactive material, excepted package" for uranium hexafluoride (UF_6) with less than 0.1 kg per package.

2. In the course of discussions, attention was drawn to the fact that the United Nations Recommendations on the Transport of Dangerous Goods, Model Regulations, contains provisions for classification of dangerous goods possessing different hazards on the basis of a system of precedence of hazard as described in section 2.0.3 of the Model Regulations.

3. At the fortieth session the IAEA presented document ST/SG/AC.10/C.3/2011/46 with a data sheet for uranium hexafluoride.

Item 6 of that document reads as follows:

"In the discussions, it was mentioned that UF_6 possesses other hazardous properties, notably toxicity and oxidizing properties. This is not an issue which

[1] In accordance with the programme of work of the Sub-Committee for 2013-2014 approved by the Committee at its sixth session (refer to ST/SG/AC.10/C.3/84, para. 86 and ST/SG/AC.10/40, para. 14).

concerns this new entry only; it is an issue which concerns also UN Nos 2977 and 2978. But at this time, it might be better to consider that only the hazards identified for UN Nos 2977 and 2978 should be taken into account for this new entry (i.e. class 8 only). But it should be borne in mind for action before the end of the biennium (end 2012) if there is evidence of additional subsidiary risks to be taken into account. As an annex to this working paper, provisional information (data sheet) is provided."

4. The data sheet contains toxicity values that require classification as toxic PG I. The document was produced shortly before the end of the 3 month time limit for an official document and some members of TRANSCC wanted to check the values; therefore the mention "under investigation" was added against some values. It was decided that the focal point for toxicity - the GHS Sub-Committee - should look at the toxicity of uranium hexafluoride. But until December 2013, no new data was provided.

5. The 18th revised edition of the Recommendations on the Transport of Dangerous Goods, Model Regulations contains the new entry UN3507 as an entry in Class 8.

6. The Safety Data Sheet of the IAEA Document is still valid. The IUCLID Data Sheet (European Commission) and the RTECS (US Government) are still unchanged.

7. The data on toxicity are quite clear and consistent in the different sources. The values are in particular based on a study from the University of Rochester under contract with the US Department of Energy in 1983 with 511 rats and 78 guinea pigs.

8. The reason for omitting the toxicity risk for UF_6 was the original understanding that a class 7 label includes toxicity (informal document INF.7, 42nd session).

9. The property TOXIC BY INHALATION is defined only for liquids (2.6.2.2.4.3) and sublimation is not considered (the vapour pressure of UF_6 is comparable to acetone, see informal document INF.36, 40th session). A change of that definition might be necessary but consequences for other substances need to be investigated so that this would be a new issue for a later session. To assign special provision 354 is therefore not proposed in this document.

10. It is known that UF_6 has oxidizing properties, but there are no data from a test as prescribed in section 34 of the Manual of Tests and Criteria. Therefore this document contains no proposal to add the subsidiary risk oxidizer. Industry is invited to test the reaction with fibrous cellulose (a small scale test at room temperature may be sufficient).

11. The production of toxic gases (HF) when in contact with water is not yet addressed in the Model Regulations.

12. Therefore the following amendments are proposed.

Proposal: (changes to the existing text in bold)

13. Amend the entries in Chapter 3.2 - Dangerous Goods List to read as follows:

UN No.	Name and description	Class	Subsidiary risk	PG	SP	Limited Quantity	Excepted Quantity	Packing Instruction
2977	RADIOACTIVE MATERIAL, URANIUM HEXAFLUORIDE, FISSILE	7	**6.1**, 8			0	E0	See Chapter 2.7 and section 4.1.9
2978	RADIOACTIVE MATERIAL, URANIUM HEXAFLUORIDE, non-fissile or fissile-excepted	7	**6.1**, 8		317	0	E0	See Chapter 2.7 and section 4.1.9
3507	URANIUM HEXAFLUORIDE, RADIOACTIVE MATERIAL, EXCEPTED PACKAGE, less than 0.1 kg per package, non-fissile or fissile-excepted	**6.1**	7, **8**	I	317 369	0	E0	P**603**

14. Chapter 3.3, amend special provision 369 to read as follows:

"In accordance with 2.0.3.2, this radioactive material in an excepted package possessing **toxic and** corrosive properties is classified in Class **6.1** with radioactive material **and corrosivity** subsidiary risk

Uranium hexafluoride may be classified under this entry only if the conditions of 2.7.2.4.1.2, 2.7.2.4.1.5, 2.7.2.4.5.2 and, for fissile-excepted material, of 2.7.2.3.6 are met.

In addition to the provisions applicable to the transport of Class 6.1 substances **with a corrosivity subsidiary risk**, the provisions of 5.1.3.2, 5.1.5.2.2, 5.1.5.4.1 (b), 7.1.8.5.1 to 7.1.8.5.4 and 7.1.8.6.1 shall apply.

No Class 7 label is required to be displayed."

15. Chapter 4.1.4.1 (Packing Instructions): Change "P805" to **"P603"** and move it between P602 and P620.

Annex

Data sheet to be submitted to the United Nations for new or amended classification of substances (Changes to the original document from the IAEA in bold italics)

Submitted by.....IAEA.....Date .....blank.....

Supply all relevant information including sources of basic classification data. Data should relate to the product in the form to be transported. State test methods. Answer all questions - if necessary state "not known" or "not applicable" - If data is not available in the form requested, provide what is available with details. Delete inappropriate words.

Section 1 Substance identity

1.1 Chemical name: Uranium hexafluoride

1.2 Chemical formula: UF_6

1.3 Other names/synonyms

1.4.1 UN number:.....left blank. 1.4.2 CAS number: .. left blank.....

1.5 Proposed classification for the Recommendations: left blank

1.5.1 Proper shipping name (3.1.2[a])... . left blank

1.5.2 Class/division: left blank

Packing group: left blank

Subsidiary risks ***5.1 (oxidizing) under investigation, 6.1 (toxic), 8 (corrosive)***

1.5.3 Proposed special provisions, if any see left blank

1.5.4 Proposed packing instruction(s)..... see left blank

Section 2 Physical properties

2.1 Melting point or range..... 64.05 °C (triple point)

2.2 Boiling point or range ..... 56.5 °C (sublimes)

2.3 Relative density at:

2.3.1 15 °C ...5.12 g/cm^3.....

2.3.2 20 °C :..5.09 g/cm^3.....

2.3.3 50 °C ....4.92. g/cm^3.....

2.4 Vapour pressure at : (20 °C is 10,58 kPa[b])

2.4.1 50 °C .....70.2.. kPa[h]

2.4.2 65 °C .....156.56.. kPa[h]

2.5 Viscosity at 20 °C[c].....NA..... m2/s

2.6 Solubility in water at 20 °C ....NA..... g/100 ml (reacts with water)

2.7 Physical state at 20°C (2.2.1.1[a]) solid[c]

2.8 Appearance at normal transport temperatures, including colour and odour:

Colourless to white deliquescent crystals.

2.9 Other relevant physical properties.....

Section 3 Flammability

3.1 Flammable vapour

3.1.1 Flash point (2.3.3[a]) ..... °C oc/cc, NA.

3.1.2 Is combustion sustained? (2.3.1.3[a]) NA

3.2 Autoignition temperature .....°C, NA

3.3 Flammability range (LEL/UEL) .....%, NA

3.4 Is the substance a flammable solid? (2.4.2[a]) no

3.4.1 If yes, give details .....

Section 4 Chemical properties

4.1 Does the substance require inhibition/stabilization or other treatment such as nitrogen blanket to prevent hazardous reactivity ? no

If yes, state:

4.1.1 Inhibitor/stabilizer used . .....

4.1.2 Alternative method .....

4.1.3 Time effective at 55 °C .....

4.1.4 Conditions rendering it ineffective .....

4.2 Is the substance an explosive according to paragraph 2.1.1.1? (2.11) no

4.2.1 If yes, give details .....

4.3 Is the substance a desensitized explosive? (2.4.2.4[a]) no

4.3.1 If yes, give details

.....

4.4 Is the substance a self-reactive substance? (2.4.11) no

If yes, state:

4.4.1 Exit box of flow chart .....

What is the self-accelerating decomposition temperature (SADT) for a 50 kg package? ..... °C

Is the temperature control required? (2.4.2.3.4[a]) no

4.4.2 Proposed control temperature for a 50 kg package ..... °C

4.4.3 Proposed emergency temperature for a 50 kg package..... °C

4.5 Is the substance pyrophoric? (2.4.31) no

4.5.1 If yes, give details .....

4.6 Is the substance liable to self-heating? (2.4.3[a]) no

4.6.1 If yes, give details .....

.....

4.7 Is the substance an organic peroxide (2.5.1[a]) no

If yes state:

4.7.1 exit box of flow chart .....

What is the self accelerating decomposition temperature (SADT) for a 50 kg package?..... °C

Is temperature control required? (2.5.3.4.1[a]) yes/no

4.7.2 proposed control temperature for a 50 kg package ..... °C

4.7.3 proposed emergency temperature for a 50 kg package..... °C

4.8 Does the substance in contact with water emit flammable gases? (2.4.4[a]) no

4.8.1 If yes, give details .....

4.9 Does the substance have oxidizing properties (2.5.11) : under investigation

4.9.1 If yes, give details: UF_6 readily oxidates organic compounds, ***e.g: violent reaction with vacuum pump (motor) oil at room temperature.***

4.10 Corrosivity (2.8[a]) to: No data available, (the test 37)

4.10.1 Mild steel .....mm/year at ..... °C

4.10.2 Aluminium.....mm/year at.....°C

4.10.3 Other packaging materials (specify)

.....mm/year at..... °C

.....mm/year at..... °C

4.11 Other relevant chemical properties:.

Uranium hexafluoride (UF_6) combines with water to form the soluble reaction products UO_2F_2 and HF. UF_6 is (essentially) inert to most metals and fluorinated plastics and rubbers. Teflon is used in the valve packing and cap gasket of UF_6 cylinders. The use of glass is not advised because the presence of trace amounts of HF in UF_6 and residual moisture on the glass can result in rapid attack of the material.

Section 5 Harmful biological effects

5.1 LD50, oral (Human) (2.6.2.1.1[a]): 1.63 mg/kg[b], [e] ~~***(under investigation)***~~

5.2 LD50, dermal (2.6.2.1.2[a]) .....mg/kg Animal species .....

5.3 LC50, inhalation (2.6.2.1.3[a]) .. 942 mg/m^3 Exposure time 10 minutes

Animal species: rat[d].... ~~***(under investigation)***~~

5.4 Saturated vapour concentration at 20 °C (2.6.2.2.4.3[a]): 104436 ml/m^3 [b]

5.5 Skin exposure (2.8[a]) results: Highly corrosive (causes severe burns), effect based on the corrosivity of HF produced by the hydrolysis of UF_6 [b]

Exposure time ..... hours/minutes

Animal species.....

5.6 Other data: Radiological toxicity, mainly emit alpha particles that have little penetrating ability, the main radiation hazard from uranium occurs when uranium compounds are ingested or inhaled.

Specific activity of UF6: $1.2x10^4$ ~ $2.3x10^6$ Bq/g (0.5% ~ 95% U-235)[e] .

Acute toxicity to aquatic organisms: Likely to be high[b] , N[f]..(Not relevant to small quantity)

5.7 Human experience: Accidents in facilities,

LC50 (Human): 0.276 mg/litre, Exposure time 1 hour[b]. ***~~(under investigation)~~***

Section 6 Supplementary information

6.1 Recommended emergency action

6.1.1 Fire (include suitable and unsuitable extinguishing agents)

6.1.2 Spillage .....

6.2 Is it proposed to transport the substance in:

6.2.1 Bulk Containers (6.8[a])

6.2.2 Intermediate Bulk Containers (6.5[a])?

6.2.3 Portable tanks (6.7[a])?

If yes, give details in Sections 7, 8 and/or 9.

Section 7 Bulk containers (only complete if yes in 6.2.1)

7.1 Proposed type(s)

Section 8. Intermediate bulk containers (IBCs) (only complete if yes in 6.2.2)

8.1 Proposed type(s).....

Section 9. Multimodal tank transport (only complete if yes in 6.2.3)

9.1 Description of proposed tank (including IMO tank type if known).....

9.2 Minimum test pressure

9.3 Minimum shell thickness

9.4 Details of bottom openings, if any

9.5 Pressure relief arrangements

9.6 Degree of filling

9.7 Unsuitable construction materials .

Endnote:

[a] This and similar references are to chapters and paragraphs in the Model Regulations on the Transport of Dangerous Goods.

[b] IUCLID: EUROPEAN COMMISSION – European Chemicals Bureau
http://esis.jrc.ec.europa.eu/doc/IUCLID/data_sheets/7783815.pdf

[c] See definition of "liquid" in 1.2.1 of the Model Regulations on the Transport of Dangerous Goods.

[d] The Registry of Toxic Effects of Chemical Substances (RETCS)
http://www.cdc.gov/niosh-rtecs/yr480580.html

[e] IAEA TECDOC – 423: RECOMMENDATIONS FOR PROVIDING PROTECTION DURING THE TRANSPORT OF URANIUM HEXAFLUORIDE
Superseded by TECDOC 608

[f] International Chemical Safety Cards 1250
http://www.cdc.gov/niosh/ipcsneng/neng1250.html

[g] Uranium hexafluoride: a survey of the physico-chemical properties, R. DeWitt, GAT-280, the GOODYEAR atomic cooperation, Portsmouth Ohio, 1960.

[h] Oliver, G. D., Milton, H.T. and Grisard, J.W., The Vapor Pressure and Critical Constants of Uranium Hexafluoride, J. Am. Chem. Soc., 75, 2827-9 (1953)

[i] IAEA – TECDOC- 608: Interim guidance on the safe transport of uranium hexafluoride
http://www-pub.iaea.org/MTCD/publications/PDF/te_608_prn.pdf