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**DETAILED REVIEW DOCUMENT ON CLASSIFICATION IN OECD MEMBER COUNTRIES OF  
SUBSTANCES AND MIXTURES WHICH IN CONTACT WITH WATER RELEASE TOXIC GASES**

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The work of the OECD related to chemical safety is carried out in the Environment, Health and Safety Programme. As part of its work on chemical testing, the OECD has issued several Council Decisions and Recommendations (the former legally binding on member countries), as well as numerous Guidance Documents and technical reports. The best known of these publications, the OECD Test Guidelines, is a collection of methods used to assess the hazards of chemicals and of chemical preparations. These methods cover tests for physical and chemical properties, effects on human health and wildlife, and accumulation and degradation in the environment. The OECD Test Guidelines are recognised world-wide as the standard reference tool for chemical testing.

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The Environment, Health and Safety Programme co-operates closely with other international organisations. This document was produced within the framework of the Inter-Organisation Programme for the Sound Management of Chemicals (IOMC).

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## **DETAILED REVIEW DOCUMENT ON CLASSIFICATION IN OECD MEMBER COUNTRIES OF SUBSTANCES AND MIXTURES WHICH IN CONTACT WITH WATER RELEASE TOXIC GASES**

### **INTRODUCTION**

1. During discussion at the *International Workshop on the Harmonization of the Classification of the Physical Hazards of Chemicals*, held in Ottawa in 1994, it was noted that the workplace system in Canada has classification criteria for substances which react on contact with water to give off toxic gases or vapours. A recommendation was made for further study.

2. This subject was revisited at the second session of the *Working Group on Harmonization of Classification Criteria for Reactive Substances* when the expert from the United States made a proposal to cover the emission of both flammable and toxic gases under the UN Recommendations for the Transport of Dangerous Goods. At the July 1997 meeting of the *UN/ILO Working Group on Harmonized Classification Criteria for Physical Hazards*, it was generally felt that cooperation with the OECD would be necessary for this matter, as reaction with water was a property falling within the competence of the group and the toxicity and corrosivity of gases evolved were properties falling within the competence of the OECD. Canada was asked to submit a proposal to the OECD Advisory Group for the Harmonization of Classification and Labelling.

3. At the 9th Meeting of the Task Force for the Harmonization of Classification and Labelling (OECD, Paris, 17-18 February 2000), the Task Force agreed to begin work on the Step 1 document to explain the rationale behind current national criteria and approaches.

4. The 31<sup>st</sup> Joint Meeting agreed that this work should be done by the Task Force for the Harmonization of Classification and Labelling.

5. The Step 1 document including comments from US, Slovenia, BIAC (European) and Canada.

### **SCOPE AND DEFINITIONS**

#### **Scope**

6. This endpoint covers substances which in contact with water releases toxic gases or vapours.

#### **Description of the classification systems in place**

##### **The Canadian System:**

7. The Canadian workplace system includes the following requirements:

Section 66 of the *Controlled Products Regulations to the Hazardous Products Act*:

A product, material or substance shall be included in Class F - Dangerously Reactive Material listed in Schedule II to the Act if it...



(c) reacts vigorously with water to release a gas that has an LC<sub>50</sub> not exceeding 2,500 parts per million by volume of gas, when tested for four hours in accordance with OECD Test Guideline No. 403, "Acute Inhalation Toxicity", dated May 12, 1981.

It is assumed that mixtures will be tested.

8. It is recognized that Section 66 covers a wide range of chemically reactive materials, including substances which react with water to form a toxic gas as described by paragraph 46(c) of the *CPR*. At present, section 66 correlates only with paragraph 46(c); i.e., paragraph 66(c) refers only to emissions of a "gas" in contact with water or water vapour. This implies the exclusion of flammable vapours and vapours with an LC<sub>50</sub> not exceeding 1,500 ppm as per paragraph 46(d) and vapours with an LC<sub>50</sub> between 1,500 and 2,500 ppm as per paragraph 49(c) of the *CPR*. Therefore, it has been agreed that section 66 of the *CPR* be amended to include the following two paragraphs:

(d) reacts vigorously with water to release a vapour that has an LC<sub>50</sub> not exceeding 1,500 ppm by volume of vapour, when tested for four hours in accordance with OECD Test Guideline 403, "Acute Inhalation Toxicity", dated May 12, 1981, and a saturated vapour concentration at normal atmospheric pressure greater than two times the value of that LC<sub>50</sub>"; or

(e) reacts vigorously with water to release a vapour that has an LC<sub>50</sub> of more than 1,500 but not exceeding 2,500 ppm by volume of vapour, when tested for 4 hours in accordance with OECD Test Guideline No. 403, "Acute Inhalation Toxicity", dated May 12, 1981, and a saturated vapour concentration at normal atmospheric pressure of more than 0.4 times the LC<sub>50</sub>";

#### **The EU System Including Slovenia:**

9. The EU system assigns additional risk phrases in accordance with the following criteria (based on experience obtained during compilation of Annex I) to substances and preparations classified by virtue of 2.2.1. to 3.2.7. above and/or chapters 4 and 5:

R29 Contact with water liberates toxic gas

For substances and preparations which in contact with water or damp air, evolve very toxic/toxic gases in potentially dangerous amounts, e.g. aluminum phosphide, phosphorus pentasulphide.

10. The EU system defines very toxic gases as less than or equal to 0.5 mg/l and toxic gases as greater than 0.5 mg/l but less than 2.0 mg/l.

#### **The US System:**

11. The U.S. Department of Transportation has legislation/classification systems based on the hazards of water activated toxic substances:

Certain substances which in contact with water emit toxic gases. Toxic gases are gases which are known to be so toxic or corrosive to humans as to pose a hazard to health or are presumed to be toxic or corrosive

to humans because they have an  $LC_{50}$  value equal to or less than  $5,000 \text{ ml/m}^3$  (ppm) when tested in accordance with UNRTDG 6.2.3.

It is assumed that mixtures will be tested.

12. The other regulatory authorities (EPA/Office of Pesticide Programs, OSHA, CPSC) regulate (classification and labeling) water activated toxic substances, but have not exercised special authority to distinguish such substances from toxic substances.

**The UN Recommendations on the Transport of Dangerous Goods – Model Regulations:**

13. The Section 2.2.2.1 (c) UN Recommendations on the Transport of Dangerous Goods – Model Regulations includes:

Division 2.3: *Toxic Gases*

Gases which:

- (i) are known to be so toxic or corrosive to humans as to pose a hazard to health; or
- (ii) are presumed to be toxic or corrosive to humans because they have an  $LC_{50}$  value (as defined in 2.6.2.1) equal to or less than  $5,000 \text{ ml.m}^3$  (ppm).

**NOTE:** Gases meeting the above criteria owing to their corrosivity are to be classified as toxic with a subsidiary corrosive risk.

**NOTE:** Gases with an  $LC_{50}$  lower than or equal to 200 ppm are referenced as “highly toxic gases”.

## ANNEX 1. COMPARISON OF THE CLASSIFICATION SCHEMES.

	Does your country/authority have any legislation for this endpoint?	Classification criteria for substances	Classification criteria for mixtures
<b>Canada</b>	Yes	Substances which react vigorously with water to release a gas that has an LC <sub>50</sub> not exceeding 2500 ppm by volume of gas, when tested for 4 hours in accordance with OECD Test Guideline No. 403, Acute Inhalation Toxicity, dated May 12, 1981.	It is assumed that mixtures will be tested.
<b>EU</b>	Yes	Substances which in contact with water or damp air, evolve very toxic/toxic gases in potentially dangerous amounts, e.g., aluminum phosphide, phosphorus pentasulphide.	It is assumed that mixtures will be tested
<b>Slovenia</b>	Yes	See EU	
<b>USA</b>	Yes	Certain substances which in contact with water emit toxic gases. Toxic gases are gases which are known to be so toxic or corrosive to humans as to pose a hazard to health or are presumed to be toxic or corrosive to humans because they have an LC <sub>50</sub> value equal to or less than 5,000 ml/m <sup>3</sup> (ppm) when tested in accordance with UNRTDG 6.2.3.	It is assumed that mixtures will be tested.

**ANNEX 2. NATIONAL LEGISLATION/CLASSIFICATION SYSTEMS IN PLACE.**

<b>COUNTRY</b>	<b>NATIONAL LEGISLATION</b>	<b>CRITERIA / GUIDELINES</b>	<b>APPLICATION OF CRITERIA</b>	<b>CONTROL IN PLACE</b>
<b>Canada</b>	Controlled Products Regulation (CPR) under the authority of Hazardous Products Act (HPA)	Professional judgement + CPR sections 33(), 66	Available data+expert judgement	Health Canada and federal, provincial & territorial occupational safety & health agencies.
<b>Germany</b>	Chemikaliengesetz v. 25 July 1994	Annexe VI :Dir. 67/548/EC	R49/Ann VI/dir. 67/548/EC	BgVV (Federal Institute on Veterinary medicine and consumer protection) BauA (Federal Institute of Occupational Safety and Hygiene)
<b>Slovenia</b>	The same as in the EU			
<b>USA</b>		49 CFR 173.124(c)	Available data +expert judgement	US Department of Transport

**ANNEX 3. DO LISTS OF SUBSTANCES WHICH ARE CLASSIFIED AS CAUSING A WATER ACTIVATED TOXIC HAZARDS EXIST?**

<b>COUNTRY</b>	<b>Do Lists Exist?</b>	<b>Reference</b>
<b>Canada</b>	No	
<b>Germany</b>	Yes	Annexe I :Dir. 67/548/EEC
<b>Slovenia</b>	No	
<b>USA</b>	Yes	Emergency Response Guidebook (see attachment)

## Attachment: From US Emergency Response Guidebook

*Water-Reactive Materials Which Produce Large Amounts of Toxic Gas(es) When in Contact with Water.*

		TIH	LC <sub>50</sub>
1162	Dimethyldichlorosilane	HCl	3124
1242	Methyldichlorosilane	HCl	3124
1250	Methyltrichlorosilane	HCl	3124
1295	Trichlorosilane	HCl	3124
1298	Trimethylchlorosilane	HCl	3124
1340	Phosphorus pentasulfide	H S	712
1360	Calcium phosphide	PH	22
1384	Sodium hydrosulfite	H S	712
1384	Sodium hydrosulfite	SO	2520
1397	Aluminum phosphide	PH	22
1412	Lithium amide	NH	7338*
1419	Magnesium aluminum	PH	22
1432	Sodium phosphide	PH	22
1433	Stannic phosphide	PH	22
1541	Acetone cyanohydrin	HCN	71
1680	Potassium cyanide	HCN	71
1689	Sodium cyanide	HCN	71
1714	Zinc phosphide	PH	22
1716	Acetyl bromide	HBr	2860
1717	Acetyl chloride	HCl	3124
1724	Allyl trichlorosilane, stabilized	HCl	3124
1725	Aluminum bromide, anhydrous	HBr	2860
1726	Aluminum chloride, anhydrous	HCl	3124
1728	Amyltrichlorosilane	HCl	3124
1732	Antimony pentafluoride	HF	1300
1736	Benzoyl chloride	HCl	3124
1745	Bromine pentafluoride	Br	310
1745	Bromine pentafluoride	HF	1300
1746	Bromine trifluoride	Br	310
1746	Bromine trifluoride	HF	1300
1747	Butyltrichlorosilane	HCl	3124
1749	Chlorine trifluoride	Cl	293
1749	Chlorine trifluoride	HF	1300
1752	Chloroacetyl chloride	HCl	3124
1754	Chlorosulfonic acid	HCl	3124
1758	Chromium oxychloride	HCl	3124
1777	Fluorosulfonic acid	HF	1300
1801	Octyltrichlorosilane	HCl	3124
		TIH	LC
1806	Phosphorus pentachloride	HCl	3124
1809	Phosphorus trichloride	HCl	3124

1810	Phosphorus oxychloride	HCl	3124
1818	Silicon tetrachloride	HCl	3124
1828	Sulfur chlorides	H S	712
1828	Sulfur chlorides	HCl	3124
1828	Sulfur chlorides	SO	2520
1829	Sulfur trioxide	H SO	470
1831	Oleum	H SO	470
1834	Sulfuryl chloride	H SO	470
1834	Sulfuryl chloride	HCl	3124
1836	Thionyl chloride	HCl	3124
1836	Thionyl chloride	SO	2520
1838	Titanium tetrachloride	HCl	3124
1898	Acetyl iodide	HI	2860
1923	Calcium hydrosulfite	H S	712
1923	Calcium hydrosulfite	SO	2520
1939	Phosphorus oxybromide,	HBr	2860
2004	Magnesium diamide	NH	7338*
2011	Magnesium phosphide	PH	22
2012	Potassium phosphide	PH	22
2013	Strontium phosphide	PH	22
2442	Trichloroacetyl chloride	HCl	3124
2495	Iodine pentafluoride	HF	1300
2691	Phosphorus pentabromide	HBr	2860
2692	Boron tribromide	HBr	2860
2806	Lithium nitride	NH	7338*
2977	Uranium hexafluoride, fissile	HF	1300
2978	Uranium hexafluoride, non-	HF	1300
2985	Chlorosilanes, n.o.s.	HCl	3124
2986	Chlorosilanes, flam., corr, n.o.s.	HCl	3124
2987	Chlorosilanes, corrosive, n.o.s.	HCl	3124
2988	Chlorosilanes, wtr-rtv, flam.,	HCl	3124
3048	Aluminum phosphide pesticide	PH	22
3049	Metal alkyl halides, n.o.s.	HCl	3124
3052	Aluminum alkyl halides	HCl	3124
9191	Chlorine dioxide, hydrate,	Cl	293

\* RTECS (US HHS, 1986) value is 4000 ppm based on rat data.  
The CGA (1995) value is 7338 ppm.