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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**  
(Twenty-first session, 1-10 July 2002,  
agenda item 6 (b))

**DRAFT AMENDMENTS TO THE MODEL REGULATIONS  
ON THE TRANSPORT OF DANGEROUS GOODS**

**Listing and Classification**

**Proposal for schematic classification of Organometallic Substances**

**Transmitted by the International Council of Chemical Associations (ICCA)**

**1. Introduction**

Last December meeting, ICCA submitted an information paper (UN/SCETDG/20/INF.20) on a classification scheme for organometallic substances, in divisions 4.2 and 4.3. A number of comments have been received and as much as possible incorporated in this proposal.

In the UN Model Regulations, organometallic substances are classified in division 4.2 as pyrophoric substances or, in diluted form, in division 4.3 as water reactive substances. These substances can be designated to a number of UN entries, but not in a systematic way. In practice the same product may be transported under different UN numbers which causes confusion. Also some UN entries may be used for both solid and liquid substances. Over the last two years, relevant industries discussed these problems and developed a systematic classification procedure for organometallic substances as submitted in this proposal.

**2. Appropriate UN numbers**

The designation of an appropriate UN number to organometallic compounds is **not** based on a generic entry system. These materials can be assigned to the following available appropriate UN entries:

GE.02-

## Division 4.2

- pyrophoric substances; the current UN numbers are based on physical state (solid/liquid) and nature (organic or inorganic) of the substances;
- pyrophoric organometallic compounds n.o.s (one UN number for both solid and liquid);
- n.o.s entries for pyrophoric metal alkyls, on the basis of their general chemical nature (alkyls general, alkyl halides, alkyl hydrides and aryl hydrides);
- n.o.s. entries for pyrophoric metal alkyls with specified metal part;
- metal alkyls listed by chemical name.

## Division 4.3

- organometallic compound or compound solution or compound dispersion, water reactive, flammable
- organometallic compound, solid, water reactive, flammable

A table of currently available UN numbers is given in Annex 1. In practice, the number of possibilities result in a non unambiguous UN number assignment. For example, a pyrophoric solution of a metal alkyl compound can be assigned to UN number 2845 (Pyrophoric liquid, n.o.s.) or UN 3203 (Pyrophoric organometallic compounds, n.o.s) or UN 2003, Metal alkyl, n.o.s. In order to classify organometallic substances in a systematic way, ICCA proposes a procedure to achieve consistent classification. Justification is given below.

### 3. Justification of proposed classification scheme

In the proposed scheme for classifying organometallic substances the following aspects are incorporated:

- individual UN entries for solid and liquid substances, which is currently not the case;
- clear distinction between pyrophoric and non-pyrophoric organometallic substances and formulations;
- clear distinction between water reactive and non-water reactive organometallic substances and formulations;
- systematic assignment of packagings, IBCs and tanks (if applicable), in line with the current requirements for these substances and air elimination from the packaging in case of a pyrophoric substance.

In the scheme, the non-pyrophoric water reactive substances have to be evaluated on :

- a) flammability for solids and liquids; and
- b) self-heating properties for the solids.

On a): the determination of the flash point to assess flammability properties of liquids is not possible due to the reactive properties of organometallic substances in air. Therefore, it is proposed to use the flash point of the solvent used (if any) in the formulation.

On b): for non pyrophoric, water reactive solid organometallic substances the self-heating properties are tested first, because these substances may react with oxygen. In case of negative result, the flammability of 4.1 is tested. This is in line with the precedence of hazards table 2.0.3.3.

At the moment, test N.5 is not applicable to pyrophoric substances. Nevertheless the water reactivity property is an essential part of the classification. In practice, the test is executed under nitrogen atmosphere to determine water reactivity properties. Therefore it is proposed to amend the introductory text (33.4.1.3.1) of test N.5 accordingly.

All the UN entries proposed for deletion are covered by the proposed organometallic substances. Nevertheless it is proposed to keep the old UN entries in the alphabetic list with reference to the relevant new UN number. For the new generic entries proposed, the wording organometallic “substance” which covers the current descriptions: compounds, solutions, dispersions because it is not always obvious which description should be used.

In case an organometallic substance is not classified according to the flow chart in division 4.2 or 4.3, with relevant subsidiary risk, classification in other classes has to be evaluated.

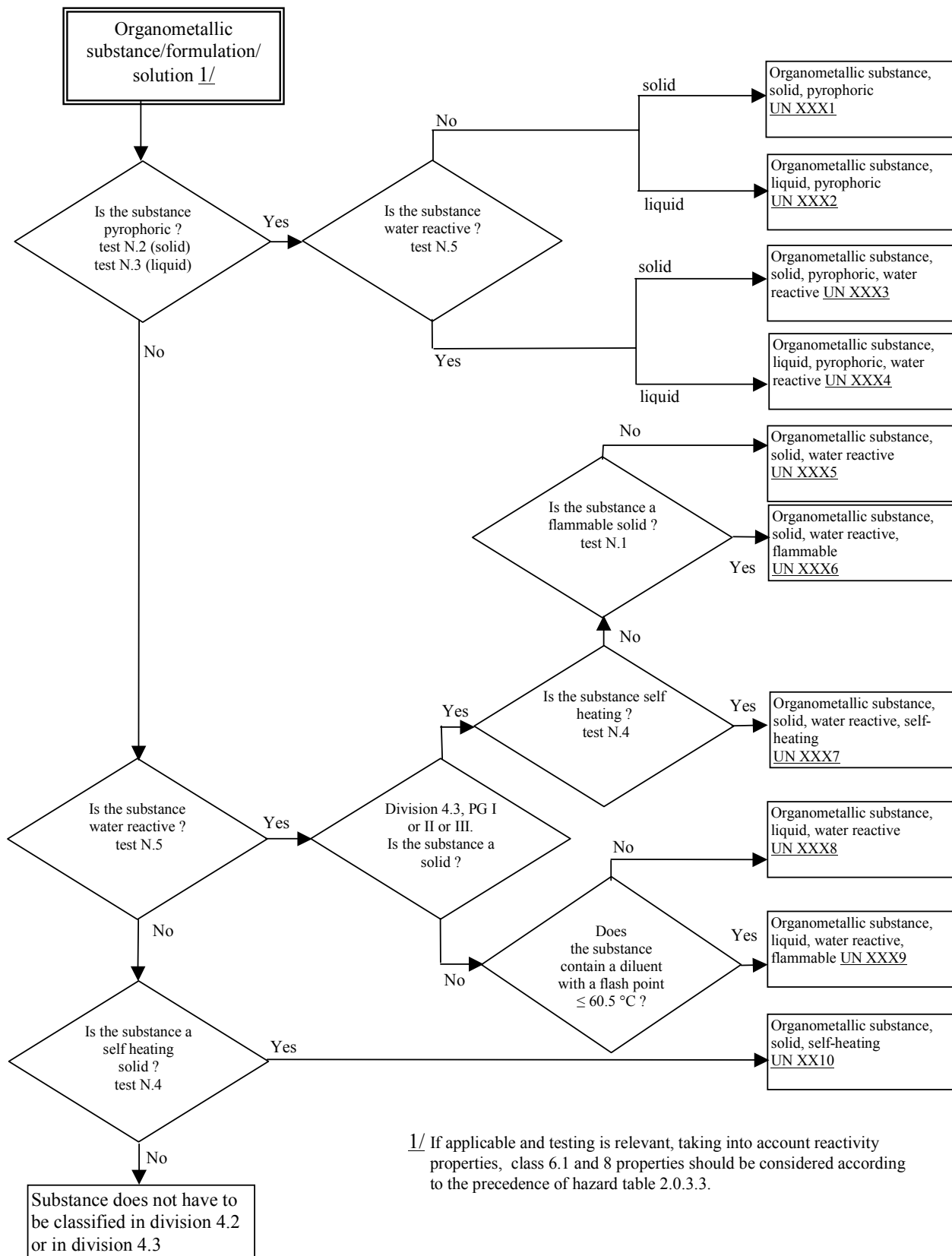
#### **4. Proposals**

4.1 Insert in chapter 2.4., under introductory notes, the following new note:

***NOTE 3:** Because Organometallic substances can be classified in division 4.2 or 4.3 with additional subsidiary risks, depending on the properties of the substance, a specific classification flow chart for these substances is given in 2.4.5*

## 4.2 Insert the following new flowchart in new 2.4.5

Figure 2.4.2: Flowchart scheme for organometallic substances



4.3 Delete the following UN numbers from Chapter 3.2, Dangerous Goods List:

1366	Diethylzinc
1370	Dimethylzinc
2003	Metal alkyls water-reactive N.O.S. or Metal aryls water reactive, N.O.S
2005	Magnesium diphenyl
2445	Lithium alkyls
3049	Metal alkyl halides, water-reactive, N.O.S., Metal aryl halides, water-reactive, N.O.S
3050	Metal alkyl hydrides, water-reactive, N.O.S., Metal aryl hydrides, water-reactive, N.O.S
3051	Aluminium alkyls
3052	Aluminium alkyl halides (liquid + solid)
3053	Magnesium alkyls
3076	Aluminium alkyl hydrides
3203	Pyrophoric organometallic compound, water reactive, N.O.S (solid + liquid)
3207	Organic metallic compound or compound solution or compound dispersion, water reactive, flammable, N.O.S
3372	Organic metallic compound solid, water reactive, flammable, N.O.S

4.4 Amend the second line of 33.4.1.3.1 of the Manual of Tests and Criteria to read as follows:

"In case a pyrophoric substance is tested, the test should be executed under nitrogen atmosphere."

4.5 Insert a new special packing provision in packing instruction P404:

"PPxx: For UN Nos. xxx1 and xxx3, air shall be eliminated from the vapour space by nitrogen or other means."

Insert a new special packing provision in packing instruction P400:

"PPxx: For UN Nos. xxx2 and xxx4, air shall be eliminated from the vapour space by nitrogen or other means."

Insert a new special packing provision in packing instruction IBC04:

"Bx: For UN Nos. xxx1 and xxx3, air shall be eliminated from the vapour space by nitrogen or other means."

## 4.6 Insert the following new UN numbers in the Dangerous Goods List of Chapter 3.2:

UN No.	Name and description	Class or division	Subsidiary risk	UN packing group	Special provisions	Limited quantities	Packagings and IBCs		Portable tanks	
							Packing instruction	Special provisions	Portable tank instruction	Portable tank special provision
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
xxx1	ORGANOMETALLIC SUBSTANCE, SOLID PYROPHORIC	4.2		I	274 yyy	NONE	P404 IBC04			
xxx2	ORGANOMETALLIC SUBSTANCE, LIQUID, PYROPHORIC	4.2		I	274 yyy	NONE	P400		T21	TP2 TP7
xxx3	ORGANOMETALLIC SUBSTANCE, SOLID PYROPHORIC, WATER REACTIVE	4.2	4.3	I	274 yyy	NONE	P404 IBC04			
xxx4	ORGANOMETALLIC SUBSTANCE, LIQUID, PYROPHORIC, WATER REACTIVE	4.2	4.3	I	274 yyy	NONE	P400		T21	TP2 TP7
xxx5	ORGANOMETALLIC SUBSTANCE, SOLID WATER REACTIVE	4.3		I	274	NONE	P403 IBC04			
		4.3		II	274	500 g	P410 IBC04			
		4.3		III	223 274	1 kg	P410 IBC06			
xxx6	ORGANOMETALLIC SUBSTANCE, LIQUID, WATER REACTIVE	4.3		I	274	NONE	P402		T13	TP2 TP7
		4.3		II	274	500 g	P001 IBC01		T7	TP2 TP7
		4.3		III	223 274	1 kg	P001 IBC02		T7	TP2 TP7
xxx7	ORGANOMETALLIC SUBSTANCE, SOLID WATER REACTIVE, FLAMMABLE	4.3	4.1	I	274	NONE	P403 IBC04			
		4.3	4.1	II	274	500 g	P410 IBC04			
		4.3	4.1	III	223 274	1 kg	P410 IBC06			
xxx8	ORGANOMETALLIC SUBSTANCE, SOLID WATER REACTIVE, SELF-HEATING	4.3	4.2	I	274	NONE	P403 IBC04			
		4.3	4.2	II	274	500 g	P410 IBC04			
		4.3	4.2	III	223 274	1 kg	P410 IBC06			
xxx9	ORGANOMETALLIC SUBSTANCE, LIQUID, WATER REACTIVE, FLAMMABLE	4.3	3	I	274	NONE	P402		T13	TP2 TP7
		4.3	3	II	274	500 g	P001 IBC01		T7	TP2 TP7
		4.3	3	III	223 274	1 kg	P001 IBC02		T7	TP2 TP7
xxx10	ORGANOMETALLIC SUBSTANCE, SOLID SELF-HEATING	4.2		II	274	500 g	P410 IBC06			
		4.2		III	223 274	1 kg	P002 IBC08			

## 5. Consequential amendments

### 5.1 Amend the following entries in the alphabetical index of substances and articles

Entry	To read as follows:
DIETHYLZINC, 4.2, 1366	Diethylzinc, see 4.2, xxx4
DIMETHYLZINC, 4.2, 1370	Dimethylzinc, 4.2, xxx4
METAL ALKYL, WATER-REACTIVE, N.O.S., 4.2, 2003	Metal alkyls, water-reactive N.O.S., see 4.2, xxx3 or xxx4
METAL ARYL, WATER-REACTIVE, N.O.S., 4.2, 2003	Metal aryls, water-reactive N.O.S., see 4.2, xxx3 or xxx4
MAGNESIUM DIPHENYL, 4.2, 2005	Magnesium diphenyl, see 4.2, xxx1
LITHIUM ALKYL, 4.2, 2445	Lithium alkyls, see 4.2, xxx4
METAL ALKYL HALIDES, WATER-REACTIVE, N.O.S., 4.2, 3049	Metal alkyl halides, water-reactive, N.O.S., see 4.2, xxx4
METAL ARYL HALIDES, WATER-REACTIVE, N.O.S., 4.2, 3049	Metal aryl halides, water-reactive, N.O.S., see 4.2, xxx4
METAL ALKYL HYDRIDES, WATER-REACTIVE, N.O.S., 4.2, 3050	Metal alkyl hydrides, water-reactive, N.O.S., see 4.2, xxx4
METAL ARYL HYDRIDES, WATER-REACTIVE, N.O.S., 4.2, 3050	Metal aryl hydrides, water-reactive, N.O.S., see 4.2, xxx4
ALUMINIUM ALKYL, 4.2, 3051	Aluminium alkyls, see 4.2, xxx4
ALUMINIUM ALKYL HALIDES, LIQUID, 4.2, 3052	Aluminium alkyl halides, liquid see 4.2, xxx4
ALUMINIUM ALKYL HALIDES, SOLID, 4.2, 3052	Aluminium alkyl halides, solid see 4.2, xxx3
MAGNESIUM ALKYL, 4.2, 3053	Magnesium alkyls, see 4.2, xxx4
ALUMINIUM ALKYL HYDRIDES, 4.2, 3076	Aluminium alkyl hydrides, see 4.2, xxx4
PYROPHORIC ORGANOMETALLIC COMPOUND, WATER REACTIVE, LIQUID, N.O.S., 4.2, 3203	Pyrophoric organometallic compound, water reactive, liquid, N.O.S., see 4.2, xxx4
PYROPHORIC ORGANOMETALLIC COMPOUND, WATER REACTIVE, SOLID, N.O.S., 4.2, 3203	Pyrophoric organometallic compound, water reactive, solid, N.O.S., see 4.2, xxx3
ORGANOMETALLIC COMPOUND DISPERSION, WATER REACTIVE, FLAMMABLE, N.O.S., 4.3, 3207	Organometallic compound dispersion, water reactive, flammable, N.O.S., see 4.3, xxx9
ORGANOMETALLIC COMPOUND SOLUTION, WATER REACTIVE, FLAMMABLE, N.O.S., 4.3, 3207	Organometallic compound solution, water reactive, flammable, N.O.S., see 4.3, xxx9
ORGANOMETALLIC COMPOUND SOLID, WATER REACTIVE, FLAMMABLE, N.O.S., 4.3, 3372	Organometallic compound solid, water reactive, flammable, N.O.S., see 4.3, xxx6

5.2 Insert the new UN numbers, as shown in 4.4, in the alphabetical index of substances and articles

5.3 In 3.1.2.2 select an other example instead of UN 3207

In 3.1.2.8.1.3: select an other example for UN 2003 Metal Alkyl, water reactive, N.O.S. (triethylgallium)

5.4 Change UN numbers in packing instruction P404 (2005 into xxx1, 3203 into xxx3, 3052 into xxx3)

**Annex 1**Possible UN numbers for organometallic compounds, division 4.2

Proper shipping name	UN number
Pyrophoric liquid, organic, N.O.S	2845
Pyrophoric solid, organic, N.O.S	2846
Pyrophoric liquid, inorganic, N.O.S	3194
Pyrophoric solid, inorganic, N.O.S	3200
Pyrophoric organometallic comp, water reactive, N.O.S ( <b>solid + liquid</b> )	3203
Metal alkyls/aryls, water reactive, N.O.S	2003
Metal alkyl/aryl halides, water reactive, N.O.S	3049
Metal alkyl/aryl hydrides, water reactive, N.O.S.	3050
Aluminium alkyls	3051
Aluminium alkyl halides ( <b>solid + liquid</b> )	3052
Aluminium alkyl hydrides	3076
Magnesium alkyls	3053
Lithium alkyls	2445
Magnesium diphenyl	2005
Diethylzinc	1366
Dimethylzinc	1370

Possible UN numbers for organometallic compounds, division 4.3

Organometallic compound or compound solution or compound dispersion, water reactive, flammable, N.O.S	3207
Organometallic compound solid, water reactive, flammable, N.O.S	3372

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