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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
(Twentieth session, 3-12 December 2001, agenda item 7 (d))

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

This information paper contains a first draft on schematic classification of organometallic substances. The intent of this paper is to inform the UN sub-committee and to collect comments from the various delegations. A brief introduction may be given, but it is not the intent to discuss this paper during this December session.

A formal proposal, incorporating the comments received, will be submitted for the July 2002 session.

**** First DRAFT ****

1. Introduction

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 practise 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. The problem was already partly highlighted in Information paper 43, December 1994, of the UN CETDG. Over the last two years, relevant industries discussed these problems and developed a systematic classification procedure for organometallic substances as submitted by 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:

Division 4.2
- pyrophoric substance; 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 bases 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 practise, 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 the a procedure to achieve consistent classification. Justification is given below.

3. Justification of classification scheme proposed

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

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

a) flammability for the liquids and
b) self-heating properties for the solids (and not flammability properties).

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 in the formulation.

On b): for non pyrophoric, water reactive solid organometallic substances the self-heating properties are relevant, because these substances react with oxygen. Also according the precedence of hazards table 2.0.3.3, self-heating of 4.2 takes precedence over flammability 4.1.

All the UN entries proposed for deletion are covered by the proposed organometallic substances, defined as substances having a metal-carbon bond. Nevertheless it is proposed to remain 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 a organometallic substance is not classified according to the flow chart in division 4.2 or 4.3, classification in other classes has to be evaluated. This is also applicable for the substances classified by the proposed scheme.

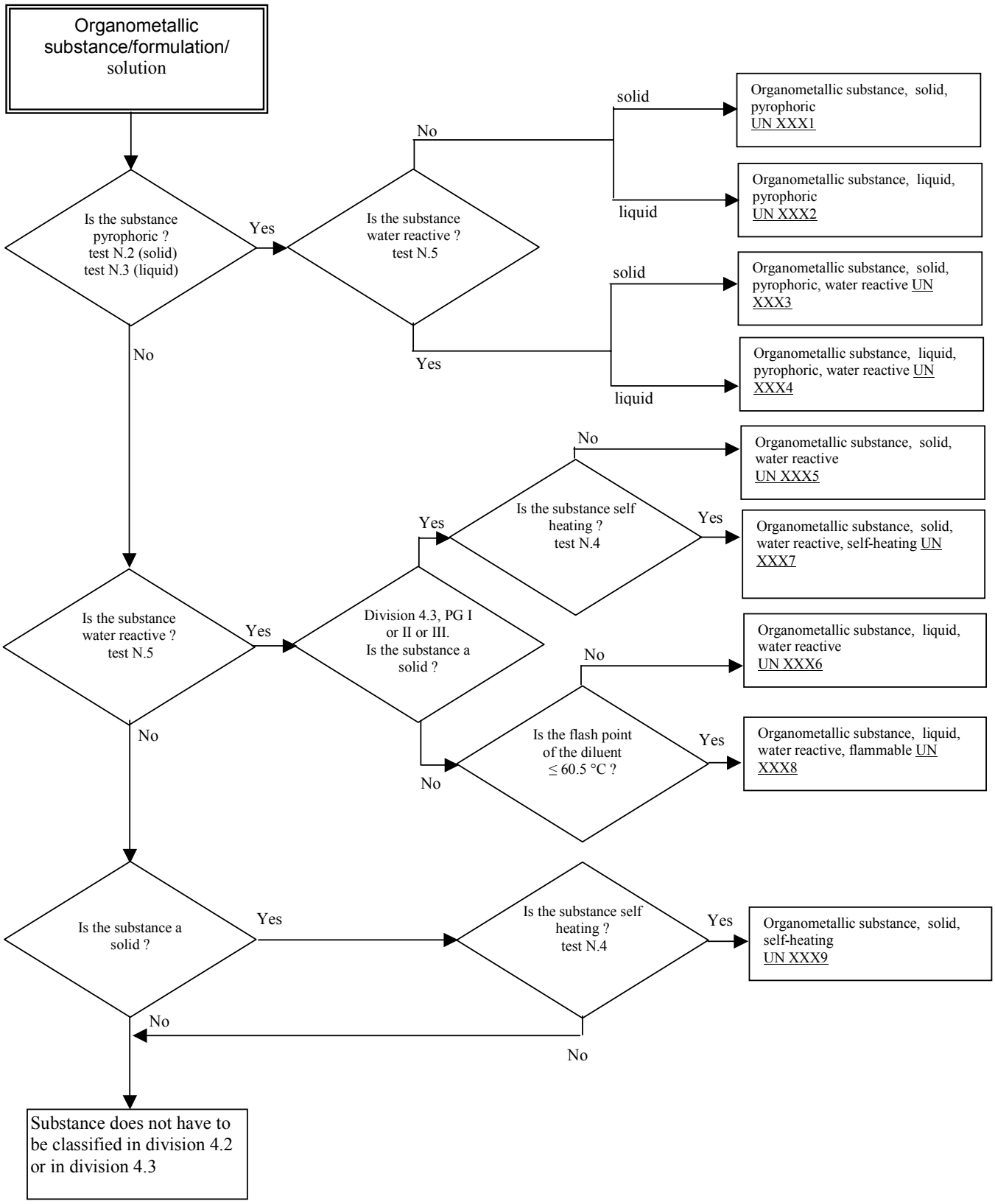
4. Proposals

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

NOTE 3: *Because Organometallic substances, defined as substances containing a metal-carbon bond, 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 (substances containing metal-carbon bonds)



4.3 Delete the following new UN numbers in chapter 3, 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 Insert the following new UN numbers in chapter 3, Dangerous Goods List:

UN No. (1)	Name and description (2)	Class or division (3)	Subsid-iary risk (4)	UN packing group (5)	Special provi-sions (6)	Limited quantities (7)	Packagings and IBCs		Portable tanks	
							Packing instruction (8)	Special provisions (9)	Portable tank instruction (10)	Portable tank special provision (11)
xxx1	Organometallic substance, solid, pyrophoric	4.2		I	274	NONE	P404			
xxx2	Organometallic substance, liquid, pyrophoric	4.2		I	274	NONE	P400		T21	TP2 TP7 TP9
xxx3	Organometallic substance, solid, pyrophoric, water reactive	4.2	4.3	I	274	NONE	P404			
xxx4	Organometallic substance, liquid, pyrophoric, water reactive	4.2	4.3	I	274	NONE	P400		T21	TP2 TP7 TP9
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 IBC99		T13	TP2 TP7 TP9
		4.3		II	274	500 g	P001 IBC01	B2	T7	TP2 TP7
		4.3		III	223 274	1 kg	P001 IBC02	B4	T7	TP2 TP7
xxx7	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			
xxx8	Organometallic substance, liquid, water reactive, flammable	4.3	3	I	274	NONE	P402 IBC99		T13	TP2 TP7 TP9
		4.3	3	II	274	500 g	P001 IBC01	B2	T7	TP2 TP7
		4.3	3	III	223 274	1 kg	P001 IBC02	B4	T7	TP2 TP7
xxx9	Organometallic substance, solid, self-heating	4.2		II	274	500 g	P410 IBC06	B2		
		4.2		III	223 274	1 kg	P002 IBC08	B3		

5. Consequential amendments

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

Entry	To be read as
DIETHYLZINC, 4.2, 1366	Diethylzinc, see 4.2, xxx4
DIMETHYLZINC, 4.2, 1370	Dimethylzinc, 4.2, xxx4
METAL ALKYLS, WATER-REACTIVE, N.O.S, 4.2, 2003	Metal alkyls, water-reactive N.O.S, see 4.2, xxx3 or xxx4
METAL ARYLS, 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 ALKYLS, 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 ALKYLS, 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 ALKYLS, 4.2, 3053	Magnesium alkyls, see 4.2, xxx4
ALMINIUM 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
ORGANIC METALLIC COMPOUND DISPERSION, WATER REACTIVE, FLAMMABLE, N.O.S, 4.3, 3207	Organic metallic compound dispersion, water reactive, flammable, N.O.S, see 4.3, xxx8
ORGANIC METALLIC COMPOUND SOLUTION, WATER REACTIVE, FLAMMABLE, N.O.S, 4.3, 3207	Organic metallic compound solution, water reactive, flammable, N.O.S, see 4.3, xxx8
ORGANIC METALLIC COMPOUND SOLID, WATER REACTIVE, FLAMMABLE, N.O.S, 4.3, 3372	Organic metallic compound solid, water reactive, flammable, N.O.S, see 4.3, xxx7

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 **(solid + liquid)**	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 **(solid + liquid)**	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

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