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COMITÉ D'EXPERTS DU TRANSPORT DES MARCHANDISES DANGEREUSES ET DU SYSTÈME GÉNÉRAL HARMONISÉ DE CLASSIFICATION ET D'ÉTIQUETAGE DES PRODUITS CHIMIQUES

Sous-Comité d'experts du transport des marchandises dangereuses

Vingt-cinquième session, 5-14 juillet 2004
Point 6 de l'ordre du jour provisoire

INSCRIPTION, CLASSEMENT ET EMBALLAGE

Proposition d'ajouter de nouvelles rubriques ONU pour l'acide formique (n° ONU 1779) et l'acide propionique (n° ONU 1848)

Communication de l'expert de l'Allemagne

Introduction

1. Lors de la session de mars 2003 du Sous-Comité des marchandises dangereuses, des cargaisons solides et des conteneurs (Sous-Comité DSC) de l'Organisation maritime internationale (OMI), l'Allemagne a attiré l'attention sur un problème se posant à propos d'une matière très courante, l'acide propionique (n° ONU 1848).

2. Pour cette matière, la liste des marchandises dangereuses du Code IMDG donne dans sa colonne 17 les informations et observations suivantes: Liquide incolore inflammable à odeur piquante. Miscible à l'eau. Corrosif pour le plomb et la plupart des autres métaux. Cause des brûlures cutanées. Les vapeurs ont des effets irritants sur les muqueuses.

3. Bien que cette matière soit décrite comme étant un liquide inflammable, aucun risque subsidiaire de la classe 3 n'est mentionné à la colonne 4 de la liste du Code IMDG.

4. L'expert de l'Allemagne a été prié de résoudre ce problème en proposant un nouveau numéro ONU au Sous-Comité d'experts de l'ONU.

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5. Au cours des travaux concernant ce document, les industriels ont attiré l'attention des experts allemands sur une matière qui présente des propriétés semblables à celles de l'acide propionique. Il s'agit de l'acide formique (n° ONU 1779).

6. Les experts allemands ont donc réuni toutes les données nécessaires pour pouvoir classer ces deux matières. Ces données sont présentées dans les fiches de renseignements figurant dans les annexes 1 et 2, et des informations supplémentaires dans l'annexe 3.

7. Pour tenir compte des données fournies par les fiches de renseignements et pour classer l'acide formique (n° ONU 1779) et l'acide propionique (n° ONU 1848) comme il convient, l'Allemagne propose d'apporter les amendements suivants à la liste des marchandises dangereuses du Règlement type de l'ONU.

Proposition

8. N° ONU 1779 ACIDE FORMIQUE
Colonne (2), modifier le nom et la description comme suit:
ACIDE FORMIQUE contenant plus de 85 % (masse) d'acide

9. N° ONU 1779 ACIDE FORMIQUE
Colonne (4), ajouter la mention «3»

10. ACIDE FORMIQUE
Ajouter une nouvelle rubrique ainsi conçue:

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
xxxx	ACIDE FORMIQUE contenant au moins 10 % et au plus 85 % (masse) d'acide	8		II		1 L	P001 IBC02		T7	TP2
	ACIDE FORMIQUE contenant au moins 5 %, mais moins de 10 % (masse) d'acide	8		III		5 L	P001 IBC03 LP01		T7	TP2

11. N° ONU 1848 ACIDE PROPIONIQUE

Colonne (2), modifier le nom et la description comme suit:
ACIDE PROPIONIQUE contenant au moins 10 %, mais moins de 90 % (masse) d'acide

12. Acide propionique

Ajouter dans la liste une nouvelle rubrique ainsi conçue:

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
yyyy	ACIDE PROPIONIQUE contenant au moins 90 % (masse) d'acide	8	3	II		1 L	P001 IBC02		T7	TP2

ANNEXES (ENGLISH ONLY)

Annex 1

DATA SHEET TO BE SUBMITTED TO THE UNITED NATIONS FOR NEW OR AMENDED CLASSIFICATION OF SUBSTANCES

Submitted by Germany Date 04-03-29

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. SUBSTANCES IDENTITY

1.1 Chemical name **Formic acid**

1.2 Chemical formula **CH_2O_2**

1.3 Other names/synonyms **none**

1.4.1 UN Number **1779** 1.4.2 CAS number **64-18-6**

1.5 Proposed classification for the Recommendations

1.5.1	proper shipping name (3.1.2)	Formic acid	
1.5.2	class/division	**8**	subsidiary risk(s) **3 for C > 85%**
	packing group	**II**	
	class/division	**8**	subsidiary risk(s) **no for 10%<C≤ 85%**
	packing group	**II**	
	class/division	**8**	subsidiary risk(s) **no for 5%<C< 10%**
	packing group	**III**	
1.5.3	proposed special provisions, if any	**none**	
1.5.4	proposed packing instruction(s)	**PG II = P001/IBC02**	
		PG III = P001/IBC03/LP01	

Section 2. PHYSICAL PROPERTIES

2.1	Melting point or range		**8 °C**
2.2	Boiling point or range		**101 °C**
2.3	Relative density at:		
2.3.1	15 °C	not known	
2.3.2	20 °C	**1.220 g/cm3**	
2.3.3	50 °C	not known	
2.4	Vapour pressure at:		
2.4.1	20°C	**4.2 kPa**	
	50 °C	**17.0 kPa**	
2.4.2	65 °C	not known	
2.5	Viscosity at 20 °C		**1.8 mPa*s**
2.6	Solubility in water at 20 °C		**complete** g/100 ml
2.7	Physical state at 20 °C (2.2.1.1)		solid / **liquid** / gas
2.8	Appearance at normal carriage temperatures, including colour and odour		
	colourless liquid, pungent odour		
2.9	Other relevant physical properties		not known

Section 3. FLAMMABILITY

3.1	Flammable vapour		
3.1.1	Flash point (2.3.3)		**see attachment**
3.1.2	Is combustion sustained? (2.3.1.2)		**yes** / no
3.2	Autoignition temperature		**480 °C**
3.3	Flammability range (LEL/UEL)		**12 / 38 %** estimated
3.4	Is the substance a flammable solid? (2.4.2)		yes / **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? yes / **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? (2.1) yes / **no**

4.2.1 If yes, give details ...

4.3 Is the substance a desensitized explosive? (2.4.2.4) yes / **no**

4.3.1 If yes, give details ...

4.4 Is the substance a self-reactive substance? (2.4.1) yes / **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) yes / **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? (2.4.3) yes / **no**

4.5.1 If yes, give details ...

4.6 Is the substance liable to self-heating? (2.4.3) yes / **no**

4.6.1 If yes, give details ...

4.7 Is the substance an organic peroxide (2.5.1) yes / **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 the temperature control required? (2.5.3.4.1) 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) yes / **no**

4.8.1 If yes, give details ...

4.9 Does the substance have oxidizing properties (2.5.1) yes / **no**

4.9.1 If yes, give details ...

4.10 Corrosivity (2.8) to:

4.10.1	mild steel ...	**C>5%**	**more than 6.25 mm/year at 55 °C**
4.10.2	aluminium ...	**C>5%**	**more than 6.25 mm/year at 55 °C**
4.10.3	other packing materials		
	(specify) **no**		... mm/year at ...
	...		... mm/year at ...

4.11 Other relevant chemical properties ...not known...

Section 5. HARMFUL BIOLOGICAL EFFECTS

5.1	LD 50, oral (2.6.2.1.1)	**730**	mg/kg	Animal species ...**rat**..
5.2	LD 50, dermal (2.6.2.1.2) .....**x..**		mg/kg	Animal species ...
	x...not published (Patty's Ind. Hyg. Toxicol. 4, 1994)			
5.3	LC 50, inhalation (2.6.2.1.3) ...**>14.8**....		mg/litre	Exposure time .**1**.. hours
		or	ml/m^3	Animal species ...

5.4 Saturated vapour concentration at 20 °C (2.6.2.2.4.3) **41.7.** ml/m^3

5.5 Skin exposure (2.8) results: **corrosive**

Exposure time ... **x x** hours/minutes

x x...not published (Patty's Ind. Hyg. Toxicol. 3, 1981)

Animal species ... **rabbit**

5.6 Other data ...

5.7 Human experience ...**medical reports of acute exposures of workers show severe skin burns (C>90%) and mild to moderate skin burns (10%<C≤ 90%).**

Section 6. SUPPLEMENTARY INFORMATION

6.1 Recommended emergency action

6.1.1 Fire (include suitable and unsuitable extinguishing agents):

suitable are dry chemical powder, carbon dioxide, water spray and appropriate foam

6.1.2 Spillage:

Absorb on sand or vermiculite and place in closed containers for disposal; ventilate area and wash spill site after material pickup is complete

6.2 Is it proposed to transport the substance in:

6.2.1 Intermediate Bulk Containers (6.5) **yes** / no

6.2.2 Portable tanks (6.7) **yes** / no

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

Section 7. INTERMEDIATE BULK CONTAINERS (IBCs) (only complete if yes in 6.2.1)

7.1 Proposed type(s)

PG II = IBC02

PG III = IBC03

Section 8. MULTIMODAL TANK TRANSPORT(only complete if yes in 6.2.2)

8.1 Description of proposed tank (including IMO tank type if known)

For 8(3), II and 8, II and 8, III

T7

8.2.	Minimum test pressure	**4.0 bar**
8.3	Minimum shell thickness	**see 6.7.2.4.2**
8.4	Details of bottom openings, if any	**see 6.7.2.6.3**
8.5	Pressure relief arrangements	**normal**
8.6	Degree of filling	**TP2**
8.7	Unsuitable construction materials	**no**

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Annex 2

DATA SHEET TO BE SUBMITTED TO THE UNITED NATIONS FOR NEW OR AMENDED CLASSIFICATION OF SUBSTANCES

Submitted by Germany Date 04-03-25

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. SUBSTANCES IDENTITY

1.1	Chemical name	**Propionic acid**
1.2	Chemical formula	**$C_3H_6O_2$**
1.3	Other names/synonyms	**Propanoic acid**
1.4.1	UN Number	**1848**
1.4.2	CAS number	**79-09-4**

1.5 Proposed classification for the Recommendations

1.5.1	proper shipping name (3.1.2)		**Propionic acid**	
1.5.2	class/division	**8**	subsidiary risk(s)	**3 for C ≥ 90%**
	packing group	**II**		
	class/division	**8**	subsidiary risk(s)	**no for 10%<C< 90%**
	packing group	**III**		

1.5.3	proposed special provisions, if any	**none**
1.5.4	proposed packing instruction(s)	**PG II = P001/IBC02**
		PG III = P001/IBC03/LP01

Section 2. PHYSICAL PROPERTIES

2.1	Melting/freezing point or range		**-20 °C**
2.2	Boiling point or range		**141 °C**
2.3	Relative density at:		
	2.3.1	15 °C	not known
	2.3.2	20 °C	**0.992 g/cm3**
	2.3.3	50 °C	not known
2.4	Vapour pressure at:		
	2.4.1	**20 °C**	**0.5 kPa**
		50 °C	not known
	2.4.2	65 °C	not known
2.5	Viscosity at 20 °C		**10 mPas**
2.6	Solubility in water at 20 °C		**complete** g/100 ml
2.7	Physical state at 20 °C (2.2.1.1)		solid / **liquid** / gas
2.9	Appearance at normal carriage temperatures, including colour and odour		
	colourless liquid, pungent odour		
2.9	Other relevant physical properties		not known

Section 3. FLAMMABILITY

3.1	Flammable vapour		
	3.1.1	Flash point (2.3.3)	**see attachment**
	3.1.2	Is combustion sustained? (2.3.1.2)	**yes** / no
3.2	Autoignition temperature		**485 °C**
3.3	Flammability range (LEL/UEL)		**2.0 / 12.0 %** estimated
3.4	Is the substance a flammable solid? (2.4.2)		yes / **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? yes / **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? (2.1) yes / **no**

4.2.1 If yes, give details ...

4.3 Is the substance a desensitized explosive? (2.4.2.4) yes / **no**

4.3.1 If yes, give details ...

4.4 Is the substance a self-reactive substance? (2.4.1) yes / **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) yes / **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? (2.4.3) yes / **no**

4.5.1 If yes, give details ...

4.6 Is the substance liable to self-heating? (2.4.3) yes / **no**

4.6.1 If yes, give details ...

4.7 Is the substance an organic peroxide (2.5.1) yes / **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 the temperature control required? (2.5.3.4.1) 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) yes / **no**

4.8.1 If yes, give details ...

4.9 Does the substance have oxidizing properties (2.5.1) yes / **no**

4.9.1 If yes, give details ...

4.10 Corrosivity (2.8) to:

4.10.1	mild steel ...	**C>10%**	**more than 6.25 mm/year at 55 °C**
4.10.2	aluminium ...	**C>10%**	**more than 6.25 mm/year at 55 °C**
4.10.3	other packing materials		
	(specify) **no**		... mm/year at ...
		…	... mm/year at ...

4.11 Other relevant chemical properties ... not known...

Section 5. HARMFUL BIOLOGICAL EFFECTS

5.1	LD 50, oral (2.6.2.1.1)	**3500-4200**	mg/kg	Animal species	**rat**..
5.2	LD 50, dermal (2.6.2.1.2)	**500....**	mg/kg	Animal species	r**abbit**
5.3	LC 50, inhalation (2.6.2.1.3)	**>19.7**....	mg/litre	Exposure time	**1**. hours
		or	ml/m^3	Animal species	**rat**..

5.4 Saturated vapour concentration at 20 °C (2.6.2.2.4.3) **4.96** ml/m^3

5.5 Skin exposure (2.8) results: **corrosive**

Exposure time ...**1 + 5 + 15** hours/**minutes**

Animal species ... **rabbit**

5.6 Other data ...

5.7 Human experience ... **medical reports of acute exposures of workers show moderate skin burns (C>25%).**

Section 6. SUPPLEMENTARY INFORMATION

6.1 Recommended emergency action

6.1.1 Fire (include suitable and unsuitable extinguishing agents):

suitable are dry chemical powder, carbon dioxide, water spray and appropriate foam

6.1.3 Spillage:

Absorb on sand or vermiculite and place in closed containers for disposal; ventilate area and wash spill site after material pickup is complete

6.2 Is it proposed to transport the substance in:

6.2.1 Intermediate Bulk Containers (6.5) **yes** / no

6.2.2 Portable tanks (6.7) **yes** / no

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

Section 7. INTERMEDIATE BULK CONTAINERS (IBCs) (only complete if yes in 6.2.1)

7.1 Proposed type(s)

PG II = IBC02

PG III = IBC03

Section 8. MULTIMODAL TANK TRANSPORT (only complete if yes in 6.2.2)

8.2 Description of proposed tank (including IMO tank type if known)

		for 8(3), II	**for 8, III**
		T7	**T4**
8.2.	Minimum test pressure	**4.0 bar**	**2.65 bar**
8.3	Minimum shell thickness	**see 6.7.2.4.2**	**see 6.7.2.4.2**
8.4	Details of bottom openings, if any	**see 6.7.2.6.3**	**see 6.7.2.6.3**
8.5	Pressure relief arrangements		**normal normal**
8.6	Degree of filling	**TP2**	**TP1**
8.7	Unsuitable construction materials	**no**	**no**

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Annex 3

UN 1779 Formic acid + UN 1848 Propionic acid

Tranport classification as a function of conventration						
Status	**UN-No.**	**Specification**	**Concentration**	**PG**	**Label**	**Comments**
New	1848	Propionic acid CH_3-CH_2-COOH	³ 90%	II	8 + 3	for Fp <61°C
Old	1848	Propionic acid	10 to < 90%	III	8	for Fp >61°C including corrosiv to metals
Status	**UN-No.**	**Specification**	**Concentration**	**PG**	**Label**	**Comments**
New	1779	Formic acid CH-OOH	> 85%	II	8 + 3	for Fp <61°C
Old	1779	Formic acid	10 to < 85%	II	8	for Fp >61°C
New	XXXX	Formic acid	5 to < 10%	III	8	corrosiv to metals
For comparison:						
Status	**UN-No.**	**Specification**	**Concentration**	**PG**	**Label**	**Comments**
Old	2789	Acetic acid CH_3-COOH	> 80%	II	8 + 3	for Fp <61°C
Old	2790	Acetic acid	50 to < 80%	II	8	for Fp >61°C
Old	2790	Acetic acid	> 10 to < 50%	III	8	corrosiv to metals

Old means the existing one.

Labelling hazard information as a function of concentration according the EU directive 67/548/EWG						
Status	**No.**	**Specification**	**Concentration**	**--**	**Symbol**	**R-Phrase**
EG	200-579-1	Formic acid CH-OOH	³ 90%	--	C	35
CAS	64-18-6	Formic acid	10 to < 90%	--	C	34
Index	607-001-00-0	Formic acid	2 to < 10%	--	Xi	36/38
Status	**No.**	**Specification**	**Concentration**	**--**	**Symbol**	**R-Phrase**
EG	200-580-7	Acetic acid CH_3-COOH	³ 90%	--	C	35
CAS	64-19-7	Acetic acid	25 to < 90%	--	C	34
Index	607-002-00-6	Acetic acid	10 to < 25%	--	Xi	36/38
Status	**No.**	**Specification**	**Concentration**	**--**	**Symbol**	**R-Phrase**
EG	201-176-3	Propionic acid CH_3-CH_2-COOH	³ 25%	--	C	34
CAS	79-09-4	Propionic acid	10 to < 25%	--	Xi	36/37/38

Flashpoint as a function of the concentration		
Concentration %	Flashpoint of formic acid (UN 1779)	Flashpoint of propionic acid (UN 1848)
100	48	50
95	51	54
90	57	61
85	65	72
80	82	91