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

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Sub-Committee of Experts on the Transport of Dangerous Goods

Forty-ninth session

Geneva, 27 June – 6 July 2016
Item 3 of the provisional agenda
Listing, classification and packing

Examples how to apply the calculation method for the classification and assignment to packing groups for mixtures as proposed in ST/SG/AC.10/C.3/2016/21 and ST/SG/AC.10/C.3/2016/21/Corr.1

Transmitted by the European Chemical Industry Council (CEFIC) and the International Association for Soaps, Detergents and Maintenance Products (AISE)

Purpose

1. At the forty-eighth session of the Sub-Committee of Experts on the Transport of Dangerous Goods (TDG), discussions continued with regards to proposed changes to Chapter 2.8 of the UN Model Regulations. Besides the progress on the discussion which test methods and alternative methods can be used to classify a mixture to class 8 and how to assign the appropriate packing group, there was the request to industry to provide examples, on how and when the calculation method can be applied and whether the method is adequate compared to testing.

2. This paper provides examples as requested in the report of the forty-eighth session meeting: "CEFIC would also provide, in an informal document, relevant data relating to mixtures containing well-known corrosive substances for which information is available in order to illustrate the adequacy of the packing group assignment methods proposed."

3. The examples contain well-known substances as well as self-classifications to show in addition to the requirements expressed above that in industry for all ingredients of a mixture, the transport classification is available.

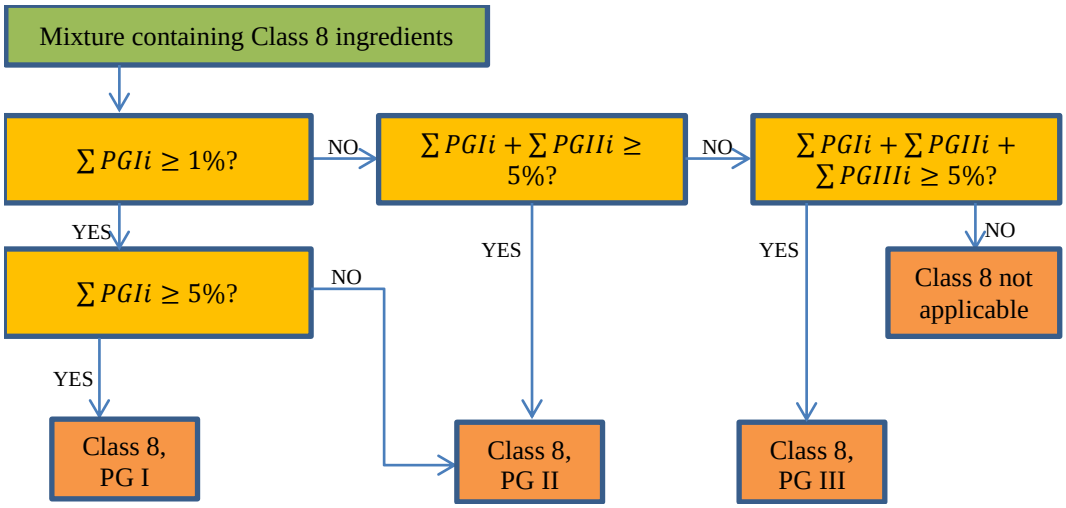
4. The calculation scheme used is as proposed in the working paper ST/SG/AC.10/C.3/2016/21. It is only applicable for mixtures where the corrosive properties of the substances in the mixture shall be considered to classify in class 8 and assign a packing group. This is possible when all substances in the mixture (i.e. present in concentrations of >1%) are considered for classification in accordance with Chapter 2. When a specific concentration limit is assigned to a substance following its entry in the Dangerous Goods List or in a Special Provision, this limit shall be used instead of the generic limits in the scheme.

5. This means that the concentration for the components which have a specific limit has to be put in correlation to this specific concentration limit, whereas the components without specific concentration limits have to be put in correlation to the general concentration limit. In case the sum of these correlations is equal or bigger than 1, the criteria has to be considered as fulfilled.

6. For example for a mixture, which contain two ingredients (1 + 2) with specific limits and one ingredient (3) without specific limit, the calculation formula is as follows:

(% ingredient 1 / SCL1) + (% ingredient 2 / SCL2) + (% ingredient 3/ GCL) ≥ 1

This approach is taken from the ECHA guideline for the application of the CLP criteria.



7. The examples provided have the following structure:

(a) Number of the example

(b) Intended use of the mixture

(c) Formulation of the mixture

(d) Additional information

i. Form

ii. pH-value

iii. special ingredients

iv. information whether the classification of the ingredient is a self-classification or whether it is listed in the UN Model Regulations

v. others

(e) Calculation

(f) Flow chart

(g) Test method applied and results

8. The following examples are attached in Annex I

no	Intended use	Classification result based on the calculation method	Classification result based on test method	remark
1	Cleaning compound	class 8, packing group II	class 8, packing group II	
2	Cleaning Solution	class 8, packing group II	Not corrosive	
3	Quat Disinfectant Cleaner Concentrate	class 8, packing group II	Not corrosive	
4	Textile auxiliary	Not class 8	Not corrosive	Component listed in the UN MR with Specific concentration limits
5	Bathroom Disinfectant Cleaner (Concentrate)	class 8, packing group II	class 8, packing group II	
6	Extra Strength No Rinse Mark Remover	class 8, packing group III	class 8, packing group III	
7	Adhesive	class 8, packing group II	Class 8, corrosive to skin / Not corrosive on skin	
8	Technical Lubricant	class 8, packing group III	class 8, packing group III	
9	Catalyst	class 8, packing group II	Not corrosive	In vitro skin corrosion test (OECD 431)
10	Hair colour component	class 8, packing group III	Not corrosive	
11	Metal treatment	class 8, packing group II	class 8, packing group II	Synergetic effects may occur, but still the calculation method gives correct results; more than one ingredient with specific concentration limits

Annex I

Example 1

Intended use: Cleaning compound

Formulation

	Ingredient name	CAS-no. (if available)	Percentage - Range	Classification according transport regulations for skin corrosion (class 8)	Listed in UN Model Regulation / self-classification
A	Surfactant		1,2	--	S
B	Sodium hypochlorite	7681-52-9	5,0	UN1791, PG II	UN MR
C	Sodium hydroxide	1310-73-2	1,0	UN1824, PG II	UN MR
D	Non dangerous ingredients		92,8	--	S

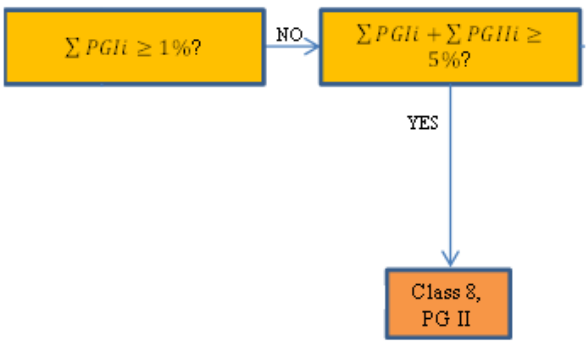
Additional information:

Form: liquid

PH-value >13

The mixture contains bases and surfactants, but there is no evidence that these have a synergetic effect. Therefore the calculation method is considered to apply.

Ingredient B and C are listed in the UN Model Regulations, Ingredient A has a self-classification as non-dangerous for transport. It is listed in the formulation and not added to the other non-dangerous ingredients (see D), as it is a surfactant.

Calculation method:		**Test data:**
No specific concentration limits Σ c (B + C) > 5%? Σ c (B + C) = 6% ➔ > 5% ➔ class 8 no ingredients assigned to PG I ingredients assigned to PG II: Σ c (B + C) = 6% 6% > 5% ➔ **<u>class 8, packing group II</u>**		OECD 435 (Corrositex®; DOT-E 10904 Rev 12/95) **<u>class 8, Packing group II</u>**

Example 2

Intended use: Cleaning Solution

Formulation:

	Ingredient name	CAS-no. (if available)	Percentage - Range	Classification according transport regulations for skin corrosion (class 8)	Listed in UN Model Regulation / self-classification
A	NaOCL	7681-52-9	5,9 – 6,3	UN1791, PG II	UN MR
B	NaOH	1310-73-2	≤ 2,0	UN1824, PG II	UN MR
C	Non dangerous ingredients				

Additional information:

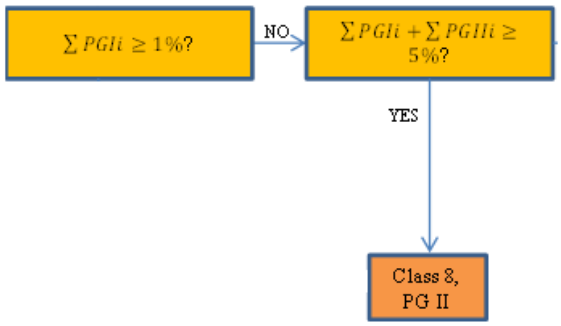
Form: liquid

pH 11,9 - 13,0%

The mixture contains bases, but there is no evidence that these have a synergetic effect. Therefore the calculation method is considered to apply.

Both relevant ingredients are listed in the UN Model Regulations.

The example shows that the calculation method is the most conservative approach.

Calculation method:		**Test data:**
No specific concentration limits Σ c (A + B) > 5%? Σ (6,3 (A) + 2,0 (B)) = 8,3 % ➔ class 8 no ingredients assigned to PG I ingredients assigned to PG II: Σ (6,3 (A) + 2,0 (B)) = 8,3 % 8,3% > 5% ➔ **<u>class 8, packing group II</u>**		OECD 435 (Corrositex®; DOT-E 10904 Rev 12/95) **<u>Non corrosive, not class 8</u>**

Example 3

Intended use:

Quat Disinfectant Cleaner Concentrate

Formulation:

	Ingredient name	CAS-no. (if available)	Percentage - Range	Classification according transport regulations for skin corrosion (class 8)	Listed in UN Model Regulation (UN) / self-classification (S)
A	WATER	7732-18-5	60 - 90	--	
B	BENZYL-C12-16-ALKYL DIMETHYL AMMONIUM CHLORIDES	68424-85-1	8,7	PG II	S
C	OCTYLDECYLDIMETHYLAMMONIUM CHLORIDE	32426-11-2	6,5	PG II	S
D	ETHOXYLATED C12-C15 ALCOHOLS	68131-39-5	5 - 10	--	S
E	ETHYL ALCOHOL	64-17-5	1 - 5	--	UN1170
F	DIDECYLDIMETHYLAMMONIUM CHLORIDE	7173-51-5	3,9	PG II	S
G	EDTA TETRASODIUM SALT	64-02-8	1 - 5	--	S
H	DIOCTYL DIMETHYL AMMONIUM CHLORIDE	5538-94-3	2,6	PG II	S
I	SODIUM METASILICATE	6834-92-0	1 - 5	PG III	UN3253

Additional information:

Form: liquid

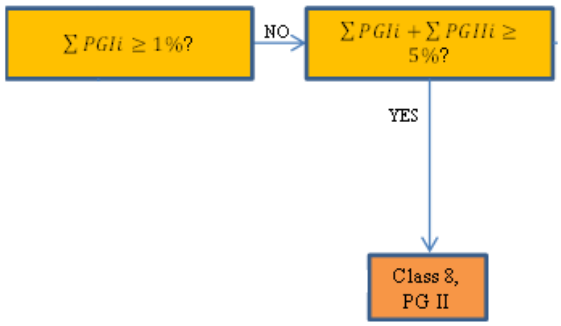
pH-value: 12,2 – 13,2

The mixture contains surfactants, but there is no evidence that these have a synergetic effect. Therefore the calculation method is considered to apply.

Substances A, D, E, and G can be disregarded for the classification in class 8, as they are not classified as class 8 materials.

One ingredients is listed in the UN Model Regulations as class 8, one is listed as UN1170, class 3 and not relevant for this calculation. All other ingredients have been classified by the consignor.

The example shows that the calculation method is the most conservative approach.

Calculation method:		**Test data:**
No specific concentration limits Σ c (B + C + F + H + I) > 5% ➔ class 8 no ingredients assigned to PG I ingredients assigned to PG II: Σ (8,7 (B) + 6,5 (C) + 3,9 (F) + 2,6 (H)) = 21,7 % 21,7% > 5% ➔ **<u>class 8, packing group II</u>** Ingredient I is not included in the calculation, as it is assigned to PG III and therefore not relevant in this step of the calculation.		OECD 435 (Corrositex®; DOT-E 10904 Rev 12/95) **<u>Non corrosive, not class 8</u>**

Example 4

Intended use: Textile auxiliary

Formulation:

	Ingredient name	CAS-no. (if available)	Percentage - Range	Classification according transport regulations for skin corrosion (class 8)	Listed in UN Model Regulation / self-classification
A	Water		68 - 70	--	
B	Polymeric aromatic sulphonate		18 - 50	--	S
C	Acetic acid		6 - 10	UN 2790, 8, II	UN MR
D	Sodium acetate		5 - 20	--	S
E	Sodium sulphate		1 - 50	--	S

Additional information:

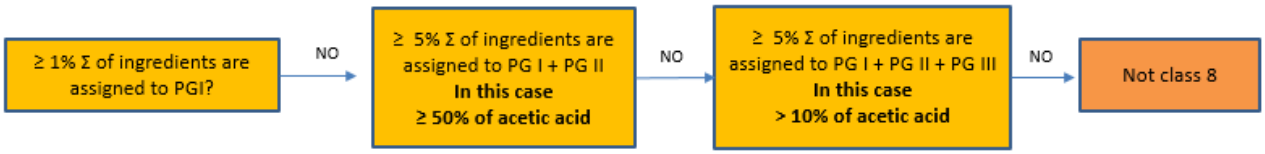
pH-value: appr. 3,5

Calculation method:

Acetic acid has specific concentration limits in the UN Model Regulations:

UN2790, PGII ACETIC ACID SOLUTION, not less than 50% but not more than 80% acid, by mass
UN2790, PGIII ACETIC ACID SOLUTION, more than 10% but not more than 50% acid, by mass

The formulation contains less than 10% (ingredient C = 6 -10 %). Therefore it is not to be classified as class 8.



Test method:

OECD 404

Test result:

Non corrosive, not class 8

Example 5

Intended use:

Bathroom Disinfectant Cleaner (Concentrate)

Formulation:

	Ingredient name	CAS-no. (if available)	Percentage - Range	Classification according transport regulations for skin corrosion (class 8)	Listed in UN Model Regulation / self-classification
A	1-OCTYL-2-PYRROLIDINONE	2687-94-7	10-30	PG II	S
B	HYDROXYACETIC ACID	79-14-1	10 - 30	PG II	S
C	MALIC ACID	6915-15-7	10 - 30	--	S
D	AMINES, COCO ALKYLDIMETHYL, N-OXIDES	61788-90-7	1 - 5	--	S
E	BENZYL-C12-16-ALKYLDIMETHYL AMMONIUM CHLORIDES	68424-85-1	2	PG II	S
F	OCTYLDECYLDIMETHYLAMMONIUM CHLORIDE	32426-11-2	1,5	PG II	S
G	DIDECYLDIMETHYLAMMONIUM CHLORIDE	7173-51-5	0,9	PG II	S
H	DIOCTYL DIMETHYL AMMONIUM CHLORIDE	5538-94-3	0,6	PG II	S
I	METHOXYACETIC ACID	625-45-6	0,1-0,5	PG II	S
J	Non corrosive ingredients (water, ethyl alcohol and fragrance)		1 - 5	--	S

Additional information:

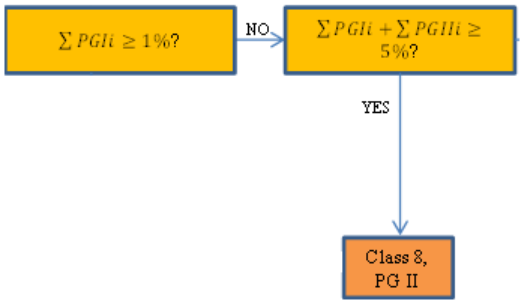
Form: liquid

pH-value: 0,9-1,5

The mixture contains acids and surfactants, but there is no evidence that these have a synergetic effect. Therefore the calculation method is considered to apply.

Substance C, D and J can be disregarded for the classification in class 8, as they are not classified as class 8 materials.

None of the ingredients is listed in the UN Model Regulations. All ingredients have been classified by the consignor.

Calculation method:		**Test data:**
No specific concentration limits Σ c (A + B + E + F + G + I) > 5%? Σ (30 (A) + 30 (B) + 2 (E) + 1,5 (F) + 0,9 (G) + 0,6 (H) + 0,5 (I)) = 65,5 % ➔ class 8 no ingredients assigned to PG I ingredients assigned to PG II: Σ (30 (A) + 30 (B) + 2 (E) + 1,5 (F) + 0,9 (G) + 0,6 (H) + 0,5 (I)) = 65,5 % 65,5% > 5% ➔ **<u>class 8, packing group II</u>**		OECD 435 (Corrositex®; DOT-E 10904 Rev 12/95) **<u>class 8, Packing group II</u>**

Example 6

Intended use: Extra Strength No Rinse Mark Remover

Formulation:

	Ingredient name	CAS-no. (if available)	Percentage - Range	Classification according transport regulations for skin corrosion (class 8)	Listed in UN Model Regulation / self-classification
A	WATER	7732-18-5	80 - 95	--	
B	2-BUTOXYETHANOL	111-76-2	3 - 7	--	S
C	ETHANOLAMINE	141-43-5	1 - 5	UN2491, PG III	UN MR
D	ALCOHOLS, C6-12, ETHOXYLATED	68439-45-2	0.5 - 1.5	--	S
E	ALCOHOLS, C12-14-SECONDARY, ETHOXYLATED	84133-50-6	0.5 - 1.5	--	S
F	Potassium Hydroxide	1310-58-3	0.1 - 1	UN1813, PG II	UN MR

Additional information:

Form: liquid

pH-value: 12.7 - 13.4

The mixture contains bases, but there is no evidence that these have a synergetic effect. Therefore the calculation method is considered to apply.

Substances A, B, D and F can be disregarded for the classification in class 8, as they are not classified as class 8 materials, although ingredient B is classified as class 6.1

All relevant ingredients are listed in the UN Model Regulations. All other ingredients have been classified by the consignor.

Calculation method:

No specific concentration limits

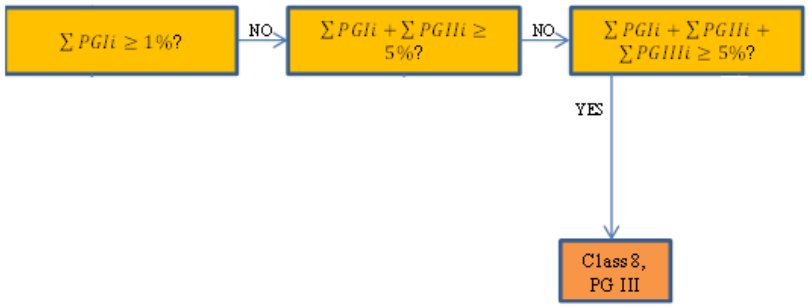
Σ c (C + F) > 5%?

Σ (5 (C) + 1 (F)) = 6 % ➔ class 8

no ingredients assigned to PG I

ingredients assigned to PG II:
Σ 1 (F) = 1%
1% < 5% ➔ not packing group II

ingredients assigned to PG II and PG III:
Σ (5 (C, PG III) + 1 (F, PG II)) = 6 %
6% > 5% ➔ **class 8, packing group III**



Test method:

OECD 435 (Corrositex®; DOT-E 10904 Rev 12/95)

Test result:

Class 8, packing group III

Example 7

Intended use: Adhesive

Formulation:

	Ingredient name	CAS-no. (if available)	Percentage - Range	Classification according transport regulations for skin corrosion (class 8)	Listed in UN Model Regulation / self classification
A	Hydroyxpropyl methacrylate	27813-02-1	25-50	--	S
B	Ethylene dimethylacrylate	97-90-5	5-10	--	S
C	Acrylic acid	79-10-7	5-10	UN 2218, PG II	UN MR
D	Methylacrylic acid	79-41-4	1-5	UN 2531, PG II	UN MR
E	Tributyl amine	102-82-9	0,1-2,5	--	UN MR
F	Cumene	98-82-8	0,1-2,5	--	UN MR
G	Ethylenedioxydiethyl dimethylacrylate	109-16-0	1-3	--	S
H	Non dangerous ingredients			--	S

Additional information:

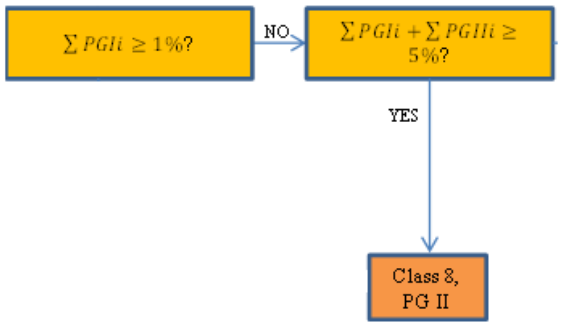
Form: liquid

pH-value: n/a (no water inside)

The mixture contains acrylic acids. There is no evidence that synergetic effects are existing. Therefore the calculation method is considered to apply.

Components E and F have dangerous properties and are named in the UN Model Regulations but they have no corrosive characteristics, so that they might be relevant for other dangerous properties but are not relevant for determination of class 8 classification.

The example shows that the calculation method is the most conservative approach.

Calculation method:		**Test result:**
No specific concentration limit for the ingredients named in the UN Model Regulations. Σ c (C+D) > 5%? Σ c (C+D) = 15% ➔ class 8 No ingredients assigned to PG I Ingredients assigned to PG II Σ (10 (C) + 5 (D)) = 15 % 15% is > 5% ➔ **<u>class 8, packing group II</u>**		OECD 431 (EpiDerm ®) **<u>Class 8, corrosive to skin</u>** OECD 404 (Test on rabbit skin) **<u>Not corrosive on skin</u>**

Example 8

Intended use: Technical Lubricant

Formulation:

	Ingredient name	CAS-no. (if available)	Percentage - Range	Classification according transport regulations for skin corrosion (class 8)	Listed in UN Model Regulation / self classification
A	Triisopropanolamine	122-20-3	1 - 5	--	S
B	Diisopropanolamine	110-97-4	1 - 5	--	S
C	adipic acid, potassium salt	25666-61-9	1 - 5	--	S
D	Amino-2-propanol, 1-	78-96-6	5 - 10	PG III	S
G	Graphite	7782-42-5	5	--	S
H	Other non-dangerous ingredients		3	--	S
I	Water	7732-18-5	70 - 80	--	

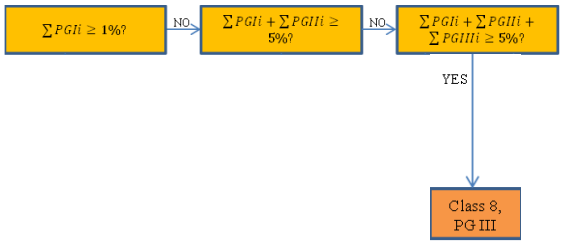
Additional information:

Form: liquid

pH-value: 9,0

There is no evidence that synergetic effects are existing. Therefore the calculation method is considered to apply.

No component is named in the UN Model Regulation.

Calculation method:		**Test result:**
No specific concentration limit available according UN Model regulations. Σ c (D) ≥ 5%? Σ c (D) = 10% ➔ class 8 No ingredients assigned to PG I or PG II Ingredients assigned to PG III Σ c (D) ≥ 5%? Σ c (D) = 10% 10% > 5% ➔ **<u>class 8, packing group III</u>**		OECD 435 (Corrositex ®) **<u>Class 8, Packing group III</u>**

Example 9

Intended use: Catalyst

Formulation:

	Ingredient name	CAS-no. (if available)	Percentage - Range	Classification according transport regulations for skin corrosion (class 8)	Listed in UN Model Regulation / self-classification
A	**n-Hexane**	110-54-3	> 25%	--	
B	**Hexane; mixture of isomers (containing a maximum of 5 % n-hexane)**	-	> 10%	--	
C	**Metal Halide 1**	-	> 3 - < 10%	UN 2869, Class 8, PG II	MR
D	**Metal Halide 2**	-	> 3 - < 10%	UN 1726, Class 8, PG II	MR
E	**Other non-dangerous ingredients**	--	>45%	--	S

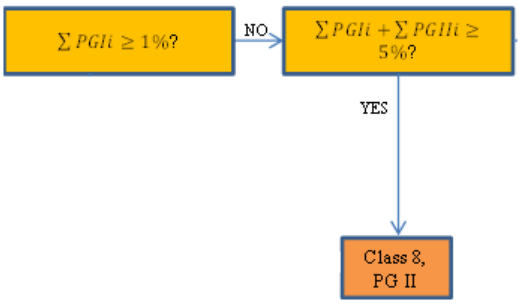
Additional information:

Form: slurry

For the mixture there is no evidence that these have a synergetic effect. Therefore the calculation method is considered to apply.

Substances A, B and E can be disregarded for the classification in class 8, as they are not classified as class 8 materials, although A and B are dangerous goods (UN1208, class3).

All relevant ingredients are listed in the UN Model Regulations. All other ingredients have been classified by the consignor as non-dangerous for transport

Calculation method:		**Test data:**
No specific concentration limits Σ c (C + D) > 5%? Σ (10 (C) + 10 (D)) = 20 % ➔ class 8 no ingredients assigned to PG I ingredients assigned to PG II: Σ (10 (C) + 10 (D)) = 20 % 20% > 5% ➔ **<u>class 8, packing group II</u>**		OECD 431 (In vitro Skin Corrosion Human Skin Model Test) **<u>Non-corrosive, not class 8</u>**

Example 10

Intended use: Hair colour component

Formulation:

	Ingredient name	CAS-no. (if available)	Percentage - Range	Classification according transport regulations for skin corrosion (class 8)	Listed in UN Model Regulation / self classification
A	Fatty alcohol C12-18	67762-25-8	10 - 25	--	S
B	Monoethanolamine	141-43-5	5 - 10	UN 2491 PG III	UN MR
C	Potassium hydroxide	1310-58-3	0,25 - 1	UN 1814 PG II	UN MR
D	Nonionic surfactant		1 - 5	--	S
E	Amino-o-cresol, p-	2835-95-2	0,25 - 1	--	S
F	2-Amino-6-chloro-4-nitrophenol	6358-09-4	0,25 - 1	UN 3077 PG III	S
G	Other non-dangerous ingredients			--	S
H	Water	7732-18-5	70 - 80		

Additional information:

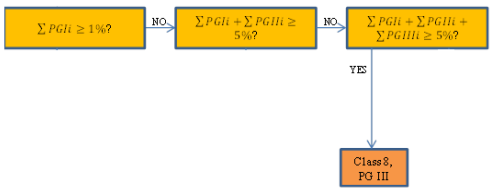
Form: liquid

pH-value: 9,8 – 10,8

The mixture contains bases, but there is no evidence that these have a synergetic effect. Therefore the calculation method is considered to apply.

Substances A, D, E, F, G and H can be disregarded for the classification in class 8, as they are not classified as class 8 materials, although ingredient F is classified as class 9.

All relevant ingredients are listed in the UN Model Regulations. All other ingredients have been classified by the consignor.

Calculation method:		**Test result:**
No specific concentration limit for the ingredients named in the UN Model Regulations. Σ c (B+C) > 5%? - yes Σ (10 (B) + 1 (C)) = 11 % ⇨ Class 8 no ingredients assigned to PG I ingredients assigned to PG II: Σ 1 (C) = 1% 1% < 5% ➔ not packing group II ingredients assigned to PG II and PG III: Σ (10 (B, PG III) + 1 (C, PG II)) = 11 % 11% is > 5% ➔ **<u>class 8, packing group III</u>**		Method: OECD 431 (EpiSkin ®) **Test result:** **<u>Not corrosive to skin</u>**

Example 11 is an example where synergistic effects may occur, but still results in the correct classification and assignment of packing group using the calculation method.

Example 11

Intended use: Metal treatment

Formulation:

	Ingredient name	CAS-no. (if available)	Percentage - Range	Classification according transport regulations for skin corrosion (class 8)	Listed in UN Model Regulation / self classification
A	Hydrofluoric acid	7664-39-3	5 – 10	UN1790, PG II (see specific concentration limit)	UN MR
B	Nitric acid	7697-37-2	5 – 10	UN2031, PG II (see specific concentration limit)	UN MR
C	Non dangerous ingredients		80 – 90	--	S

Additional information:

Form: liquid

pH-value: < 1

The mixture contains strong acids, synergetic effect is possible.

Therefore, if “Bridging principles” are not applicable, a test needs to be carried out in case the mixture should not be assigned into PG I.

The example shows that even in such situations the calculation method would give the correct assignment for the packing group, so that an under-classification is not expected.

Ingredient A and B are listed in the UN Model Regulations.

As already mentioned the introduction, for mixtures containing ingredients with specific concentration limits, the following formula can be used:

(% ingredient A / SCL1) + (% ingredient B / SCL2) ≥ 1

<table>
<tr><th colspan="2">Calculation method:</th><th>Test result:</th></tr>
<tr>
<td>Specific concentration limit for

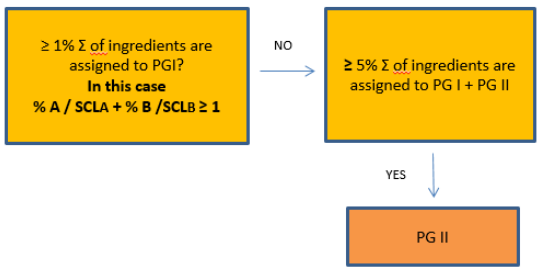
UN1790
> 60% ➔ PG I
< 60% ➔ PG II ➔ PG II is applicable for the mixture (A =10%)

UN2031
> 70% ➔ PG I
< 70% ➔ PG II ➔ is applicable for the mixture (B = 10%)

Packing group I?
Since for both components specific concentration limits for the assignment of PG I exist, these specific concentration limits have to be considered instead of the general concentration limit of 1% to decide if PG I is applicable

(10 (A) /SCL UN1790 = 60) + (10 (B) /SCL UN2031 = 70) = 0,3
➔ 0,3 ➔ less than 1
⇨ Not class 8, packing group I

Packing group II?
Since no specific (lower) concentration limits in regard to PG II for any component in the mixture is mentioned in the UN Model Regulation the general concentration limit is applicable.

Σ c (A + B) > 5%?
(10 (A) + 10 (B)) = 20%
20% > 5%
➔
<u>Class 8, Packing group II</u></td>
<td> 
</td>
<td>OECD 435 (Corrositex ®)

<u>Class 8, Packing group II</u></td>
</tr>
</table>