

Helsinki, 25 August 2022
RAC/62/2022/04

62ND MEETING OF THE COMMITTEE FOR RISK ASSESSMENT

12-15 September 2022

Face-to-face meeting

Concerns: **RAC Guidance Note:**
Assessing physical hazards as part of CLP

Agenda Point: **8.1.2**

Action requested: **For agreement**

The document was presented at RAC-61, after which it was updated based on the discussion. No comments were received from RAC during the written consultation from 15 July to 12 August and the document is thus presented to RAC 62 and agreed.

1. Introduction

This document aims to provide advice on the screening procedures for assessing the physical hazard classes. Such information is spread over several sources and this document attempts to bring them together in a more convenient manner for assessing physical hazards under CLP. The information included comes from the CLP Regulation, Guidance on the Application of the CLP Criteria and REACH Guidance on Information Requirements and Chemical Safety Assessment. Quoted passages from these documents are given in italics.

It covers in detail only the screening procedures for the individual hazard classes; if tests others than EU A. series are included in the CLP dossier, please refer to the CLP Regulation and Guidance and/or consult with the ECHA team.

2. Physical hazards

2.1. Explosives (relevant for solids and liquids)

According to the CLP Regulation, this hazard class is assessed by:

- a screening procedure, see Annex I 2.1.4.2 & 2.1.4.3 (a-c), (also copied below),
- the acceptance procedure (using UN test series 2 to 8 Part I of the UN RTDG, see Annex I, 2.1.2.3.)

Note: If the substance is (or is proposed to be) classified as an organic peroxide or self-reactive substance, it shall not be considered for classification as explosive, see CLP Annex I 2.1, or CLP Guidance 2.15.3

Note: if the substance is (or is proposed to be) classified as an explosive, no other physical hazard class needs to be evaluated

Description of the assessment

Screening procedure

According to CLP Annex I, 2.1.4.3, no classification if **any** of the following (a-c) is met:

- There are no chemical groups associated with explosives properties present in the molecule. Examples of groups which may indicate explosive properties are given in Table A6.1 in Appendix 6 of the UN RTDG, Manual of Tests and Criteria; or*

Such groups are present and

- The substance contains groups associated with explosive properties which include oxygen and the oxygen balance is less than -200; [see formula in CLP Regulation or the excel file below];*
- For an organic substance, or a homogenous mixture of organic substances, containing a chemical group (or groups) associated with explosive properties:*
 - *the exothermic decomposition energy is below 500 J/g, or*

- onset of exothermic decomposition is 500 °C or above as indicated in Table 2.1.3

The table with the examples of explosive groups has been included in the file, and can be found on the UN Manual of test and criteria at the following link

http://www.unece.org/fileadmin/DAM/trans/danger/publi/manual/Rev7/Manual_Rev7_E.pdf.

Table A6.1 EXAMPLES OF CHEMICAL GROUPS INDICATING EXPLOSIVE PROPERTIES IN ORGANIC MATERIALS

Structural feature	Examples
C-C unsaturation	Acetylenes, acetylides, 1,2-dienes
C-Metal, N-Metal	Grignard reagents, organo-lithium compounds
Contiguous nitrogen atoms	Azides, aliphatic azo compounds, diazonium salts, hydrazines, sulphonylhydrazides
Contiguous oxygen atoms	Peroxides, ozonides
N-O	Hydroxylamines, nitrates, nitro compounds, nitroso compounds, N-oxides, 1,2-oxazoles
N-halogen	Chloramines, fluoroamines
O-halogen	Chlorates, perchlorates, iodosyl compounds

Structural feature	Examples
C-C unsaturation: C=C or C≡C	Alkynes -C≡C- Acetylide MC≡CH, MC≡CM; M metal 1,2 dienes -C=C=C-
C-Metal, N-Metal	Grignard reagents R-Mg-X Organo-lithium compounds R-Li
Contiguous nitrogen atoms N-N or N=N	Azides N=N=N or N ₃ Aliphatic azo compounds R _{al} -N=N-R _{al} Diazonium salts R-N ₂ X Hydrazines R ₂ N-NR ₂ , RHN-NR ₂ , RHN-NHR, RHN-NH ₂ Sulfonyl hydrazine R-SO ₂ -NH-NH ₂ , R-SO ₂ -NH-NHR: note the S-N bond (example)
Contiguous oxygen atoms O-O	Peroxides R-O-O-R, R-O-O-H, R-C(=O)-O-O-H (example) Oxide cyclic structures containing 3 contiguous oxygens eg: a 5 atoms ring C-O-O-O-C the 2 carbons bonded
N-O	Hydroxylamines R-NH-OH, R ₂ N-OH, i.e. N-OH bond Nitrates -ONO ₂ Nitro compounds R-NO ₂

	<p>Nitroso compounds R-N=O</p> <p>N-oxides R₃NO</p> <p>1,2-oxazoles 5 atoms ring with N-O bond (example)</p>
N-halogen	<p>Chloramines N-Cl, NCl₂, i.e. N-Cl bond</p> <p>Fluoramines N-F, NF₂, i.e. N-F bond</p>

R: aliphatic or aromatic structure, R_{al}: aliphatic structure (usually non cyclic, or cyclic with few C-C unsaturation), X: halogen

b. Calculation of the oxygen balance, see formula in Annex I, 2.1.4.3b, or use the Excel file below.



DSSP_calculation.xls

This website calculates the molecular weight from the SIMLE notation:
<https://www.lenntech.com/calculators/molecular/molecular-weight-calculator.htm>

c. Table 2.1.3 with the combination of exothermic decomposition and decomposition energy (Annex I, 2.1.4.3, c).

Table 2.1.3

Decision to apply the acceptance procedure for the hazard class “Explosives” for an organic substance or a homogenous mixture of organic substances

Decomposition energy (J/g)	Decomposition onset temperature (°C)	Apply acceptance procedure? (Yes/No)
< 500	< 500	No
< 500	≥ 500	No
≥ 500	< 500	Yes
≥ 500	≥ 500	No

Note: experience in manufacture and handling is not part of the screening procedure

Acceptance procedure

According to the CLP Regulation Annex I, 2.1.2.3, a substance is tested using UN test series 1 to 8. Test 1 is a screening test, based on the results of which, an additional test

from the acceptance procedure (2 to 8) is chosen if needed; see related scheme on the Regulation.

Assessing the hazard class

The first step of the screening procedure (see CLP Annex I, 2.1.4.3a) is to check the chemical structure of the substances against the chemical groups indicating explosive properties (chemical groups IEP) in table A6.1 in the UN Manual of test and criteria.

RAC agrees that when there is a match between structural features (column 1 in table A6.1) and the substance under assessment, independently of the chemical groups IEP (column 2 in table A6.1), the criterion in CLP Annex I, 2.1.4.3 a is considered not fulfilled. However, expert judgment could change the outcome on a case by case way, for example an aromatic ring do contain C-C unsaturation however this is not per se indicative of explosive properties. Overall if:

- There are no chemical groups IEP → screening step fulfilled, no classification
- There are chemical groups IEP → assess the next steps in the procedure see above, i.e.:

2.1.4.3 b. oxygen balance (formula in the Regulation or the Excel above)

2.1.4.3 c. combination of exothermic decomposition and decomposition energy, see table 2.1.3 above

If there are chemical groups indicating explosive properties and 2.1.4.3 b or c are not fulfilled → no classification due to inconclusive data

What to do if there is only an EU A.14 study available?

Results from the EU A.14 method are not conclusive, so the screening procedure should be followed, see 2.1.4.3, or above.

2.2. Flammable gases

Not included: not generally seen in CLH proposals.

2.3. Aerosols

Not included: not generally seen in CLH proposals.

2.4. Oxidising gases

Not included: not generally seen in CLH proposals.

2.5. Gases under pressure

Not included: not generally seen in CLH proposals.

2.6. Flammable liquids

Flammability for liquids is tested using flash point and initial boiling point; no screening procedure is applicable. The substance viscosity drives the choice of the method, see tables 2.6.3 and 2.6.4 in the CLP Regulation.

Note: the substance shall not be considered for classification as flammable liquid, if it is (will be) classified as explosive, or inorganic oxidising liquids.

Note: experience in manufacture and handling is not part of the screening procedure as per CLP Regulation.

2.7. Flammable solids

Flammability for solids is tested using UN test N.1, see Annex I, 2.7.2.; no screening procedure is applicable.

Note: the substance shall not be considered for classification as a flammable solid, if it is (will be) classified as explosive, organic peroxide, self-reactive substance, pyrophoric, oxidising solids, or an inorganic oxidising solid.

Test method EC A.10 might or not be conclusive

If the assessment is performed using the A.10 method and the result is “not highly flammable”, then it complies with the ECHA Guidance, see ECHA Chapter R.7a: Endpoint specific Guidance, R.7.1.10.3: *If available data from an A.10 test method indicate that a classification as a flammable solid does not apply (result: not highly flammable), no more testing is necessary.* However, if the A.10 test method has come to the conclusion ‘highly flammable’, it will be necessary to also determine the influence of the wetted zone as described in the UN Test N.1.

Note that sometimes the DS states the test result is “not flammable” instead of “not highly flammable”.

Attention: solid substances with low melting point

If a solid substance has a low melting point, it is not possible to perform the test to assess flammable solids. Therefore, it is possible that the hazard class was assessed using the flash point test as if the substance was a liquid. This is not uncommon for low melting point solids and should generally be acceptable.

Note: experience in manufacture and handling is not part of the screening procedure.

2.8. Self reactive substances and mixtures (relevant for solids and liquids)

According to the CLP Regulation, self-reactive properties are assessed using:

- screening procedure, see CLP Annex I, 2.8.4.2, or below, **or**
- UN RTDG test series A to H.

Note: the substance shall not be considered for classification as 'self-reactive', if it is (will be) classified as an explosive, oxidising liquids or solid or organic peroxides.

Screening procedure

According to CLP Annex I 2.8.4.2, *The classification procedures for self-reactive substances and mixtures need not be applied if:*

- a. *There are no chemical groups present in the molecule associated with explosive or self-reactive properties. Examples of such groups are given in Tables A6.1 and A6.2 in Appendix 6 of the UN RTDG, Manual of Tests and Criteria; or*
- a. *For a single organic substance or a homogeneous mixture of organic substance,*
 - *the estimated SADT [self-accelerating decomposition temperature] for a 50 kg package is greater than 75°C, OR*
 - *exothermic decomposition energy is less than 300 J/g*

The table with the examples of explosive and self-reactive groups can be found in this document, above and below and in the UN Manual of test and criteria at the following link

http://www.unece.org/fileadmin/DAM/trans/danger/publi/manual/Rev7/Manual_Rev7_E.pdf.

Please note that the CLP Regulation has not (yet) updated the table number from (old) A6.2 to (new) A6.3 after the update in the UN RTGD text.

Table A6.3: Examples of chemical groups indicating self-reactive properties in organic materials

Structural feature	Examples
Mutually reactive groups	Aminonitriles, haloanilines, organic salts of oxidizing acids
S=O	Sulphonyl halides, sulphonyl cyanides, sulphonyl hydrazides
P-O	Phosphites
Strained rings	Epoxides, aziridines
Unsaturation	Olefins, cyanates

Structural feature	Examples
Mutually reactive groups	Aminonitriles $R_2N-C\equiv N$ (example) Haloanilines aniline with halogen in the ring (example) Organic salts of oxidizing acids no fixed structure
S=O	Sulphonyl halides $R-SO_2-X$ Sulphonyl cyanides $R-SO_2-C\equiv N$

	Sulphonyl hydrazides R-SO ₂ -NH-NH ₂ , R-SO ₂ -NR-NH ₂ , R-SO ₂ -NH-NRH, ... (example)
P-O	Phosphides contains P ₃ ⁻ ion (example)
Strained rings	Epoxides 3 atom ring with an oxygen (example) Aziridines 3 atom ring with a nitrogen (example)
Unsaturation	Olefins chemicals made up of hydrogens and carbons only with one or more pairs of carbon atoms linked by a double bond Cyanates [O=C=N] ⁻ , -O-C≡N, (example , example)

□ = rigid or flexible core, R: aliphatic or aromatic structure, X: halogen

Note: The criterion in CLP Annex I 2.8.4.2 a is considered not fulfilled if the chemical under assessment contains one of the structural features included in the first column of table A6.3 above. However, based on expert judgement on a case by case assessment, exceptions could apply.

Note: experience in manufacture and handling is not part of the screening procedure.

2.9. Pyrophoric liquid

According to the CLP Regulation, this hazard class is assessed by:

- screening procedure in CLP Annex I, 2.9.4.1, i.e. based on experience in manufacturing or handling, OR
- UN RTDG test N.3

Note: the substance shall not be considered for classification in this hazard class, if it is (will be) classified as explosive, or inorganic oxidising liquid.

Screening procedure

The classification procedure for pyrophoric liquids need not be applied when experience in manufacture or handling shows that the substance or mixture does not ignite spontaneously on coming into contact with air at normal temperatures (i.e. the substance is known to be stable at room temperature for prolonged periods of time (days)).

Test method EC A.13 is conclusive

Test method EU A.13 is considered equivalent to test method N.3, thus it can provide sufficient information to conclusively assess this hazard class, see REACH Guidance R.7.1.10.5.

2.10. Pyrophoric solids

According to the CLP Regulation, this hazard class is assessed by:

- The screening procedure in CLP Annex I, 2.10.4.1, i.e. based on experience in manufacturing or handling, OR
- UN RTDG test N.2

Note: the substance shall not be considered for classification in this hazard class, if it is (will be) classified as explosive, or inorganic oxidising solid.

Screening procedure

The classification procedure for pyrophoric solids need not be applied when experience in manufacture or handling shows that the substance or mixture does not ignite spontaneously on coming into contact with air at normal temperatures (i.e. the substance is known to be stable at room temperature for prolonged periods of time (days)).

Test method EC A.13 is conclusive

Test method EU A.13 is considered equivalent to test method UN RTDG N.2, thus it can provide sufficient information to conclusively assess this hazard class, see REACH Guidance R.7.1.10.6.

Waiver needs 'not highly flammable' result to be applicable

The following is not included in the CLP Regulation or the Guidance, however it has been considered an acceptable waiver by RAC previously.

If a substance does not ignite upon contact with a very hot flame (as in UN N.2 or EU A.10) or upon heating, it will not ignite spontaneously at room temperature. Thus, the substance does not meet the criteria for classification.

2.11. Self-heating substances and mixtures (relevant for solids and liquids)

According to the CLP Regulation, this hazard class is assessed using:

- screening procedure, see CLP Annex I, 2.11.4.1, or below, OR
- UN RTDG test N.4.

Note: the substance shall not be considered for classification in this hazard class, if it is (will be) classified as explosive, pyrophoric liquid or solid.

Screening procedure CLP guidance 2.11.4.2

Melting point: *substances or mixtures with a low melting point (< 160 °C) should not be considered for classification in this hazard class since the melting process is endothermic and the substance-air surface is drastically reduced. However, this criterion is only applicable if the substance or mixture is **completely molten** up to this temperature.*

Note: experience in manufacture and handling is not part of the screening procedure.

Test methods

Results from Grewer Oven or Bulk Powder Screening Tests are considered conclusive.

Test method EC A.16 may be conclusive.

It differs from UN test N.4 by the amount of substance which is heated up and the temperature progression. Due to these differences, a negative EC A.16 is conclusive for

no classification, while a positive result is inconclusive for classification and consequently, a test according to N.4 would need to be conducted.

2.12. Substances which in contact with water emit flammable gases (relevant for solids and liquids)

According to the CLP Regulation, this hazard class is assessed using:

- screening procedure, see CLP Annex I, 2.12.4.1, or below, OR
- UN RTDG test N.5.

Note: the substance shall not be considered for classification in this hazard class, if it is (will be) classified as explosive.

Screening procedure

According to CLP Annex I 2.12.4.1, *The classification procedure for this class need not be applied if:*

- the chemical structure of the substance or mixture does not contain metals or metalloids; or*
- experience in production or handling shows that the substance or mixture does not react with water, e.g. the substance is manufactured with water or washed with water; or*
- the substance or mixture is known to be soluble in water to form a stable mixture.*

Please note that the screening criteria for this hazard class includes considerations on the chemical structure, therefore an assessment can be performed based on such considerations.

2.13. Oxidising liquids

According to the CLP Regulation, this hazard class is assessed using:

- screening procedure, see CLP Annex I, 2.13.4.1, or below, OR
- UN RTDG test O.2

Note: the substance shall not be considered for classification in this hazard class, if it is (will be) classified as explosive or organic peroxide.

Screening procedure

According to CLP Annex I, *The classification procedure for this class shall not apply if:*

For an organic substance (2.13.4.1):

- the substance or mixture does not contain oxygen, fluorine or chlorine; or*
- the substance or mixture contains oxygen, fluorine or chlorine and these elements are chemically bonded only to carbon or hydrogen*

For an inorganic substance (2.13.4.2):

No classification if the inorganic substances *do not contain oxygen or halogen atoms.*

Test method EC A.21 maybe conclusive

Test method A.21 is in general similar to UN test O.2 (<https://www.enfo.hu/sites/default/files/A21web2004.pdf>). However, it requires comparison with only one reference substance. This means that it can be used only to conclude if a certain liquid substance does not have oxidising properties leading to a classification (i.e. negative result) but cannot be used in case of a positive result, as A.21 does not lead to a discrete classification category. If the latter is the case, UN test O.2 results need to be present in the CLH report.

Note: In the event of a divergence between test results and known experience in the handling and use of substances or mixtures which shows them to be oxidising, judgment based on known experience shall take precedence over test results.

Note: experience in manufacture and handling is not part of the screening procedure.

2.14. Oxidising solids

According to the CLP Regulation, this hazard class is assessed using:

- screening procedure, see CLP Annex I, 2.14.4.1, or 2.14.4.2, or below, OR
- UN RTDG test O.1 or O.3

Note: the substance shall not be considered for classification in this hazard class, if it is (will be) classified as explosive or organic peroxide.

Screening procedure

According to CLP Annex I, *The classification procedure for this class shall not apply if:*

For an organic substance (2.14.4.1):

- the substance or mixture does not contain oxygen, fluorine or chlorine; or*
- the substance or mixture contains oxygen, fluorine or chlorine and these elements are chemically bonded only to carbon or hydrogen*

For an inorganic substance (2.14.4.2):

No classification if the inorganic substances *do not contain oxygen or halogen atoms.*

Note: experience in manufacture and handling is not part of the screening procedure.

Note: results from test method EC A.17 cannot be used for classification.

ECHA guidance R7.1.13.3 (page 137): *'In the DSD, the A.17 test method of Regulation (EC) 440/2008 is used for the assessment of oxidising properties of solids. Although the principle of this method is to a large extent the same as that of the UN Test O.1 of the UN-MTC, the experimental set-up, reference substance (barium nitrate) and measured quantity differ. Furthermore, the DSD does not make any division corresponding to the categories of the CLP. Since the CLP Regulation is used for classification of substances, it is not advisable to use the A.17 method (which belongs to the DSD classification system). Instead, the UN Test O.1 should be used, which will also give more detailed information on the oxidising behaviour of a substance (or mixture), since more reference mixtures are used.'*

2.15. Organic peroxides (relevant for solids, liquids and gases)

According to the CLP Regulation, this hazard class is assessed using:

- screening procedure
 - o there is no peroxide group (-O-O), OR
 - o if there is a peroxide group, the calculation method
- test method

Note: the substance shall not be considered for classification in this hazard class, if it is (will be) classified as explosive.

Screening procedure

No classification if the chemical peroxide group (-O-O-) is absent. A conclusion from the assessment of this hazard class as "Not applicable" is also acceptable in this case.

Calculation method, see CLP Regulation Annex I 2.15.2.1.

If the peroxide group is present, classification can be assessed based on a calculation method, see CLP Annex I, 2.15.2.1.

Note: experience in manufacture and handling is not part of the screening procedure.

2.16. Corrosive to metals (relevant for solids and liquids)

According to the CLP Regulation or Guidance, this hazard class is assessed using:

- screening procedure from the CLP Guidance not present in the Regulation:
 - o for solids: based on the melting point, then according to the information below
 - o for liquids: acid or basic, see below
- UN test C.1

Note: the substance shall not be considered for classification in this hazard class, if it is (will be) classified as explosive.

Screening procedure: this screening procedure is contained in the CLP Guidance (2.16.4.1.), not in the CLP Regulation

Solid: Only solids with a melting point below 55°C need to be tested, see CLP Guidance 2.16.4.1. → A "no classification" proposal based on a melting point > 55°C is acceptable, and the overall conclusion is conclusive but not sufficient for classification.

Solids and liquids: substances having acid or basic functional groups, containing halogens or able to form complexes with metals should be considered for this hazard class. E.g. usually extreme pH points towards the likelihood of corrosivity.

Note: experience in manufacture and handling is not part of the screening procedure.

2.17. Desensitised explosive (relevant for solids and liquids)

Not included: not generally seen in CLH proposals.