## UN/SCETDG/51/INF.7 UN/SCEGHS/33/INF.3

## 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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Issues relating to the Globally Harmonized System of Classification and Labelling of Chemicals: Use of the Manual of Tests and Criteria in the context of the GHS

**Sub-Committee of Experts on the Globally Harmonized System of Classification and Labelling of Chemicals** 

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Item 2 (a) of the provisional agenda

Work of the TDG Sub-Committee on matters of interest to the GHS Sub-Committee

### Revision of the Manual of Tests and Criteria: Section 1

Transmitted by the Chairman of the Working Group on Explosives on behalf of the Working Group

Note by the secretariat:

This document takes account of the amendments to the  $6^{th}$  revised edition of the Manual of Tests and Criteria adopted by the Committee at its eighth session (see ST/SG/AC.10/44/Add.2).

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#### **SECTION 1**

#### GENERAL INTRODUCTION

**NOTE:** This general introduction relates only to Parts I to III of the Manual of Tests and Criteria and its Appendices I to 9. At its second session (10 December 2004), the Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals decided to add a new Part IV relating to tests methods concerning transport equipment. At its seventh session, the Committee of Experts on the Transport of Dangerous Goods and the Globally Harmonized System of Classification and Labelling of Chemicals decided to add a new Part V relating to classification procedures, test methods and criteria relating to sectors other than transport.

#### 1.1 Introduction

- 1.1.1 The purpose of the Manual of Tests and Criteria (hereafter referred to as the "Manual") this text is to present the United Nations schemes for the classification of certain types of dangerous goods and to give descriptions of the test methods and procedures considered to be the most useful for providing competent authorities with the necessary information to arrive at a proper classification of substances and articles for transport.
- 1.1.2 This Manual was originally intended to be used for transport and continues to be the source of classification testing and criteria for dangerous goods in transport. Hence, in Editions 1 to 6 of the Manual frequent reference is made to "as packaged for transport" and "as offered for transport". Because, for physical hazards, GHS also refers to the tests contained in this Manual, to facilitate the use of the Manual in the context of GHS the phrase "as offered for classification" is used instead. For example, if the classification to be determined is for products packaged for transport, "as offered for classification" means "as offered for transport". On the other hand, if the classification to be determined is for non-transport GHS use, then "as offered for classification" means "in the condition relevant to the particular application". More details on the reasons for this change are provided below.
- 1.1.3 The outcome of the tests in this Manual is predominantly related to the intrinsic properties of the material being tested. However the test results may also be affected by other physical parameters such as: density; particle size (distribution) and humidity. For some physical hazards the outcome of the tests and hence the classification can also be dependent on the quantity of the sample and the packaging.

For these reasons, the above mentioned parameters and circumstances should be taken into account when considering test results, particularly for classification for sectors other than transport.

<u>Note by the secretariat</u>: It is unclear whether this paragraph relates both to 1.1.2 and 1.1.3 or only to 1.1.3. If it relates only to 1.1.3, the secretariat recommends placing it as the last sentence of this paragraph (instead of as an individual paragraph without numbering). If it relates both to 1.1.2 and 1.1.3, the secretariat recommends numbering it as 1.1.4.

- 1.1.4 Thise Manual of Tests and Criteria should be used in conjunction with the latest versions of:
  - the Recommendations on the Transport of Dangerous Goods (hereafter referred to as the Recommendations) and of the Model Regulations on the Transport of Dangerous Goods annexed there to these Recommendations (hereafter referred to as the Model Regulations):

    and
  - (a)(b) the Globally Harmonized System of Classification and Labelling of Chemicals (hereafter referred to as the GHS).
- 1.1.25 It should be noted that the Manual of Tests and Criteria is not a concise formulation of testing procedures that will unerringly lead to a proper classification of products. It therefore assumes technical competence on the part of the testing body. The competent authority has discretion to dispense with certain tests, to vary the details of tests, and to require additional tests when this is justified to obtain a reliable and realistic assessment of the hazard of a product. In some cases, a small scale screening procedure may be used to decide whether or not it is necessary to

perform larger scale classification tests. Suitable examples of procedures are given in the introductions to some test series and in Appendix 6. Examples which may be listed within various test procedures are for illustrative purposes and are provided for guidance only.

- 1.1.36 In situations where the proper classification of substances and articles of certain hazard classes of Divisions for transport is the responsibility of the Competent Authority, it is normal and accepted practice that due consideration will be given to testing or classification results of other Competent Authorities when provided.
- 1.1.7 Definitions of terms used in the Manual may be found in Chapter 1.2 of the Model Regulations and of the GHS and in Appendix B of the Model Regulations.
- 1.1.8 The term substance as it is used in this Manual comprises both substances and mixtures, unless otherwise stated.

## Hazard classes in the Model Regulations and in the GHS Hazard classes in the Model Regulations 1.2.1 Substances and articles subject to the Model Regulations are assigned to one of nine classes according to the hazard or the predominant hazard they present for transport. Some of these classes are subdivided into divisions addressing a more specific type of hazard within a given class. The numerical order of the classes and divisions does however not reflect the degree of hazard. In addition, for packing purposes, some dangerous goods are assigned to one of three packing groups in accordance with the degree of danger they present: Packing group I: high hazard Packing group II: medium hazard Packing group III: low hazard The packing group to which a substance is assigned is indicated in the Dangerous Goods List in Chapter 3.2 of the Model Regulations. Articles are not assigned to packing groups. Dangerous goods meeting the criteria of more than one hazard class or division and which are not listed in the Dangerous Goods List are assigned to a transport class and division and subsidiary hazard(s) on the basis of the precedence of hazards characteristics. 1.2.1.4 Precedence of hazard characteristics for transport purposes 1.2.1.4.1 The table in 2.0.3.3 of Chapter 2.0 of the Model Regulations may be used as a guide in determining the class of a substance having more than one hazard, when it is not named in the Dangerous Goods List in Chapter 3.2 of the Model Regulations. For goods having multiple hazards, which are not specifically listed by name in Chapter 3.2 of the Model Regulations, the most stringent packing group denoted to the respective hazard of the goods takes precedence over other packing groups, irrespective of the precedence of hazard table in 2.0.3.3 of Chapter 2.0 of the Model Regulations. The precedence of hazard characteristics of the following are not dealt with in the Precedence of hazard table in Chapter 2.0 of the Model Regulations, since these primary characteristics always take precedence: Substances and articles of Class 1; Gases of Class 2; Liquid desensitized explosives of Class 3; Self-reactive substances and solid desensitized explosives of Division 4.1; Pyrophoric substances of Division 4.2; Substances of Division 5.2; Substances of Division 6.1 with a packing group I inhalation toxicity: Substances of Division 6.2; and Radioactive material of Class 7. Self-reactive substances, except for type G, giving a positive result in the self-heating test N.4, should not be classified as pyrophoric liquids or solids but as self-reactive substances (see paragraph 2.4.2.3.1.1 of the Model Regulations). Organic peroxides of type G having properties of another hazard class (e.g. UN 3149) should be classified according to the requirements of that hazard class.

#### 1.2.2 Hazard classes in the GHS

The GHS addresses classification of substances by the type of chemical hazard (e.g. flammability, toxicity, corrosivity) which are grouped into physical hazards, health hazards and environmental hazards. The GHS hazard classes each reflect a type of hazard, and they are sometimes specific to a certain aggregation state (solid, liquid or gaseous). Most of the GHS hazard classes are further subdivided into hazard categories reflecting the severity of the hazard, with Category 1 indicating the most severe hazard

#### 1.2.3 Relationship between the Model Regulations and the GHS

1.2.3.1 Since the GHS addresses also sectors other than transport (e.g. storage, supply and use), it includes hazards not considered relevant to transport, such as several non-acute health hazards. In addition, because the GHS covers only chemical hazards, not all the transport classes defined in the Model Regulations have an equivalent GHS hazard class. Furthermore, with the exception of explosive articles, the GHS does not cover articles (see 1.3.2.1.1 of the GHS). The differences in scope for GHS and the Model Regulations means that not all hazards addressed in the GHS have their counterparts in the Model Regulations, and *vice versa*. For instance, there is not a specific hazard class in the GHS for radioactive material (Class 7 in transport), and some of the dangerous goods classified for transport in Class 9 are either not addressed by the GHS at all (e.g. many articles) or are covered by other GHS hazard classes (e.g.: environmentally hazardous substances of Class 9, which may fall under the GHS hazard class Hazardous to the aquatic environment).

1.2.3.2 In addition, while one transport class may cover several different types of hazards, GHS hazard classes usually address one type of hazard each. For instance, substances of Class 4 in transport belong to seven individual GHS hazard classes. Furthermore, while transport classes are identified by a number (1-to 9), GHS hazard classes are identified by a name reflecting the type of chemical hazard (e.g. "Flammable solids"). Moreover, the concept of precedence of hazards as defined in the Model Regulations (see 1.1.4.1.4) does not exist in the GHS.

# Note by the secretariat: The Sub-Committee is invited to check whether the correct reference to be indicated here is 1.2.1.4.

1.2.3.3 The overarching correlation between GHS hazard classes and the transport classes addressed in the Model Regulations is indicated in Table 1.1. The table is indicative only and is not intended to be used as the sole basis in translating the classification of any substance or article between the GHS and the Model Regulations, or *vice versa*.

#### <u>Table 1.1 :</u> Correlation between GHS chemical hazards and Model Regulations transport classes

| GHS hazard classes                            | Hazard classes in the Model Regulations |
|---|---|
| Explosives, Divisions 1.1 to 1.6              | Class 1, Divisions 1.1 to 1.6           |
| Flammable gases, Category 1                   | Class 2, Division 2.1                   |
| <u>Aerosols</u>                               | Class 2, Division 2.1 and 2.2           |
| Oxidizing gases                               | Class 2, Division 2.2                   |
| Gases under pressure                          | Class 2                                 |
| Flammable liquids                             | Class 3                                 |
| Flammable solids                              | Class 4, Division 4.1                   |
| Self-reactive substances                      | Class 4, Division 4.1                   |
| Pyrophoric liquids                            | Class 4, Division 4.2                   |
| Pyrophoric solids                             | Class 4, Division 4.2                   |
| Self-heating substances                       | Class 4, Division 4.2                   |
| Substances which, in contact with water, emit | Class 4, Division 4.3                   |
| <u>flammable gases</u>                        |   |
| Oxidizing liquids                             | Class 5, Division 5.1                   |
| Oxidizing solids                              | Class 5, Division 5.1                   |
|   |   |

Organic peroxides Class 5, Division 5.2

<u>Corrosive to metals</u> <u>Class 8</u>

<u>Desensitized explosives</u> <u>Class 3 (liquids)</u>

Class 4, Division 4.1 (solids)

Acute toxicity, Categories 1, 2 and 3 Class 6, Division 6.1 (solids and liquids)

Class 2, Division 2.3 (gases)

Skin corrosion, Category 1 Class 8

Hazardous to the aquatic environment, Acute 1 and Class 9 (environmentally hazardous substances)

Chronic 1 and 2

#### 1.23 Layout

1.23.1 The elassification procedures, test methods and criteria are Manual is divided into three five parts:

Part I: those relating to assignment of explosives to Class 1;

Part II: those relating to assignment of self-reactive substances to Division 4.1 and of to organic

peroxides to Division 5.2;

Part III: those relating to aerosols, desensitized explosives (relating to transport only), flammable

<u>liquids</u>, flammable solids, pyrophoric liquids and solids, substances which in contact with water emit flammable gases, oxidizing liquids and solids, unstable gases and gas mixtures, substances corrosive to metals, and substances and articles of transport Class 9 (ammonium

nitrate fertilizers, lithium metal and lithium ion batteries-);

Part IV: test methods concerning transport equipment

Part V: classification procedures, test methods and criteria relating to sectors other than transport.

Part III contains some classification procedures, test methods and criteria which are also given in the Model Regulations.

1.3.2 There are also a number of appendices which give information common to a number of different types of tests, on the National Contacts for Test Details, on an example method for emergency relief vent sizing of portable tanks for the transport of organic peroxides and self-reactive substances, and on screening procedures, on flash composition tests for the classification of fireworks, response descriptors and the ballistic projection energy test for cartridges, small arms.

1. $\frac{23}{2}$ . The methods of test identification are given in Table 1. $\frac{42}{2}$ .

Table 1.42: TEST IDENTIFICATION CODES

| Part of Manual | Test series | Test type      | Test number                  | Example of test identification code |
|----------------|-------------|----------------|------------------------------|-------------------------------------|
| I              | 1 - 8       | (a), (b), etc. | (i), (ii), etc. <sup>a</sup> | 2 (a) (i)                           |
| II             | A - H       | -              | 1, 2, etc.                   | A.l                                 |
| III            | L - T       | -              | 1, 2, etc.                   | L.l                                 |

If only one test is given for a test type, the Roman numerals are not used.

1.2.33.4 Each test is given a unique identification code and is edited as follows:

x.1 Introduction

x.2 Apparatus and materials

- Procedure (including observations to be made and data to be collected) x.3
- Test criteria and method of assessing results x.4
- Examples of results x.5

NOTE: Examples of results are not normally given for tests on articles as these are too specific to the article tested and do not allow validation of the test procedure. Results on substances test samples may vary from those given in the "Examples of results" if the physical form, composition, purity etc. of the substance-test sample is different. The results given should not be regarded as standard values.

**Figures** x.1, x.2, x.3 etc. (i.e. diagrams of apparatus etc.)

**NOTE:** Unless otherwise indicated, the dimensions given on the diagrams are in millimetres.

## 1.3 Precedence of hazard characteristics 1.3.1 The table in 2.0.3.3 of Chapter 2.0 of the Model Regulations may be used as a guide in determining the class of a substance, mixture or solution having more than one risk, when it is not named in the Dangerous Goods List in Chapter 3.2 of the Model Regulations. For goods having multiple risks, which are not specifically listed by name in Chapter 3.2 of the Model Regulations, the most stringent packing group denoted to the respective hazard of the goods takes precedence over other packing groups, irrespective of the precedence of hazard table in 2.0.3.3 of Chapter 2.0 of the **Model Regulations.** 1.3.2 The precedence of hazard characteristics of the following are not dealt with in the Precedence of Hazard Table in

Chapter 2.0 of the Model Regulations, since these primary characteristics always take precedence:

| <br>Substances and articles of Class 1;   |
|---|
| <br>Gases of Class 2;   |
| <br>Liquid desensitized explosives of Class 3;                                  |
| <br>Self reactive substances and solid desensitized explosives of Division 4.1; |
| <br>Pyrophoric substances of Division 4.2;                                      |
| <br>Substances of Division 5.2;   |
| <br>Substances of Division 6.1 with a packing group I inhalation toxicity;      |
| <br>Substances of Division 6.2; and   |
| <br>Material of Class 7.  |

1.3.3 Self reactive substances, except for type G, giving a positive result in the self heating test for Division 4.2, should not be classified in Division 4.2 but in Division 4.1 (see paragraph 2.4.2.3.1.1 of the Model Regulations). Organic peroxides of type G having properties of another class or division (e.g. UN 3149) should be classified according to the requirements of that class or division.

#### 1.4 **Safety**

- 1.4.1 For the safety of laboratory personnel, the producer or other applicant for classification of a new product should provide all available safety data on the product e.g. the toxicity data (see Chapter 1.5 and Annex 4 of the GHS for guidance on the preparation of Safety Data Sheets).
- 1.4.2 Particularly when explosive properties are suspected, it is essential for the safety of workers that small scale preliminary tests are carried out before attempting to handle larger quantities. This involves tests for determining the sensitiveness of the substance to mechanical stimuli (impact and friction), and to heat and flame.
- 1.4.3 In tests involving initiation of potentially explosive substances or articles, a safe waiting period, prescribed by the test agency, should be observed after initiation.

1.4.4 Extra care should be taken when handling samples which have been tested since changes may have occurred rendering the substance more sensitive or unstable. Tested samples should be destroyed as soon as possible after the test.

#### 1.5 General conditions for testing

- 1.5.1 The conditions given in the test prescriptions should be followed as closely as possible. If a parameter is not specified in the test prescription then the conditions given <a href="here-below">here-below</a> should be applied. Where tolerances are not specified in the test prescription, it is implied that the accuracy is according to the number of decimal places given in any dimension e.g. 1.1 implies 1.05 to 1.15. In cases where conditions during a test deviate from those prescribed, the reason for the deviation should be stated in the report.
- 1.5.2 The composition of the test sample should be representative for the product being classified as close as possible to the concentration of the substance intended for transport. The contents of active substance(s) and diluent(s) should be specified in the test report with at least an accuracy of  $\pm 2$  % by mass. Components which can have a major effect on a test result, such as moisture, should be specified as accurately as possible in the test report.
- 1.5.3 All test materials in contact with the test substance should be such that, as far as possible, they do not affect the test results e.g. catalyse decomposition. In cases where such an effect cannot be excluded, special precautions should be taken to prevent the result being affected, e.g. passivation. The precautions taken should be specified in the test report.
- 1.5.4 The tests should be performed under the conditions (temperature, density etc.) which are representative of the expected circumstances <u>e.g.</u> of transport <u>or storage</u>. If the<u>se circumstances transport conditions</u> are not covered by the test conditions specified, supplementary tests may need to be performed which are specifically designed for the anticipated transport conditions e.g. elevated temperature. Where appropriate, e.g. when the result is particle size dependent, the physical conditions should be specified in the test report.

#### 1.6 Recommended tests

- 1.6.1 The Manual gives descriptions of tests and criteria used to provide the necessary information to arrive at a proper classification. In some cases, there is more than one test for a particular property. As a result of comparative work with some of these tests, it has been possible to identify one test as the recommended test in a set of equivalent tests. The recommended tests for classifying explosive substances and articles (Part I of the Manual) are listed in Table 1.2-3 and for classifying self-reactive substances and organic peroxides (Part II of the Manual) in Table 1.34. Unless otherwise specified, all test methods given in Part III of the Manual are recommended tests as only one test is given for each property. The other tests in a set are considered to be alternative tests and may continue to be used for classification purposes.
- 1.6.2 As a result of comparative work, some tests have been deleted. However, as some countries maintain databases referenced by the test number, the tests currently given in the Manual have not been renumbered unless existing tests have been assigned to different test types.
- 1.6.3 The aim is to have only one United Nations test, or combination of tests, for each property. However, until the recommended tests have been used more widely, it is not possible to do this in all cases at present.
- 1.6.4 If new tests are proposed for inclusion in the Manual, the proposer should be able to provide justification that the new test is a significant improvement on the existing recommended test. In such cases, the new test may be included as an alternative test until it has been tried by laboratories of other countries.

Table 1.23: RECOMMENDED TESTS FOR EXPLOSIVES AND EXPLOSIVE ARTICLES IN PART I

| Test<br>series | Test<br>type | Test code | Test name   |
|----------------|--------------|-----------|-------------|
| 1              | (a)          | 1 (a)     | UN gap test |

| Test     | Test       | Test code    | Test name   |
|----------|------------|--------------|---|
| series   | type       |              |   |
| 1        | (b)        | 1 (b)        | Koenen test   |
| 1        | (c)        | 1 (c) (i)    | Time / pressure test  |
| 2        | (a)        | 2 (a)        | UN gap test   |
| 2        | (b)        | 2 (b)        | Koenen test   |
| 2        | (c)        | 2 (c) (i)    | Time / pressure test  |
| 3        | (a)        | 3 (a) (ii)   | BAM Fallhammer  |
| 3        | (b)        | 3 (b) (i)    | BAM Friction apparatus  |
| 3        | (c)        | 3 (c)        | Thermal stability test at 75 °C   |
| 3        | (d)        | 3 (d)        | Small-scale burning test  |
| 4        | (a)        | 4 (a)        | Thermal stability test for unpackaged articles and packaged articles                      |
| 4        | (b)        | 4 (b) (i)    | Steel tube drop test for liquids  |
| 4        | (b)        | 4 (b) (ii)   | Twelve metre drop test for unpackaged articles, packaged articles and packaged substances |
| 5        | (a)        | 5 (a)        | Cap sensitivity test  |
| 5        | (b)        | 5 (b) (ii)   | USA DDT test  |
| 5        | (c)        | 5 (c)        | External fire test for Division 1.5   |
| 6        | (a)        | 6 (a)        | Single package test   |
| 6        | (b)        | 6 (b)        | Stack test  |
| 6        | (c)        | 6 (c)        | External fire (bonfire) test  |
| 6        | (d)        | 6 (d)        | Unconfined package test   |
| 7        | (a)        | 7 (a)        | EIS cap test  |
| 7        | (b)        | 7 (b)        | EIS gap test  |
| 7        | (c)        | 7 (c) (ii)   | Friability test   |
| 7        | (d)        | 7 (d) (i)    | EIS bullet impact test  |
| 7        | (e)        | 7 (e)        | EIS external fire test  |
| 7        | (f)        | 7 (f)        | EIS slow cook-off test  |
| 7        | (g)        | 7 (g)        | 1.6 article external fire test  |
| 7        | (h)        | 7 (h)        | 1.6 article slow cook-off test  |
| 7        | (j)        | 7 (j)        | 1.6 article bullet impact test  |
| 7        | (k)        | 7 (k)        | 1.6 article stack test  |
| <u>7</u> | <u>(1)</u> | <u>7 (1)</u> | 1.6 article (or component) fragment impact test   |
| 8        | (a)        | 8 (a)        | Thermal stability test for ANE  |
| 8        | (b)        | 8 (b)        | ANE gap test  |
| 8        | (c)        | 8 (c)        | Koenen test   |
| 8        | (d)        | 8 (d)        | Vented pipe tests <sup>a</sup>  |

These tests are intended for evaluating the suitability for transport containment in portable tanks as an oxidizing substance.

Table 1.34: RECOMMENDED TESTS FOR SELF-REACTIVE SUBSTANCES AND ORGANIC PEROXIDES IN PART II

| Test series | Test code | Test name                  |
|-------------|-----------|----------------------------|
| A           | A.6       | UN detonation test         |
| В           | B.1       | Detonation test in package |

#### UN/SCETDG/51/INF.7 UN/SCEGHS/33/INF.3

| C | C.1 | Time/pressure test  |
|---|-----|---|
| C | C.2 | Deflagration test   |
| D | D.1 | Deflagration test in the package                                    |
| E | E.1 | Koenen test   |
| E | E.2 | Dutch pressure vessel test  |
| F | F.4 | Modified Trauzl test  |
| G | G.1 | Thermal explosion test in package                                   |
| Н | H.1 | United States SADT test (for packages)                              |
| Н | H.2 | Adiabatic storage test (for packages, IBCs and tanks)               |
| Н | H.4 | Heat accumulation storage test (for packages, IBCs and small tanks) |

### 1.7 Reporting

1.7.1 Classifications for <u>inclusion in the list of dangerous goods for transport in Chapter 3.2</u> of the Model Regulations are made on the basis of consideration of data submitted to the Committee by governments, intergovernmental organisations and other international organisations in the form recommended in Figure 1 of the Recommendations. Supplementary data is required for the classification of:

Explosive sSubstances and articles of Class 1 (see 10.5); Self-reactive substances of Division 4.1 (see 20.5); and Organic peroxides of Division 5.2 (see 20.5).

1.7.2 Where tests are performed on packaged substances or articles, the test report should contain the quantity of substance or number of articles per package and the type and construction of the packaging.