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

Sub-Committee of Experts on the Transport of Dangerous Goods **23 November 2017**

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Issues relating to the Globally Harmonized System of Classification and Labelling of Chemicals: testing of oxidizing substances

Tests for oxidizing liquids (UN Test O.2) and oxidizing solids (UN Tests O.1 and O.3)

Consequential amendments of cellulose replacement to test descriptions: additional information to document ST/SG/AC.10/C.3/2017/45

Transmitted by the expert from France

Introduction

1. The purpose of this informal document is to provide the Sub-Committee with additional information in support of the document ST/SG/AC.10/C.3/2017/45 on the consequential amendments of cellulose replacement to tests descriptions for oxidizing liquids (UN Test O.2) and oxidizing solids (UN Tests O.1 and O.3).

2. The following paragraphs give an overview of the progress for the four items identified for consideration (see UN/SCETDG/51/INF.12). They take into account the outcome of the meeting between experts and laboratories held on 25 September 2017 in Germany.

UN Test O.2 – Reference substances

3. The first way of improvement considered was the replacement the reference substances for allocation of PGII (i.e. 40% aqueous sodium chlorate solution) and of PGIII (i.e. 65% aqueous nitric acid) by diluted aqueous solutions of perchloric acid[1] in the range of 30-40%. Preliminary promising results were presented by INERIS to other laboratories in September. Although most of the laboratories expressed their sympathy for the idea of replacing three reference substances by only one in the test method, it was also recognized that this operation will required additional work and a longer time frame before it can be validated through Round Robin Tests (RRT).

4. The second way considered was an improvement of the test description in particular of the section 34.4.2.3 of the Manual of Tests and Criteria, ST/SG/AC.10/11/Rev.6. In

[1] A 50% aqueous solution of perchloric acid is already the reference substance for allocation of PGI

preparation of that a questionnaire was circulated between the nine laboratories that participated to a RRT (see UN/SCETDG/49/INF.47, annex 1) on UN Test O.2 in 2015 to collect details of their best practices. Feedback gained from the answers to the questionnaire allow to make proposal to improve the wording of section 34.4.2.3.1.

Proposal 1 relating to UN Test O.2 – Reference substances

5. Modify the text in the UN Test O.2 description, i.e. in section 34.4.2.3.1 of the Manual of Tests and Criteria, ST/SG/AC.10/11/Rev.6, as follow:

> The apparatus, assembled complete with pressure transducer and heating system but without the bursting disc in position, is supported firing plug end down. [The tightness of apparatus could be checked by any suitable leakage testing on an empty vessel beforehand]. 2.50 ± 0.01 g of the liquid to be tested is mixed with 2.50 ± 0.01 g of dried cellulose in a glass beaker using a glass stirring rod [or any appropriate mixing tool for at least two minutes. The time for mixing should be tracked by a timer and kept uniform for both, reference or sample mixtures]. **For safety, the mixing should be performed with a safety shield between the operator and mixture.** (If the mixture ignites during mixing or filling, no further testing is necessary.) The mixture is added, in small portions with tapping, to the pressure vessel making sure that the mixture is packed around the ignition coil and is in good contact with it. It is important that the coil is not distorted during the packing process [and should be covered completely by the mixture after loading]. The bursting disc is placed in position and the retaining plug is screwed in tightly. The charged vessel is transferred to the firing support stand, bursting disc uppermost, which should be located in a suitable, armoured fume cupboard or firing cell. The power supply is connected to the external terminals of the firing plug and 10 A applied. The time between the start of mixing and switching the power on should [~~be about 10 minutes~~ not exceed 15 minutes in total and should be the same for each test].

UN Test O.3 – Reference oxidizer

6. The reference oxidizer (i.e. calcium peroxide 75%) for the test may originate from different sources i.e. suppliers in Europe or in other parts of the world which may not respect the whole specifications given in the test description.

7. Determination of the concentration in calcium peroxide by different methods is possible for the reference oxidizer. However, it was judged that making this determination mandatory prior to each testing campaign would increase the level of complexity of UN Test O.3 methodology, require further interlaboratory studies and create an unnecessary burden. It was considered that the quality of the calcium peroxide shall be based on the certificate of analysis from the supplier and its date of expiry. It was also recognized that the tolerance given for the concentration of calcium peroxide as specification could be changed from 0.5% to 1.0% with no impact on the outcome of the test and that will extend the period of usage of calcium peroxide according to the actual specifications of the suppliers.

Proposal 2 relating to UN Test O.3 – Reference oxidizer

8. Replace in the UN Test O.3 description, i.e. in section 34.4.3.2.1 of the Manual of Tests and Criteria, ST/SG/AC.10/11/Rev.6, the following specification:

"CaO_2: 75% ± 0.5%"

by

"CaO_2: 75% ± 1.0%".

UN Test O.3 – Coefficient of correlation and standard deviation of test results

9. Requirements in the UN Test O.3 description (see section 34.4.3.5.3 of the Manual of Tests and Criteria ST/SG/AC.10/11/Rev.6) are set for the coefficient of correlation R^2 (i.e. at least 0.95) and the standard deviation (i.e. not exceeding 10%). From a practical point of view, to respect the strictness of these criteria has for consequence the necessity to repeat burning trials a very numerous time before both criteria can be met at once.

10. Following a RRT on UN Test O.3 (see UN/SCETDG/49/INF.47, annex 2) and analysis of its results, these criteria were, indeed, seen to be too limiting by the majority of the thirteen participating laboratories.

11. The impact and consequence of a possible relaxation of these criteria were studied based on test results gained during the hereinbefore RRT. The study showed that no significant alteration of the overall results (i.e. classification of the tested substances) were noticeable in the case where the criteria are changed from "at least 0.95" to "at least 0.90" for the coefficient of correlation R^2 and from "not exceeding 10%" to "not exceeding 20%" for the standard deviation.

Proposal 3 relating to UN Test O.3 – Coefficient of correlation and standard deviation of test results

12. Modify the text in the UN Test O.3 description, i.e. in section 34.4.3.5.3 of the Manual of Tests and Criteria, ST/SG/AC.10/11/Rev.6, as follow:

> The profile of each burning test has to be examined by plotting the mass loss as a function of time. The graph can also be used for decision making and should be used in case of doubt. The coefficient of correlation (R^2) of the mass curve of each burning test should be at least ~~0.95~~ 0.90 between 20% to 80% mass loss, otherwise the burning trial has to be repeated. Five valid tests should be performed with each reference and test substance mixture. The standard deviation of the burning rates within these five tests should not exceed ~~10%~~ 20% in total.

Test UN O.3 – Inert metal wire as ignition source

13. During the RRT exercise, various types of metal wire were used – see UN/SCETDG/49/INF.47, annex 2, para 2.5.1.1 -. Up to 50% of participants i.e. 6 participants observed more or less frequent breakages of the wire during the runs.

14. The possible reasons of these breakages were explored in more details by France. It is known from the literature[2] that this issue is more frequent with nitrate compounds or with low melting point samples. In this latter case, the melted portion of the sample may fuse to the ignition wire and the fused portion possibly reaches a temperature higher than the melting point of the ignition wire.

15. Different natures of ignition wires are already used by the different laboratories. Information on the performance of these wires are available in a published RRT report (see UN/SCETDG/49/INF.47, annex 2) and can be used as guidance for the selection of a wire on a case by case based on the laboratory experience. Based on that it is seen not necessary to change the specifications given in section 34.4.3.3.2.

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[2] Hiroshi Koseki in Journal of Loss Prevention in the Process Industries 14 (2001) 431–434