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## 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

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Item 3 of the provisional agenda

#### Listing, classification and packing

## Further information related to ST/SG/AC.10/C.3/2021/39 – Quinone dioxime and other unintentionally energetic substances

### Submitted by the Council on Safe Transportation of Hazardous Articles (COSTHA)

#### Introduction

1. This paper includes more information on the testing leading to a classification of quinone dioxime (QDO) as a Division 1.4 explosive concluded this year.
2. We also identify inconsistencies and potential solutions related to the classification of unintentionally energetic substances which are impacting quinone dioxime and a wide range of other chemicals. This is because the thermal criteria for exit from Class 1 would forbid the fire behaviour of other dangerous goods.
3. Due to the trend towards more competent authority oversight of self-classification, the assignment of unintentionally energetic substances to Class 1 will become increasingly common. Classification options based on configurations can already provide safe and flexible solutions. Regulatory amendments may be necessary to enhance these options for a safe and equitable classification system.

#### Testing of QDO with Division 1.4 explosive results

4. During the REACH registration process, an ECHA reviewer found that QDO did not pass the screening criteria in UNMTC Appendix 6, and testing was required to re-evaluate the historical classification of flammable solid (and classified as non-regulated by many manufacturers according to safety data sheets). Conversations with the IGUS-EOS<sup>1</sup> group of experts indicate that the oxygen balance equation is not useful in a strong majority of cases. Other experts question the current decomposition thermal screening criteria, at least for research and development. The screening criteria are oriented towards intrinsic properties.
5. Test Series 3 was performed with passing results for stability and sensitivity.
6. QDO underwent small scale laboratory energy testing and passed the Test Series 1(a) gap test, indicating that it will not detonate. However, it failed the Koenen 2(b) test with a limiting diameter of 5 mm instead of 2 mm, indicating the potential to deflagrate by overcoming venting. A similar indication for the potential of deflagration was provided by borderline passing results in the Test Series 2(c) time-pressure test.

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<sup>1</sup> The International Group of Experts on the Explosion Risks of Unstable Substances, Working Group on Energetic and Oxidising Substances (EOS), <http://www.igus-experts.org/>

7. QDO was tested in the Test Series 6(a) single package test with a negative result, and then the 6(c) bonfire test was performed four times in various packagings ranging from 45 kg down to 2 kg. The largest packaging of 45 kg net quantity exhibited a 2 m flame radius, which dissipated to zero in the subsequent tests of smaller packagings. No explosion behaviour was observed, but the burn times and heat flux measurements aligned with a Division 1.4 classification based on thermal effects. Noticeable smoke and vertical flames occurred.
8. QDO was classified as a Division 1.4 explosive based on thermal characteristics alone.

## Classification path

9. Class 1 is defined in 2.1.1.1 (a) to comprise explosive substances<sup>2</sup>, excluding dust cloud explosion potential, forbidden explosives and those where the predominant hazard is appropriate to another class. The decision of whether the hazard is appropriate to another class belongs to competent authorities and is not a matter for self-classification by industry. There are generally no "de minimis" quantities or concentrations allowed to exit Class 1. Section 2.1.3.6.2<sup>3</sup> of the UN Model Regulations (UNMR) concludes the process with the following statement:

“Where a substance provisionally accepted into Class 1 is excluded from Class 1 by performing Test Series 6 on a specific type and size of package, this substance, when meeting the classification criteria or definition for another class or division, should be listed in the Dangerous Goods List of Chapter 3.2 in that class or division with a special provision restricting it to the type and size of package tested.”

10. No quantitative criteria are given in Test Series 6 for exclusion from Class 1. The UN Manual of Tests and Criteria (UNMTC) states in 16.6.1.4.7 a qualitative criterion of “no hazardous effect”. From a practical standpoint, no flammable dangerous good, and perhaps no dangerous good of any type, can pass this criterion in a fire. Passing results in Test Series 2 (i.e., not Class 1) do not equate to “no hazardous effects” or 1.4S results in a bonfire (1 meter radius horizontal flame), so the UNMTC criterion is more severe than for non-explosives.

## Current workaround

11. Some competent authorities interpret the requirement for “no hazardous effect” literally. Others, based on the flow chart in UNMTC Figure 10.3 Box 35, require a 1.4S result to grant an exit from Class 1 for an unintentionally energetic substance. Within the UNMTC, the flow chart may be considered out of alignment with the text of 16.6.1.4.7, or vice versa.

12. Most flammable goods probably exhibit thermal behaviour more in the range of Division 1.4 or 1.3. Formal results are not available to COSTHA, as flammable and other dangerous goods are not subject to Test Series 6(c), however, even small flammable liquid packagings show Division 1.3 fireball behaviour in informal testing.

## Small scale testing for intrinsic properties versus large scale empirical evaluations

13. The following information is provided as a basis for potentially giving more weight to the results of Test Series 6 and the value of packaging-based assessments versus small scale test information.

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<sup>2</sup> The word “substance” is intended to include a mixture of substances. See UNMTC section 1.1.3.

<sup>3</sup> This paper deals with the UN Model Regulations rather than regional or national regulations, in which there are significant differences. For example, ADR omits equivalent texts for UNMR 2.1.3.6.2 or 2.1.3.6.3 concerning the use of Test Series 6 for classifications based on packaging or desensitization, and instead gives broad discretion in ADR 2.2.1.1.8.1, the equivalent of UNMR 2.1.3.6.1.

14. Test Series 2 consists of small-scale laboratory<sup>4</sup> tests which evaluate energy characteristics of a substance. The purpose is to identify intrinsic properties<sup>5</sup> to forecast the potential for explosive behaviour. If no explosive behaviour is found, further testing is not necessary and configuration-based requirements do not apply, other than the packing instruction. A knowledge of the physical hazard intrinsic properties of a chemical are useful beyond the transport sector; their application extends outside the scope of transport into manufacturing and storage regulations.

15. As recently discussed extensively by the GHS, with the assistance of the Explosives Working Group and agreed with 100% consensus, intrinsic properties of explosives are superseded by empirical knowledge for specific configurations.<sup>6</sup> This is because an explosives classification system based on intrinsic properties alone would assign all chemicals within its scope to Sub-Category 2A / Division 1.1 or Category 1 / forbidden for transport. A knowledge of intrinsic properties helps to ensure safety throughout the life cycle, but its application to transport without accounting for the mitigating effect of configurations is burdensome.

16. The Globally Harmonized System of classification and labelling of chemicals (GHS) states in 2.1.1.3.4:

“As the assignment to a division depends on the configuration, the classification of an explosive may change over its life cycle as a result of reconfiguration.”

17. Substances undergoing the 6(c) bonfire test are empirically proven to give certain results with a certain single or combination packaging and a maximum net quantity, i.e. a particular configuration. Empirical testing captures all parameters, known or unknown. Intentional explosives do not use small scale energy tests, and move straight into empirical evaluation of a configuration.

18. Small scale tests are performed because they are safer, easier and cheaper to perform than the large scale tests in Test Series 6, with the hopeful result that Test Series 6 will not be necessary. In those cases where Test Series 6 is performed, empirical results supersede small scale test data.

## Future Work

19. COSTHA seeks interim relief for QDO's exit from Class 1 on the basis that it has been proven not to explode in certain configurations and displays thermal behaviour aligned with other flammable dangerous goods.

20. Should the Sub-Committee support the logic provided in the COSTHA proposals, we would return with further proposals to amend the Model Regulations.

21. IGUS-EOS recognizes the general nature of the challenges faced by QDO, and has included this work in their ad-hoc working group “Classification of energetic substances”. COSTHA is proposing research to EOS in support of future UN proposals for new UN entries:

- (a) Research and development operations are often not realistically able to perform the current classification testing requirements in Test Series 2 or Test Series 6. The screening procedure thresholds, while they may be appropriate from an intrinsic property viewpoint, may be too narrow to avoid testing of materials which could likely benefit from configuration-based classification.

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<sup>4</sup> Test Series 2(b) and 2(c) may be performed in a normal building without special expertise in explosives. Test Series 2(a) and Test Series 6 require specialized expertise and facilities.

<sup>5</sup> Intrinsic properties of explosives are not intrinsic in the same sense as for health hazards. The test results are specific to the test apparatus, and are still configuration-based, e.g., dependent on particle size distribution. The test results are useful because the conditions may be more severe than those encountered in transport.

<sup>6</sup> Forms of the word “configuration” are used 33 times in the new GHS Chapter 2.1.

(b) A tiered approach to configuration-based exits from Class 1 could be developed based on combinations of prescribed energy limits, quantities and specialized packaging. Hypotheses could be validated with large scale testing, resulting in new UN entries which, once complete, would only require realistically performable small scale tests.

## **Proposal**

22. COSTHA requests a discussion of the possibilities for interim relief for QDO. The Sub-Committee is invited to consider pursuing further work.

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