Introduction of new entries for 1,4-benzoquinone dioxime

Transmitted by the Council on the Safe Transportation of Hazardous Articles (COSTHA)*

I. Introduction

1. By provision of testing through two independent laboratories, 1,4-benzoquinone dioxime (QDO) satisfies the defining criteria of an explosive substance class 1. This conclusion was verified by the competent authority in Germany (BAM) and subsequently by the United States (US) of America competent authority (PHMSA). However, QDO is manufactured globally and distributed to end users throughout the world under various dangerous and non-dangerous classifications. This document proposes to harmonize the transport classification, against the backdrop of empirical testing and application of the classification criteria, by introduction of new UN entry.

II. Background

2. During the REACH registration process in 2016 an ECHA reviewer found that QDO did not pass the screening criteria in appendix 6 of the Manual of Tests and Criteria, and testing was required to re-evaluate the historical classification (UN 1325, flammable solid, 4.1, PG II, and/or classified as non-regulated by some). Test series 3 was performed with passing results for stability and sensitivity.

3. 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.

4. 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.

* A/77/6 (Sect, 20), table 20.6
(COSTHA will provide test report in a later submission of an informal document), 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 flux measurements.

5. The flame radius measurements, however, ranged from a maximum of 2 meters for a 45 kg per unit quantity to less than 1 meter for smaller unit quantities (COSTHA will provide test report in a later submission of an informal document). The latter is a 1.4S result, in which case a chemical like QDO which is not intentionally energetic would exit class 1 (see section 2.1.3.6.2 of the Model Regulations). These results are much less energetic than those seen for propellants.

6. Flux measurements continued to control the classification even for smaller packages. Such measurements are frequently not employed by test laboratories, in favour of the flame radius measurement. Some experts question whether the flux measurement should result in stricter transport controls than for other flammable goods, especially considering the critical nature of these goods for rubber manufacturing. An explosive classification may preclude normal use by industry. As mentioned above, the practice of non-dangerous declaration of QDO continues. We wonder if a more pragmatic solution could be achieved.

7. QDO was hence classified as a Division 1.4 explosive based on thermal flux characteristics alone. Explosives acceptance testing was repeated by a US laboratory in 2021 with identical results.

III. Discussion

8. The disconnect in terms of classification at the substance level calls into question transportation safety first and foremost, as well as commercial competitiveness. Classification globally should be harmonized when substances of identical composition are manufactured and tested in different regions. As a result of regional testing, this material which is used in the vehicle tire manufacturing and specialty rubber industries has been regionally re-classified from a Division 4.1 material to a Division 1.4, resulting in significant transportation complications.

9. Based on certain testing, the product could be identified in some cases as a Division 1.4 Compatibility Group C material. However, it is also recognized that this classification is not being used universally. COSTHA believes it is important to properly classify and identify relevant hazards when shipping QDO. To remove ambiguity with the classification of the QDO, we believe a new entry be should be introduced reflecting a Division 1.4 Compatibility Group C classification.

10. The value of new entries was discussed by the Explosives Working Group (EWG) during the sixty-second session of the Sub-Committee based on an informal document (UN/SCETDG/62/INF.62). In the report from the EWG (informal document UN/SCETDG/62/INF.47), the group provided support for two entries to be considered by the Sub-Committee.

11. COSTHA proposes two new entries for 1,4-benzoquinone dioxime (QDO) that reflect the hazards this material represents and would allow for safe and proper packaging and hazard communication.

IV. Data sheet to be submitted to the United Nations for new or amended classification of substances

Section 1. SUBSTANCE IDENTITY

1.1 Chemical name: 1,4-benzoquinone dioxime

1.2 Chemical formula: \( \text{C}_8\text{H}_4\text{N}_2\text{O}_2 \)

1.3 Other names/synonyms: p-benzoquinone dioxime; 2,5-Cyclohexadiene-1,4-dione, 1,4-dioxide; QDO
1.3.1 CAS number: **105-11-3**

1.4 Proposed classification for the Recommendations

1.5.1 Proper shipping name (3.1.2): **1,4-benzoquinone dioxime**

1.5.2 Class/division: **1.4C** Subsidiary risk(s): *None* Packing group: **N/A**

1.5.2 Class/division: **4.1** Subsidiary risk(s): *None* Packing group: **II**

**V. Proposal**

12. Amend 2.4.2.4.1 to include “*UN 35XX*” in the list of solid desensitized explosives (new text is underlined, deleted text in strike-through).

13. Amend the Dangerous Good List to include the following entries:

<table>
<thead>
<tr>
<th>UN No.</th>
<th>Name and description</th>
<th>Class or division</th>
<th>Subsidiary hazard</th>
<th>UN packing group</th>
<th>Special provisions</th>
<th>Limited and excepted quantities</th>
<th>Packagings and IBCs</th>
<th>Portable tanks and bulk containers</th>
</tr>
</thead>
<tbody>
<tr>
<td>05XX</td>
<td>1,4-BENZOQUINONE DIOXIME</td>
<td>1.4C</td>
<td></td>
<td></td>
<td></td>
<td>0 E0</td>
<td>P114(b)</td>
<td>PP48</td>
</tr>
<tr>
<td>35XX</td>
<td>1,4-BENZOQUINONE DIOXIME, DESSENSITIZED</td>
<td>4.1</td>
<td>II</td>
<td>XYZ</td>
<td>0 E0</td>
<td>P406</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

14. Add in 3.3 a new special provision XYZ to read:

“**XYZ**  This entry is permitted only when testing of the product meets the exclusion criteria from Class 1 in 2.1.3.6. If the material does not meet the exclusion criteria, the entry UN 05XX shall be used.”

15. Amend 4.1.4.1, P114(b), PP48 to read:

“**PP48**  For UN Nos. 0508 and 0509, and 05XX, metal packagings shall not be used. Packagings of other material with a small amount of metal, for example metal closures or other metal fittings such as those mentioned in 6.1.4, are not considered metal packagings.”

16. The entry name in the alphabetical index should be amended as follows:

<table>
<thead>
<tr>
<th>Name and description</th>
<th>Class</th>
<th>UN No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-Benzoquinone dioxime</td>
<td>1.4C</td>
<td>05XX</td>
</tr>
<tr>
<td>1,4-Benzoquinone dioxime, desensitized</td>
<td>4.1</td>
<td>35XX</td>
</tr>
</tbody>
</table>