



**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****Fifty-ninth session**

Geneva, 29 November – 8 December 2021

Item 3 of the provisional agenda

Listing, classification and packing**New UN entry for Quinone dioxime (also known as
1,4-benzoquinone dioxime, or p-benzoquinone dioxime;
CAS no. 105-11-3)****Submitted by the Council on Safe Transportation of Hazardous Articles
(COSTHA)*****Introduction**

1. Quinone dioxime (QDO; Chemical Abstracts Service (CAS) no. 105-11-3) is a solid that is manufactured worldwide by some forty companies and is variously classified as unregulated or as Division 4.1, packing group PG II or PG III as confirmed by the current European Chemicals Agency (ECHA) classification data.¹
2. First patented in 1945, beginning in 1956, QDO has been manufactured and safely transported without any known incident for more than sixty years. A predominant use of QDO is in the manufacture of tires. QDO is a rubber vulcanization curative and accelerator producing unique properties. QDO is important to tire safety and hence transport safety in that it imparts to tire rubber a high impermeability through high-density polymer / molecular cross-linking, and resistance to de-crosslinking when attacked by heat or chemicals. These same advantages are also relevant to other essential industries such as those engaged in manufacturing medical bottle closures, worker chemical personal protection equipment (PPE), high voltage insulators, as well as for production of pharmaceuticals.
3. It is estimated that worldwide over 1350 tons of QDO are manufactured annually with known manufacturing locations in the United States of America, Germany, China, Russia, and India.
4. Uncertainty over the classification of QDO has recently arisen based on REACH testing showing QDO to meet criteria in test series 6(c). More than likely, many substances classified as flammable liquids or flammable solids demonstrate more severe or similar burning behaviour than that of QDO, especially when evaluated by thermal flux alone.

* A/75/6 (Sect.20), para. 20.51

¹ See [p-benzoquinone dioxime - Substance Information - ECHA \(europa.eu\)](https://echa.europa.eu)

5. As discussed below in more detail, QDO is not intended to function as an explosive or as a pyrotechnic and does not pose a hazard warranting its consideration as an explosive substance based on the UN definition in 2.1.1.3(a) and will not "... cause damage to the surroundings" by explosion. Classification of QDO as a Class 1 explosive would misrepresent its predominant hazard of flammable solid, per 2.1.1.1(a): "... except those ... where the predominant hazard is appropriate to another class".

6. Assignment of a UN number and proper shipping name to QDO is proposed to resolve the current uncertainty regarding its correct classification. The purpose of this proposal is to establish a uniform classification for QDO as a Packing Group II, Division 4.1 flammable solid. A completed data sheet is attached as an annex.

Classification of substances not intended to function as explosives

7. The Model Regulations identifies which substances, though not intended to function as explosives, must nevertheless still be considered explosives substances. Under 2.1.1.3(a), a substance which, though not intended to function as an explosive, is considered to be an explosive substance when the substance:

"is in itself capable, by chemical reaction, of producing gas at such a temperature and pressure and at such a speed as to cause damage to the surroundings."

Further as also noted under 2.1.1.1(a), substances are excluded from Class 1 when the "predominant hazard is appropriate to another class".

8. Analogously other regulations define explosive substances in a similar manner.

(a) The ADR defines explosives substances as "solid or liquid substances (or mixtures of substances) capable by chemical reaction of producing gases at such a temperature and pressure and at such a speed as to cause damage to the surroundings".

(b) The United States Department of Transportation regulations defines explosive substances as including:

"an explosive means any substance or article, including a device, which is designed to function by explosion (i.e., an extremely rapid release of gas and heat) or which, by chemical reaction within itself, is able to function in a similar manner even if not designed to function by explosion, unless the substance or article is otherwise classed under the provisions of this subchapter".

(c) Likewise, the Canadian Transport of Dangerous Goods regulations include substances not intended to function as explosives when they are:

"capable, by chemical reaction, of producing gas at a temperature, pressure and speed that would damage the surroundings;"

9. From the above regulation excerpts, it is seen that the transport regulations consistently exclude a substance not intended to function as an explosive unless it is:

"itself capable, by chemical reaction, of producing gas at such a temperature and pressure and at such a speed as to cause damage to the surroundings".

10. Significantly, there is no criterion indicating a substance not intended to function as an explosive is considered an explosive substance on the basis of ordinary burning characteristics which do not produce "gas at a temperature and pressure at such a speed as to cause damage to the surroundings". Rather, substances where the "predominant hazard" is ordinary burning are appropriately covered in other classes (e.g., Classes 2.1, 3 and 4). Still others with energetic properties may be classified as self-reactive substances or organic peroxides.

Testing/classification of QDO

11. *QDO Fire Behaviour*. A fire test of more than 135.2 kg mass in three 45 kg fibreboard drums of QDO in accordance with the UN 6(c) test showed that it produced a flame radius of 2 meters (see figure 1).

Figure 1. External fire test

Wood shavings were inserted between the wooden slats and soaked with a gasoline/diesel mixture.



Test set-up for external fire test, full fire phase (maximum flame) after ignition

12. As can be seen from photos (see figure 1), the burning behaviour of QDO in combination with wood shavings soaked with a gasoline/diesel mixture and wood is less severe than might be expected of many flammable liquids (e.g., diesel oil) when tested under similar conditions. Further, fire intensity is not even a classification criterion that is applicable to dangerous goods other than substances or articles intended to function as explosives.

13. Such burning behaviour is not unlike that of many flammable liquids and solids for which the appropriate hazard classification is other than Class 1. QDO does not detonate based on the Test Series 1 gap test, a test more severe than that required for transport. Importantly, from testing there was no indication that QDO will produce “gas at such a temperature and pressure and at such a speed as to cause damage to the surroundings”. As such there is no basis for considering it as an explosive substance in that, as a substance not intended to function as an explosive, it does not meet the defining criteria for an explosive substance in 2.1.1.3.

14. *QDO SADT.* QDO was tested by a German laboratory and determined to have a self-accelerating decomposition temperature (SADT) of greater than 75 °C when tested using the heat accumulation storage test (UN H.4). Further QDO was determined to have an onset decomposition temperature of 227 °C indicating on the basis of new provisions in the UN Manual of Tests and Criteria (see para. 20.3.4 of the 7th revised edition, as amended by Amendment 1) that its SADT is significantly higher (i.e., on the order of 120 °C or more). In any case QDO does not qualify as a Division 4.1 self-reactive substance at any level.

15. *Division 4.1 Flammable Solid Testing.* QDO was subjected to the burning rate test for flammable solids and determined to meet the criteria for a Packing Group II Flammable Solid on the basis of a burning time of 2 seconds and the flame passing the wetted zone.

Proposal

16. On the basis of the above, it is proposed to amend the 3.2 Dangerous Goods List by introducing a new Division 4.1 UN entry for QDO, as follows:

UN No. Substance	Class	Subsidiary Hazard	UN packing group	Special provisions	Limited and excepted quantities		Packagings and IBCs		Portable tanks and bulk containers	
							Packing instruction	Special packing provisions	Instructions	Special provisions
UN XXXX QUINONE DIOXIME	4.1		II		1 kg	E2	P002			

Annex

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

Submitted by: COSTHA Date: July 16, 2021

Section 1. SUBSTANCE IDENTITY

- 1.1 Chemical name: 1,4-benzoquinone dioxime
 1.2 Chemical formula: C₆H₆N₂O₂
- 1.3 Other names/synonyms: p-benzoquinone dioxime; 2,5-Cyclohexadiene-1,4-dione, 1,4-dioxime
 1.4.1 UN number: **1325** 1.4.2 CAS number: **105-11-3**
- 1.5 Proposed classification for the Recommendations
 1.5.1 Proper shipping name (3.1.2): **1,4-benzoquinone dioxime**
 1.5.2 class/division: **4.1** Subsidiary risk(s): **None** Packing group: **II**
 1.5.3 proposed special provisions, if any: **None**
 1.5.4 proposed packing instruction(s): **P002**

Section 2. PHYSICAL PROPERTIES

- 2.1 Melting point or range: Not determined
 2.2 Boiling point or range: Not determined
 2.3 Relative density at:
 2.3.1 15 °C: Not determined
 2.3.2 20 °C: 1.47 g/cm³ (12.26 lb/gal)
 2.3.3 50 °C: Not determined
- 2.4 Vapour pressure at:
 2.4.1 50 °C: Not determined
 2.4.2 65 °C: Not determined
- 2.5 Viscosity at 20 °C²: Not determined
 2.6 Solubility in water at 20 °C: Insoluble
 2.7 Physical state at 20 °C (2.2.1.1): Solid (solid/liquid/gas)
 2.8 Appearance at normal transportation temperatures, including colour and odour: Very slight chemical odour, but not offensive. Fine particles - brown powder.
 2.9 Other relevant physical properties: N/A

Section 3. Flammability

- 3.1 Flammable vapour
 3.1.1 Flash point (2.3.3): \geq 93 °C cc
 3.1.2 Is combustion sustained? (2.3.1.3): Yes
- 3.2 Autoignition temperature: \geq 165.5 °C
 3.3 Flammability range (LEL/UEL): Not Determined
 3.4 Is the substance a flammable solid? (2.4.2): YES
 3.4.1 If yes, give details: **UN Test N.1, Test Method for Readily Combustible Solids, demonstrated that 1,4-benzoquinone dioxime propagated combustion for a length of 100 mm in less than 45 seconds, and the flame passed the wetted zone. See also attached test report #21048.**

Section 4. CHEMICAL PROPERTIES

- 4.1 Does the substance require inhibition/stabilization or other treatment such as nitrogen blanket to prevent hazardous reactivity? No
 4.2 Is the substance explosive according to paragraph 2.1.1.1? (2.1) No
 4.3 Is the substance a desensitized explosive? (2.4.2.4) No

² See definition of "liquid" in 1.2.1 of the Model Regulations on the Transport of Dangerous Goods.

- 4.4 Is the substance a self-reactive substance? (2.4.1) No
- 4.5 Is the substance pyrophoric? (2.4.3) No
- 4.6 Is the substance liable to self-heating? (2.4.3) No
- 4.7 Is the substance an organic peroxide? (2.5.1) No
- 4.8 Does the substance in contact with water emit flammable gasses? (2.4.4) No
- 4.9 Does the substance have oxidizing properties? (2.5.1) No
- 4.10 Corrosivity (2.8) to: **There are no corrosive properties associated with this substance**
 - 4.10.1 Mild steelmm/year at °C N/A
 - 4.10.2 Aluminummm/year at °C N/A
 - 4.10.1 Other packaging materials (specify)
 -mm/year at °C
 -mm/year at °C
- 4.11 Other relevant chemical properties: N/A

Section 5. HARMFUL BIOLOGICAL EFFECTS

- 5.1 LD50, Oral (2.6.2.1.1) 464 mg/kg Animal species? Rat
- 5.2 LD50, Dermal (2.6.2.1.2) Not determined
- 5.3 LC50, Inhalation (2.6.2.1.3) 55 mg/litre Exposure time: Not listed
- 5.4 Saturated vapour concentration at 20 °C (2.6.2.2.4.3) Not determined
- 5.5 Skin exposure (2.8) results: Not determined
- 5.6 Other data: N/A
- 5.7 Human experience: Not determined

Section 6. SUPPLEMENTARY INFORMATION

- 6.1 Recommended emergency action
 - 6.1.1 Fire (include suitable and unsuitable extinguishing agent): Carbon Dioxide, Dry Chemical, Foam, Water Fog
 - 6.1.2 Spillage: Remove all sources of ignition. Avoid breathing dust and keep dust to a minimum. Wet with water if necessary. Contain and remove with a broom and non-sparking tools.
- 6.2 Is it proposed to transport the substance in:
 - 6.2.1 Bulk Containers (6.8) No
 - 6.2.2 Intermediate Bulk Containers (6.5) No
 - 6.2.3 Portable tanks (6.7) No

***If yes provide details in Sections 7, 8 and/or 9

Section 7. BULK CONTAINERS (Only complete if yes 6.2.1) ...N/A

Section 8. INTERMEDIATE BULK CONTAINERS (Only complete if yes in 6.2.2) ...N/A

Section 9. MULTIMODAL TANK TRANSPORT (Only complete if yes in 6.2.3) ...N/A

Appendix

[English only]

STRESAU TEST REPORT # 21048



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LABORATORY REPORT # 21048

"DIVISION 4.1 READILY COMBUSTIBLE SOLID ANALYSIS"

May 25, 2021

for

Parker Hannifin Corporation

601 South Street

Saegertown, PA 16433

USA

Attn: Mr. Erik Steinbeck

Prepared by: *Thomas E. Basham*

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Russell Spry
Hazardous Materials Technician

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Prepared for: Parker Hannifin Corporation
 601 South Street
 Saegertown, PA 16433

DIVISION 4.1 READILY COMBUSTIBLE SOLIDS ANALYSIS

1.0 OBJECT

One sample, identified below, was subjected to Division 4.1 Readily Combustible Solid Testing in accordance with the *United Nations Transport of Dangerous Goods, Manual of Tests and Criteria, Seventh Revised Edition (2019)*, as requested by Erik Steinbeck of Parker Hannifin Corporation, Inc. **Credit Card Payment.**

2.0 IDENTIFICATION AND PHYSICAL APPEARANCE

<p>SAMPLE IDENTIFICATION</p>	<p>Material: 2002677 Batch Number: 0012143386 Date Sampled: 5/11/21</p>
<p>STRESAU LABORATORY, INC. ID NO.</p>	<p>21048</p>
<p>APPEARANCE</p> <p>The sample arrived at Stresau Laboratory, Inc. in plastic containers at ambient temperature and was tested in the form received.</p>	<p>Brown Powder</p> 

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3.0 TEST CONDUCTED

3.1 UN Test N.1, Test Method for Readily Combustible Solids

3.1.1 SCOPE

As intended by the United Nations, this test is performed to identify the ability of a substance to propagate combustion with different criteria for performing and assessing the results of testing for metal powders or powders of metal alloys and non-metallic pastes, powders and granular substances (United Nations, 2015, p. 371).

The test is divided into two parts:

PART I PRELIMINARY SCREENING

The first part is a Preliminary Screening to rule out substances that do not meet the criteria of Division 4.1 immediately. If a sample passes the Preliminary Screening, no further testing is required (United Nations, 2015, p. 371).

PART II BURN RATE TEST

The second part is the Burn Rate Test and is required for substances that are not ruled out by the Preliminary Screening process (United Nations, 2015, p. 371).

Alternatively, if a substance is known to have a fast Burn Rate, the Preliminary Screening may be omitted from testing.

3.1.2 PART I PRELIMINARY SCREENING

3.1.2.1 Procedure

A portion of the sample is poured into a rectangular mould and then inverted onto a cool impervious base plate to form an unbroken train with a height of 10 mm, width of 20 mm, and a length of 250 mm (United Nations, 2015, p. 367).

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If a mould cannot be used, the sample is formed into the correct dimensions. A gas burner or a Nickel-Chromium wire is then placed at one end of the sample and ignition is attempted for a maximum of two minutes or 5 minutes for metal powders in order to determine the burning rate along a 200 mm distance (United Nations, 2015, p. 367).

3.1.2.2 Criteria

If a sample propagates combustion by burning or smoldering for a length of 200 mm in less than 2 minutes or for the entire length of the sample train in less than 20 minutes for metal powders, the Burn Rate test should be carried out (United Nations, 2015, p. 368).

3.1.2.3 Results

NOTE: The sample was tested under the assumption that it was not a metal powder.

FIG. 1 Pre Test

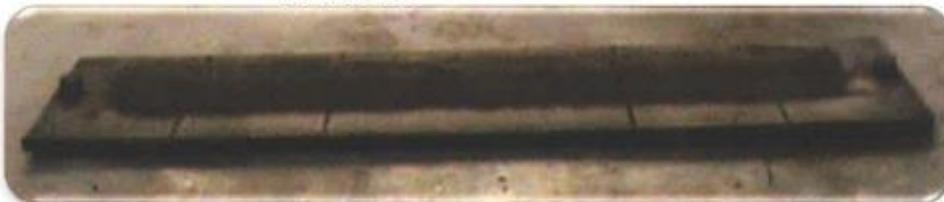
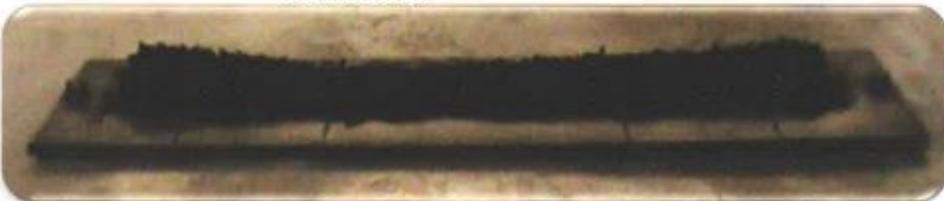


FIG. 2 Post Test



3.1.2.3 Results

Trial	Sample No.	Observations	Perform Burn
		Ambient Conditions 71.1 °F/68.7 % RH	Rate Test?
1	21048	Heat was applied with a flame for 2 minutes. The sample ignited in approximately 4 seconds and propagated 200 mm in 9 seconds.	YES

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3.1.2.4 Discussion

Because sample # 21048 propagated combustion across 200 mm length of the sample train in less than 2 minutes, further testing was required.

3.1.3 PART II BURN RATE TEST

3.1.3.1 Procedure

As described by the United Nations, a portion of the sample is poured into a rectangular mould 200 mm long with a triangular cross section that has a height of 10 mm and a width of 20 mm at the base of the triangle. Pasty substances are formed into a rope with a cross section of approximately 100 mm² (United Nations, 2019, p 367).

The sample is then inverted onto a cool impervious base plate and a gas burner is placed at one end in an attempt to ignite the sample and when the pile has burned a distance of 80 mm, the burning time along a 100 mm distance is observed (United Nations, 2019, p 367).

If the powder is not a metal powder, a wetting agent is added approximately 25 mm beyond the timed zone in order to determine if the propagation of combustion will be inhibited by a wetting agent and to determine a packing group if the substance is determined to be a flammable solid. (United Nations, 2019, pp. 367).

A total of 6 trials per sample are performed unless any trial results in a positively flammable material. No further trials will be performed if the substance is found to be flammable during any trial (United Nations, 2019, pp. 367).

3.1.3.2 Criteria

Classified as Division 4.1 when:	Packing Group II assigned if:	Packing Group III assigned if:
Powdered, granular or pasty substances the time of burning for any of 6 trials performed is less than 45 s or the rate of burning is more than 2.2 mm/s.	the burning time is less than 45 sec. and the flame passes the wetted zone.	the burning time is less than 45 s and the wetted zone stops the flame propagation for at least four minutes.

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Powders of metals or metal alloys	the sample can be ignited and the reaction spreads over the entire length of the sample in 10 minutes or less;	the zone of the reaction spreads over the entire length of the sample in 5 minutes or less;	the zone of the reaction spreads over the entire length of the sample in more than 5 minutes, but not more than 10 minutes.
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(United Nations, 2019, p. 368)

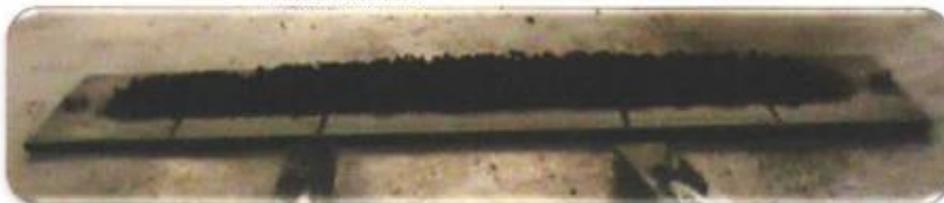
3.1.3.3 Results

Trial	Sample	Time until ignition	Observations	PG
			Ambient Conditions Temperature: 71.1 °C Humidity: 68.7 %	
1	21048	2 sec.	When heat was applied with a flame the sample ignited and propagated 100 mm with flame across the top of the train in 4 seconds and the flame passed the wetted zone.	II

FIG. 1 Pre Test



FIG. 2 Post Test



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4.0 CONCLUSIONS

Based on the test results, the following conclusion was made:

- 1) The material represented by sample # 21048 appeared to be a Division 4.1 Flammable Solid, Packing Group II, as defined by UN/DOT criteria. This is because the sample propagated combustion for a length of 100 mm in less than 45 seconds and the flame passed the wetted zone, when the UN Test N.1, Test Method for Readily Combustible Solids, Burn Rate was performed on the material.

The conclusions represent our interpretation of the test data, as defined by the listed test specifications. The conclusions contained in this report are for the customer's informational purposes only.

5.0 DATA STORAGE

The field data for this report is contained in Data Book #SLF 2021-1, and will be filed with Stresau Laboratory Document Control. No video documentation was made.

6.0 TEST SERVICES

For the benefit of our customers, Stresau Laboratory, Inc. will, on occasion, use outside testing services to either expedite or qualify our own testing capabilities.

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References

United Nations. (2019). *Recommendations on the Transport of Dangerous Goods Manual of Tests and Criteria* (7th ed.). New York and Geneva: United Nations.



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Report # 21048 Appendix A
EQUIPMENT QUALITY TRACEABILITY FORM

Customer: Parker Hannifin Corporation

Job Code: 4000

Stresau Report #: HMT 21048

Procedure #: TP 169

Date: May 25, 2021

Report by: Thomas E. Basham

Item	Mfg.	Model	Stresau Equip. #	Quality Status
TP 169:				
Test Plate	Stresau Lab	P/N 1301001-8	1171	2
Stopwatch	Fisher Scientific	06-662-50	2086	2
Stopwatch	Fisher Scientific	06-662-50	2087	2
Temperature & Humidity	Omega	TH6P2	2096	2

Attach additional forms if needed

Equipment # = Traceable to Stresau Quality System

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