



U.S. Department
of Transportation

**Pipeline and Hazardous
Materials Safety
Administration**

1200 New Jersey Avenue, SE
Washington, DC 20590

May 6, 2020

Mr. James V. McManus
Principal Engineer
Dangerous Goods Safety Advisor
Entegris, Inc.
7 Commerce Drive
Danbury, CT 06810

Reference No. 19-0114

Dear Mr. McManus:

This letter is in response to your September 24, 2019, letter requesting clarification of the Hazardous Materials Regulations (HMR; 49 CFR Parts 171-180) applicable to empty packagings. Specifically, you ask whether a 50-liter Department of Transportation (DOT) 3AA-2400 specification cylinder containing “UN 2199, Phosphine, 2.3 (poisonous gas), 2.1 (flammable gas),” residue is subject to the HMR after the cylinder is cleaned of residue and purged of vapors using a vacuum pump and nitrogen purging.

You state the 100 ppmv phosphine/nitrogen mixture within the cylinder has a calculated LC₅₀ of 200,000 ppm and the pressure within the cylinder is less than 200 kPa (29.0 psig/43.8 psia) at 20 °C (68 °F). You seek confirmation that the gas mixture you describe is not subject to the HMR.

Section 173.22 states it is the responsibility of the shipper to classify a hazardous material. However, based on the information you provided, this Office agrees that a phosphine/nitrogen mixture within a cylinder that has a calculated LC₅₀ of 200,000 ppm and a pressure less than 200 kPa does not meet the definition of a Division 2.1 or Division 2.3 material under the HMR. Paragraphs (b)(2)(ii) and (iii) of § 173.29 state a packaging that is sufficiently cleaned of residue and purged of vapors to remove any potential hazard, or that is refilled with a material that is not subject to the HMR to the extent that any residue that remains in the packaging no longer poses any hazard, is not subject to the requirements of the HMR.

I hope this information is helpful. Please contact us if we can be of further assistance.

Sincerely,

T. Glenn Foster
Chief, Regulatory Review and Reinvention Branch
Standards and Rulemaking Division

Dodd, Alice (PHMSA)

From: INFOCNTR (PHMSA)
Sent: Wednesday, September 25, 2019 10:46 AM
To: Hazmat Interps
Subject: FW: Request for Interpretation
Attachments: Entegris Request for Interpretation 49 CFR Section 173.29 Empty Packaging.pdf

Hello Alice and Ikeya,

Please see attached for letter of interpretation request. The requester sent in for a letter and Josh called to provide letters 15-0157 and 18-0011 which we deemed relevant. The requestor said that the 15 letter was close, however, he is still going through with this letter request since his material is a 2.3 and he wants that specifically addressed.

Please contact our office with any questions.

Thanks,

Kathryn, HMIC

From: Jim McManus [mailto:Jim.McManus@entegris.com]
Sent: Tuesday, September 24, 2019 4:15 PM
To: INFOCNTR (PHMSA) <INFOCNTR.INFOCNTR@dot.gov>
Subject: Request for Interpretation

Notes from Josh's call with Jim 9/25/19:

- Has 2.3 material-toxic by inhalation
- wants a letter specific to this hazard class
- there is a complex calculation in this situation
- a lot of people will mistakenly classify this material as hazmat even when its considered empty

Dear Sir or Madame:

Pursuant to 49 CFR §105.20, this letter is being submitted by e-mail to PHMSA to request an interpretation of a question I have related to §173.29 of the Hazardous Materials Regulations (HMR). Specifically, the question is related to a DOT specification cylinder package containing the residue of UN2199, phosphine and whether the package is subject to the requirements of the HMR after a cleaning and purging process.

I greatly appreciate PHMSA's attention to this matter and look forward to a response that furthers my understanding of the Hazardous Materials Regulations.

Should PHMSA require additional details to process this interpretation, please contact me using the information listed below.

Regards,

Jim

Jim McManus
Principal Engineer
Dangerous Goods Safety Advisor (DGSA)
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September 24, 2019

Standards and Rulemaking Division
Pipeline and Hazardous Materials Safety Administration, Attn: PHH-10
U.S. Department of Transportation
East Building
1200 New Jersey Avenue, SE
Washington, DC 20590-0001
infocntr@dot.gov

Re: Request for Interpretation

Dear Sir or Madame:

Pursuant to 49 CFR §105.20, this letter is being submitted by e-mail to PHMSA to request an interpretation of a question I have related to §173.29 of the Hazardous Materials Regulations (HMR). Specifically, the question is related to a DOT specification cylinder package containing the residue of UN2199, phosphine and whether the package is subject to the requirements of the HMR after a cleaning and purging process.

Cylinder Cleaning and Purging Process

A 50 liter DOT-3AA 2400 cylinder package contains the residue of UN 2199, phosphine. The cylinder package is cleaned of residues and purged of vapors using a vacuum pump and nitrogen purging to remove any potential hazard such that the cylinder package should not be subject to the requirements of the Hazardous Materials Regulations as it conforms with provisions (ii) and (iii) of §173.29(b)(2).

After the cleaning and purging process, the remaining gas within the cylinder is analyzed and found to contain 100 parts-per-million by volume (ppmv) of phosphine and the remaining balance of gas in the cylinder is nitrogen. The pressure of the phosphine/nitrogen gas mixture contained in the cylinder is 103.4 kPa (15 psig) at 20 °C (68 °F).

In order to determine if the cylinder contents pose any potential hazard, the toxicity of the phosphine/nitrogen gas mixture is determined using the method of calculation specified for gas mixtures in §173.115(c)(2).

§173.115(c)(2) specifies that the LC₅₀ values for mixtures may be determined using the formula in §173.133(b)(1)(i) or CGA P-20 (IBR, see §171.7).

The formula given in CGA P-20 for determining the LC₅₀ of a binary mixture is as follows:

$$\text{LC}_{50} = \frac{\text{ppm LC}_{50} \text{ of toxic component}}{\text{ppm of toxic component}} \times 1\,000\,000$$

As the LC₅₀ for pure phosphine is 20 ppm, the LC₅₀ for the 100 ppmv phosphine/nitrogen mixture described above is calculated as follows:

$$\text{LC}_{50} \text{ phosphine/nitrogen mixture} = 20 \text{ ppm} / 100 \text{ ppm} \times 1\,000\,000 = \underline{\underline{200,000 \text{ ppm}}}$$

Classification of Cleaned and Purged Cylinder

§173.116 assigns the four hazard zones for Division 2.3 materials depending on the LC₅₀ of the gas. The criteria used to determine the hazard zone for a Division 2.3 material is shown in the table below:

Hazard zone	Inhalation toxicity
A	LC ₅₀ less than or equal to 200 ppm.
B	LC ₅₀ greater than 200 ppm and less than or equal to 1000 ppm.
C	LC ₅₀ greater than 1000 ppm and less than or equal to 3000 ppm.
D	LC ₅₀ greater than 3000 ppm or less than or equal to 5000 ppm.

For a gas to be considered Division 2.3 material, it must fall within one of the four hazard zones. A material with an inhalation toxicity > 5000 ppm would fall outside this criteria and would not be considered a Division 2.3 material.

Therefore, I conclude the phosphine/nitrogen mixture is not classified as a hazardous material for the following reasons:

- ✓ The calculated LC₅₀ (200,000 ppm) for the phosphine/nitrogen mixture does not fall within any of the hazard zone criteria and therefore the 100 ppm phosphine/nitrogen mixture would not be classified as a Division 2.3 material.
- ✓ Since the pressure of the phosphine/nitrogen mixture inside the cylinder is less than 200 kPa (29.0 psig/43.8 psia) at 20 °C (68 °F), it would not be classified as a Division 2.2 material.

Question:

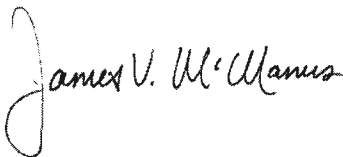
Based on the information in the preceding discussion, does PHMSA agree with the following statement?

Since the 100 ppmv phosphine/nitrogen mixture has a calculated LC₅₀ of 200,000 ppm and the cylinder pressure is less than 200 kPa (29.0 psig/43.8 psia) at 20 °C (68 °F), the gas mixture contained in the cylinder should not be subject to the Hazardous Materials Regulations.

I greatly appreciate PHMSA's attention to this matter and look forward to a response that furthers my understanding of the Hazardous Materials Regulations.

Should PHMSA require additional details to process this interpretation, please contact me using the information listed below.

Sincerely,



James (Jim) V. McManus
Principal Engineer
Dangerous Goods Safety Advisor (DGSA)
Entegris Inc.
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