



U.S. Department
of Transportation

**Pipeline and Hazardous
Materials Safety
Administration**

1200 New Jersey Avenue, SE
Washington, DC 20590

May 29, 2019

Mr. Kevin Skerrett
Senior Regulatory Specialist
UL Supply Chain & Sustainability
23 British American Boulevard
Latham, NY 12110

Reference No. 16-0116

Dear Mr. Skerrett:

This letter is in response to your June 29, 2016, email and subsequent telephone conversation with a member of my staff requesting clarification of the Hazardous Materials Regulations (HMR; 49 CFR Parts 171-180) applicable to methanol solutions when shipped domestically and internationally.

In your email, you note that methanol has two entries in the Hazardous Materials Table (HMT):

- The first entry describes methanol as a Class 3, PG II material. The letter “D” in Column 1 of the HMT identifies this material as being suitable for domestic transportation.
- The second entry describes methanol as a Class 3, (6.1), PG II material. Column 1 of the HMT depicts both the letter “I” and the “plus” (+) sign. The letter “I” identifies proper shipping names appropriate for describing materials in international transportation. The (+) sign fixes the proper shipping name, hazard class, and packing group for that entry without regard to whether the material meets the definition of that class, packing group, or any other hazard class definition.

You ask a series of questions related to the applicability of the Division 6.1 (Toxic) subsidiary hazard to methanol. Your questions are paraphrased and answered below:

- Q1. You ask whether human health experience takes precedent over the classification criteria determined by animal testing presented in § 173.132(a)(1) through (c).
- A1. The answer is yes. Animal testing data obtained in accordance with § 173.132 may be used when there is an absence of data on human toxicity. For the purposes of the HMR, a Division 6.1 (Toxic) material is a material, other than a gas, which is known to be so toxic to humans as to afford a hazard to health during transportation, or which, in the absence of adequate data on human toxicity is *presumed* [emphasis added] to be toxic to humans because it falls within any of the categories presented in § 173.132 when tested on laboratory animals.

- Q2. You ask whether the International Maritime Dangerous Goods Code (IMDG Code), the International Civil Aviation Organization Technical Instructions for the Safe Transport of Dangerous Goods by Air (ICAO Technical Instructions), and the United Nations Model Regulations on the Transport of Dangerous Goods (UN Model Regulations) concur with the HMR with respect to the use of human health experience over animal testing data.
- A2. The answer is yes. The IMDG Code in 2.6.2.2.2, the ICAO Technical Instructions in 2.6.2.2.2, and the UN Model Regulations in 2.6.2.2.2 state that in making packing group assignments, account shall be taken of human experience in instances of accidental poisoning and special properties possessed by any individual substance, such as liquid state, high volatility, any special likelihood of penetration, and special biological effects. Paragraph 2.6.2.2.3 of all three standards further states that in the absence of human experience the groupings shall be based on data obtained from animal experiments.
- Q3. You ask whether the statements in § 173.132(a) and 2.6.2.2.2 of the IMDG Code, the ICAO Technical Instructions, and the UN Model Regulations apply only to the listed “pure” material or is it implied for all mixtures and solutions of the material.
- A3. The statements in § 173.132(a) and 2.6.2.2.2 of the IMDG Code, the ICAO Technical Instructions, and the UN Model Regulations regarding the use of human experience is not specific to a listed “pure” material and can be applied to materials listed in the HMT and their solutions.
- Q4. In your email, you note that no experimental oral, dermal, or inhalation human toxicity values exist for methanol. You ask if a shipper can apply animal testing data for a mixture or solution of a listed substance, such as methanol, for which there is no human experience data for a specific concentration.
- A4. It is the shipper’s responsibility to properly classify and describe a hazardous material. The international entry for methanol is assigned a (+) sign in Column 1 of the HMT, and this means that the material is known to pose a risk to humans. The (+) sign no longer needs to be considered when the mixture or solution does not exhibit the same hazard to humans. In this example, the material may be described using an alternative proper shipping name that represents the hazards posed by the material. See § 172.101(b)(1).
- Q5. You ask what constitutes acceptable evidence that a mixture or solution is significantly different or poses no hazard to humans.
- A5. To make that determination, you must identify available human toxicity data for methanol and use that data to determine if a mixture or solution is still toxic. If you find that the hazards to humans are significantly different from that of the pure methanol or

that no hazard to humans is posed, the material may be described using an alternative shipping name that represents the hazards posed by the material.

- Q6. You ask whether § 172.101(b)(1) allows the shipper to omit the Division 6.1 (Toxic) subsidiary hazard or only select an alternative shipping name that describes the material as toxic.
- A6. See A5.
- Q7. You ask whether a shipper must describe a solution that contains methanol and assigned an alternate proper shipping name with a Division 6.1 (Toxic) subsidiary hazard.
- A7. A solution containing methanol must be described by an appropriate proper shipping name from the HMT that reflects the hazards of the solution. If you find that the hazards to humans are significantly different from that of the pure methanol or that no hazard to humans is posed, the material may be described using an alternative shipping name that represents the hazards posed by the material. In this instance, the most appropriate description for the material shall be determined in accordance with § 172.101(c)(10).
- Q8. You ask whether an approval from the Associate Administrator is required to use an alternate proper shipping name.
- A8. The approval from the Associate Administrator to use an alternate proper shipping name is required for instances when a (+) sign is assigned to a mixture or solution according to § 172.101(b)(1). In the case of methanol, the (+) sign is affixed to a pure substance. If you were to dilute that pure substance in a solution to a point at which the hazard to humans is significantly different than the pure substance or where no hazard to humans is posed, the (+) sign would no longer be applied to that material, and the shipper would be required to assign a new proper shipping name to the material based on its current properties and hazard characteristics.
- Q9. You ask whether the answers to A6 through A8 differ if the material is offered for international transport.
- A9. The answer is no. The IMDG Code in 3.1.3, the ICAO Technical Instructions in 3.1.3, and the UN Model Regulations in 3.1.3 state that a mixture or solution is not subject to the regulations if the characteristics, properties, form or physical state of the mixture or solution are such that it does not meet the criteria, including human experience criteria, for inclusion in any class.
- Q10. In your email, you note that in 2003 the United States submitted a proposal to the United Nations Sub-Committee of Experts on the Transport of Dangerous Goods (the Sub-

Committee) to amend the existing entries for methanol to add a PG III entry for methanol and methanol solutions without the Division 6.1 (Toxic) subsidiary hazard. You further noted that this proposal was not adopted because the Sub-Committee determined that the Division 6.1 (Toxic) subsidiary hazard label was justified by human experience not only for the pure substance, but also for dilute solutions. Based on this, you ask whether dilution is an acceptable method to omit the Division 6.1 (Toxic) subsidiary hazard from methanol solutions in international transport.

- A10. The criteria for assigning a UN number and a proper shipping name are outlined in Chapter 2 of the IMDG Code, the ICAO Technical Instructions, and the UN Model Regulations. As described in 2.0.2.6 in both the UN Model Regulations and the IMDG Code (2.0.3.6 in the ICAO Technical Instructions), for a solution or mixture when the hazard class, the physical state or the packing group is changed in comparison with the listed substance, the appropriate n.o.s. entry shall be used including its packaging and labelling provisions. A solution or mixture of methanol may not be subject to the IMDG Code, the ICAO Technical Instructions, or the UN Model Regulations if the characteristics, properties, form or physical state of the mixture or solution are such that it does not meet the criteria, including human experience criteria, for inclusion in any class. The fact that the Sub-Committee did not adopt the 2003 proposal has no impact on how mixtures or solutions should be classified.
- Q11. You ask whether there is a negligible or de minimis concentration of methanol below which the toxic hazard has dropped to a negligible risk.
- A11. There is no definitive concentration that would exempt a mixture or solution containing methanol from the HMR; however, if the concentrations are so low that the material no longer meets the criteria for any hazard class, the material may no longer be considered hazardous. Each mixture or solution must be evaluated in the form it will be shipped to determine whether it should be considered a hazardous material.
- Q12. You ask whether there was any indication from the Sub-Committee, including approval, for calculating or testing to omit the Division 6.1 (Toxic) subsidiary hazard for mixtures or solutions containing methanol.
- A12. The criteria for assigning a UN number and a proper shipping name are outlined in Chapter 2 of the IMDG Code, the ICAO Technical Instructions, and the UN Model Regulations. As described in 2.0.2.6 in both the UN Model Regulations and the IMDG Code (2.0.3.6 in the ICAO Technical Instructions), for a solution or mixture when the hazard class, the physical state or the packing group is changed in comparison with the listed substance, the appropriate n.o.s. entry shall be used including its packaging and labelling provisions. A solution or mixture of methanol may not be subject to the IMDG Code, the ICAO Technical Instructions, or the UN Model Regulations if the

characteristics, properties, form or physical state of the mixture or solution are such that it does not meet the criteria, including human experience criteria, for inclusion in any class.

Q13. You ask whether the Sub-Committee has further discussed the classification of mixtures and solutions of methanol since 2003.

A13. The answer is no. Since 2003 there have been no further discussions specific to the transport of mixtures or solutions of methanol.

Q14. You ask whether a shipper can use calculations and methods authorized by the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

A14. The answer is no. When an entry is assigned a (+) sign in Column 1 of the HMT, the hazard class and packing group are fixed, regardless of whether that material meets the definition of that hazard class, packing group, or any other hazard class definition. For materials not assigned a (+) sign in Column 1 of the HMT, transport classification decisions must utilize the criteria described in § 173.132 of the HMR and Chapter 2 of the IMDG Code, the ICAO Technical Instructions, and the UN Model Regulations.

Q15. Paragraph 2.2.61.1.14 of the European Agreement Concerning the International Carriage of Dangerous Goods by Road (ADR) includes a provision that exempts certain substances, mixtures and solutions from consideration as a Division 6.1 (Toxic) material. You ask whether this rationale is appropriate for the classification of methanol mixtures or solutions.

A15. Paragraph 2.2.61.1.14 of the ADR references two European Council directives. It is the opinion of this Office that provided those directives specifically address methanol mixtures and solutions it may be appropriate to utilize these directives in making classification decisions for transport between ADR contracting parties. However, the U.S. is not a contracting party to the ADR and we recommend directing this question to an appropriate ADR contracting party. A List of Competent Authorities for the application of ADR is available through the following URL:
http://www.unece.org/trans/danger/publi/adr/country-info_e.html (last visited May 16, 2019).

Q16. You ask whether there have been any proposals to provide a similar reference in the GHS or the UN Model Regulations.

A16. We are not aware of any proposals to extend references to these European Council Directives to the GHS or the UN Model Regulations.

- Q17. In letter of interpretation (LOI) 04-0204 PHMSA agreed that the concentration of methanol in various mixtures described in LOI 04-0134 was sufficiently diluted such that the mixture posed no toxicity hazard to humans. You ask what was the methanol concentration in the product discussed in LOI 04-0134.
- A17. The product described in LOI 04-0134 contains various concentrations of hydrogen peroxide (20% – 39%), methanol (4% – 13%), and water (48% – 76%).
- Q18. You ask what was the rationale for agreeing that the mixture described in LOI 04-0134 did not pose a hazard to humans.
- A18. The review of the mixtures described in LOI 04-0134 (i.e., that they did not pose a hazard to humans) was based on our assessment of the information provided for that product at that time.

I hope this information is helpful. If you have further questions, please do not hesitate to contact this office.

Sincerely,

A handwritten signature in black ink, appearing to read "S.C. Kelley", with a long, sweeping horizontal line extending to the right.

Shane C. Kelley
Director,
Standards and Rulemaking Division

Goodall, Shante CTR (PHMSA)

Alary
173.132
Class 6 Definition
16-0116

From: Rivera, Jordan CTR (PHMSA)
Sent: Wednesday, June 29, 2016 5:20 PM
To: Hazmat Interps
Subject: FW: PHMSA Interpretation request - International classification of methanol mixtures

Hi Shante/Alice,

Please submit this as a letter of interpretation. Mr. Skerrett has spoken multiple individuals in the Info Center on this issue.

Please let me know if you have any questions.

Thanks,
Jordan

From: Skerrett, Kevin [mailto:Kevin.Skerrett@ul.com]
Sent: Wednesday, June 29, 2016 3:41 PM
To: PHMSA HM InfoCenter
Subject: PHMSA Interpretation request - International classification of methanol mixtures

We are looking for some guidelines regarding the dilution of the toxicity of methanol for dilutions and solutions shipped internationally.

Since we currently have reviews on hold for these issues, which can block shipping of product, we would like to request an informal response (by phone or email) as quickly as possible, followed by a formal letter of interpretation in your normal timeframe.

We review supplier classifications for the benefit of downstream users, and this issue has been increasingly difficult to deal with.

Suppliers provide a variety of rationales for why their product dilution does not require the 6.1 subsidiary hazard for methanol shipped internationally.

We want to know which of these are acceptable, and whether acceptability requires an approval or other authorization from a Competent Authority (CA), such as PHMSA, or if the supplier's professional judgment alone is sufficient.

The problem is the "human experience" indicated for methanol by the "plus sign" in column A (DOT), Special Provision A113 (ICAO/IATA) and Special Provision 279 (IMDG and UN Model Regs).

173.132 (a) appears to indicate that human health experience is precedent over the LD50 calculations presented in the rest of 173.132 – but provides no means of calculating packing group, or dilution of the hazard to a non-regulated level, when "human experience" is involved.

This is a problem for all 20+ materials carrying this indication, but methanol is particularly a concern, since:

- 1) DOT allows a domestic alternative that does NOT include the 6.1 subsidiary hazard
- 2) Methanol is very common in many consumer and retail products, in a wide variety of concentrations.

We are primarily interested in the international shipment methanol, but if the answers to any of the questions below would differ for methanol relative to the other "human experience" case, please do indicate that if possible.

Below are the questions we believe would help us understand this better:

- A) 173.132 (a) indicates that 6.1 applies to a material "...which is known to be so toxic to humans as to afford a hazard to health during transportation, or which, in the absence of adequate data on human toxicity:", it then provides the LD50 definitions and calculations.
- This appears to indicate that human health experience is precedent over the LD50 calculations presented in the rest of 173.132 - is that correct?
 - Do the international regs (specifically IMDG and ICAO and TDG) have this same understanding?
 - Does this only apply to the listed (pure) material, or is it implied for all dilutions and solutions of it?
 - Suppliers correctly point out that there is no human LD50 data for methanol - nor should there be. For a solution of a material listed by its technical name (like methanol), if there is no human experience data for the specific concentration, can the animal LD50 calculations then be applied?
 - It is clear that in the absence of human experience, no approval by PHMSA or other CA is required for a shipper to apply the LD50 calculations. Is that still true if "human experience" is involved? Can a LD50 rationale be allowed without approval, or only with it?
- B) 172.101 (b)(1) defines the "plus sign" in Column A of the 172.101 table. It is clear that this locks in the classification for the listed material – but less clear for dilutions and other solutions. It indicates "When a plus sign is assigned to mixtures or solutions containing a material where the hazard to humans is significantly different from that of the pure material or where no hazard to humans is posed, the material may be described using an alternative shipping name that represents the hazards posed by the material. An appropriate alternate proper shipping name and hazard class may be authorized by the Associate Administrator."
- What is considered acceptable evidence that the hazard to humans is "significantly different" or "no hazard"? No guidance for this appears in 173.132.
 - This appears to allow dropping the 6.1 subsidiary hazard, as opposed to just selecting an alternate name that continues to carry the 6.1 hazard – is that correct?
 - Suppliers have told us that this (the plus sign) does not apply if a different UN# must be selected based on other hazards the material presents – is this correct? Or does the 6.1 carry through unless specifically addressed?
 - Is an approval or authorization by the Associate Administrator required for use of an alternate shipping name? The word "may" makes this appear optional, and thus not necessary for the supplier to pursue.
 - Do the answers to these questions differ for international shipment vs. domestic?
- C) On 14 April 2003 the expert from the US submitted to the UN a request (ST/SG/AC.10/C.3/2003/23) to add, internationally, a Methanol PG III listing that would drop the 6.1 subsidiary hazard based on dilution. The UN response (ST/SG/AC.10/C.3/46 of 16 July 2003) indicated, in part, "76. Many experts said that they could not support the proposal because it was well known that methanol was responsible for numerous deaths due to ingestion of adulterated alcohol and therefore they considered that the Division 6.1 label was justified by human experience not only for pure methanol but also its solutions." The US expert then withdrew the proposal.
- This appears to indicate that the international community does not consider dilution to be acceptable for dropping the 6.1 subsidiary, at least not without an approval – is that correct?
 - "Common sense" is often quoted by suppliers as a rationale for declassification by dilution – is there at least a "deminimis" threshold below which the international experts agree that the hazard has dropped to negligible risk?
 - In these negotiations, was ANY route, including approval, indicated for calculating or testing to a reduction of the 6.1 hazard?
 - Has anything further occurred along these lines with the UN?
- D) GHS calculations are increasingly used as justification for dropping the 6.1 subsidiary hazard for methanol solutions – including aspects that are not in the HMR. Can these be used, or only with approval, or not at all?
- Since Rat LD50 values might not reflect human toxicity, ATE values are drawn from Table 3.1.1 (GHS 5th ed.) and then used in the calculations. It is felt that this would address human toxicity, since the 6.1 would be assigned based on "human toxicity" – effectively a stand-in for "human LD50". Analogy is made between GHS Category 3 and HMR PG III, and so then Category 3 ATEs are used to calculate the solution's LD50 and this is used to determine PG. Is this an acceptable approach? With or without approval?
 - Given methanol's flashpoint (12°C) and the precedence table (173.2(b)), it is possible that the toxicity of methanol could have been assigned as PG II – we cannot tell on what basis the 6.1 was assigned to Methanol – could the Category 2 ATEs be used as a "worst case" calculation instead?

- c. GHS (5th ed.) includes 3.1.3.6.2.1(b), which appears to specifically address the “human toxicity” issue. It specifies that the tox roll-up calculation (similar to 173.132(c)(3) may use ATEs in cases when: “(b) Evidence from human exposure that indicates toxic effects but does not provide lethal dose data”. Does this provide an acceptable rationale for transport classification by ATEs? Is this under consideration for the HMR or other transport regs?
- E) ADR (and RID and ADN) include a clause in their 6.1 classification sections as 2.2.61.1.14 that addresses using the EU DSD and DPD classifications in transport: “Substances, solutions and mixtures, with the exception of substances and preparations used as pesticides, which do not meet the criteria of Directives 67/548/EEC3 or 1999/45/EC4 as amended and which are not therefore classified as highly toxic, toxic or harmful according to these directives, as amended, may be considered as substances not belonging to Class 6.1.”
 - a. This appears to be specific to EU regs, and I do not find similar wording elsewhere. Is this a valid rationale for declassifying 6.1 for methanol mixtures?
 - b. Has there been any discussion of extending this to GHS and the UN Model regs?
- F) PHMSA interpretation 04-0204 appears to be an example of PHMSA agreeing with the dropping of the 6.1 subsidiary for methanol for international shipment based on dilution.
 - a. No concentrations were given – were these available on the original request (04-0134)? I could not find a copy of that.
 - b. No rationale or calculation was given by the requestor or by PHMSA – was any determined, and could this be the basis of guidance?

I apologize for the degree of detail, but these are all rationales that we have been presented with.

After verbal discussion with the HMIC, our understanding was that an approval or authorization would be necessary for any of the above – but we would be happy to be wrong about that!

Although we recognize that a receiver is entitled to reship material as received from a supplier per 171.2(b), as long as there is no reason to believe it is incorrect, we believe that due diligence regarding this issue requires that it be clarified.

I can be reached by cellphone at (518) 229-7302 or by email at kevin.skerrett@ul.com

Thank you very much for your attention to this request!

Kevin Skerrett

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