

# Hydrogen Sulphide (H<sub>2</sub>S) in Petroleum Crude Oil

## Background

In light of the results obtained during the Transport Canada 2014-2015 crude oil sampling and testing campaign, Transport Canada (TC) is proposing to amend the *Transportation of Dangerous Goods Regulations* (TDG Regulations) to address safety hazards related to the high levels of H<sub>2</sub>S in petroleum crude oil transported in Canada.

Hydrogen sulphide is a colourless natural gas found in some petroleum crude oils. It is heavier than air, toxic, corrosive, flammable, explosive, and toxic when inhaled. According to the TDG Regulations, crude oil containing high levels of H<sub>2</sub>S can be classified as UN3494, PETROLEUM CRUDE OIL, FLAMMABLE, TOXIC (Class 3 with a subsidiary Class 6.1) and require consignors to include the words "toxic by inhalation" or "toxic-inhalation hazard" on a large means of containment, next to the placard; and on the shipping document. However, this UN number is not used by industry since there exists no threshold level for using UN3494, PETROLEUM CRUDE OIL, FLAMMABLE, TOXIC (added to the *Recommendations on the transportation of dangerous goods - Model Regulations* in 2008 and the 49 CFR in 2012) versus UN1267, PETROLEUM CRUDE OIL. This is mainly because there are no established field test methods to accurately determine H<sub>2</sub>S level in the vapour phase. However, there are existing laboratory-based test methods to measure H<sub>2</sub>S levels in the liquid phase, which can then be used to estimate the vapour phase concentration by applying partition coefficients. Test methods used for monitoring H<sub>2</sub>S vapour in the workplace exist but, when used for field testing, can lead to widely variable and therefore unreliable results.

At the Spring 2016 General Policy Advisory Council meeting, industry was made aware of a regulatory amendment proposing H<sub>2</sub>S thresholds of 2 ppm in the liquid phase for the identification of a toxic by inhalation hazard and 5 ppm in the liquid phase for the assignment of UN3494, PETROLEUM CRUDE OIL, FLAMMABLE, TOXIC. The proposal was shared via email for their review and comments. TC also held discussions with a first group of stakeholders because of the potential impacts on road and rail transport.

One comment received indicated that the 2 ppm and 5 ppm threshold levels for H<sub>2</sub>S in the liquid phase were too low and suggested a level greater than 100 ppm in the liquid phase as an appropriate cut-off mark for crude oil to be classified as UN3494, PETROLEUM CRUDE OIL, FLAMMABLE, TOXIC.

A second comment stated that distinct requirements to classify crude oil (UN1267, PETROLEUM CRUDE OIL with inhalation hazard marking for crude containing between 2ppm and 5 ppm of H<sub>2</sub>S in the liquid phase and UN3494, PETROLEUM CRUDE OIL, FLAMMABLE, TOXIC for concentrations over 5 ppm) would create confusion among first responders when viewing dangerous goods safety marks from a distance.

A third comment stressed the importance of ensuring regulatory alignment with the United States, in particular harmonization related to classification requirements, tank car schedules, and TDG regulations.

Additionally, based on a recommendation made during a recent Canadian Standards Association CSA B620 (highway tanks) committee meeting, it was proposed that UN3494, PETROLEUM CRUDE OIL, FLAMMABLE, TOXIC should be transported in TC 407 (25 psi) highway tanks and that establishing a reasonable threshold for using UN3494, PETROLEUM CRUDE OIL, FLAMMABLE, TOXIC should not be overly onerous to industry given the availability of TC 407 (25 psi) highway tanks.

## Analysis/ Considerations

- Pursuant to the TDG Regulations, a mixture is a dangerous good when it meets the criteria for inclusion in at least one of the nine classes of dangerous goods. The nine classes represent the physical hazards posed by the dangerous good as they are offered for transport – these hazards are posed by the dangerous good as prepared for transport and during transport. The system of classes exists to direct the type of packaging to be used in containing the hazard, to give information on the physical and chemical characteristics of the substances, and to guide first responders on the response procedures that would be most appropriate in the event of a release.

- Commonly, petroleum crude oil meets the criteria to be included in Class 3, Flammable Liquids and, in some cases, Class 6.1, Toxic Substances. A mixture of petroleum crude oil is included in Class 6.1, Toxic Substances if it is liable either to cause death or serious injury or to harm human health when inhaled.
- For the classification of petroleum crude oil, account is taken of human experience in instances of accidental intoxication and of special properties possessed by any individual substance in a mixture such as high volatility and special biological effects when assessing the toxicity of a dangerous goods. For example, methanol, phenol and thiophosgene are toxic substances due to human experience even if they do not meet the criteria (based on lethal concentration  $LC_{50}$ ) for inclusion in Class 6.1.
- Given that the  $H_2S$  contained in petroleum crude oil is a toxic substance and that the vapour phase concentration of  $H_2S$  as measured in the petroleum crude oil samples obtained from the Crude Oil Sampling and Testing campaign ranged from 0 to 65,000 ppm in the vapour phase, TC deems it necessary to address these safety considerations and hazards.
- Specifically, of the 68 samples tested, 33 had  $H_2S$  values in the vapour phase that were below 100 ppm in the vapour phase, and 35 had  $H_2S$  values in the vapour phase that were above 100 ppm in the vapour phase. Of particular importance, 31 of the samples taken had values that were above 500 ppm in the vapour phase. It is important to note that exposure to levels of 100 ppm or more in the vapour phase are considered immediately dangerous to life and health (IDLH), and exposure above 500 ppm in the vapour phase is lethal.
- Exposure to  $H_2S$  remains a concern since human experience has shown that workers, especially truck drivers, have become unconscious after inhaling  $H_2S$ . Occupational data received from the Association of Worker Compensation Boards of Canada (2008-2014) and various provincial worker Compensation Boards (ranging from 2004-2015) have demonstrated a higher number of reported work place incidents in the transport sector than in most other sectors (although not a higher number of deaths, which are rare in all sectors).
- In light of consultations over summer 2016, the current proposal has been revised with a threshold of 10 ppm in the liquid phase for UN3494, PETROLEUM CRUDE OIL, FLAMMABLE, TOXIC. Given that the partition coefficient between  $H_2S$  in the liquid phase to  $H_2S$  in the vapour phase is not a precise measure, pending the development of an accurate field tester, a threshold of 10 ppm in the liquid phase may be relatively high (corresponding to concentrations of 500 – 3000 ppm in the vapour phase). However, this proposed liquid phase threshold of 10 ppm in the context of exposure in transportation is considered a reasonable precautionary measure given the analysis of data from the 2014 Sampling and Testing Campaign.
  - Future studies will continue to examine the presence and behaviour of  $H_2S$  in crude oils. TC is also currently working with the Canadian Crude Quality Technical Association to develop a more accurate and robust test method for  $H_2S$  in the vapour phase. Once this is developed, TC would be able to establish a more definitive threshold level of  $H_2S$  to classify crude oils as UN 3494, PETROLEUM CRUDE OIL, FLAMMABLE, TOXIC based on a standardized test method.
- Based on current data, TC estimates that approximately 25% to 45% of the crude oil samples would be classified as UN3494, PETROLEUM CRUDE OIL, FLAMMABLE, TOXIC if a 10 ppm liquid phase threshold level for  $H_2S$  is implemented.

## **Recommendation**

It is proposed to adopt these proposed regulatory requirements:

### Threshold levels:

TC proposes that:

- 1) Petroleum crude oils that have an H<sub>2</sub>S concentration of 10 ppm or above in the liquid phase be classified as UN3494, PETROLEUM SOUR CRUDE OIL, FLAMMABLE, TOXIC, which is a Class 3, subclass 6.1 dangerous goods.
- 2) Crude oils that have an H<sub>2</sub>S concentration below 10 ppm in the liquid phase be classified as UN1267, PETROLEUM CRUDE OIL, which is a Class 3 dangerous goods.

#### Tank car selection:

It is proposed that assigning UN3494, PETROLEUM SOUR CRUDE OIL, FLAMMABLE, TOXIC to petroleum crude oil with high H<sub>2</sub>S content would trigger different tank car selection and use requirements and would require an exemption from pressure tank car requirements. In other words, an amendment is required to specify the use of a TC 117 tank car when crude oil is classified as UN3494, PETROLEUM SOUR CRUDE OIL, FLAMMABLE, TOXIC. Crude oil classified as UN 1267, PETROLEUM CRUDE OIL, under this proposal would permit the use of CPC 1232 (non-jacketed and jacketed) tank cars until these are eliminated based on the current phase-out schedule. For more details please see the Protective Direction 38 ( <http://www.tc.gc.ca/eng/tdg/safety-menu-1289.html> ) and the Regulations Amending the Transportation of Dangerous Goods Regulations (TC 117 Tank Cars) SOR/2015-100 (<http://www.tc.gc.ca/eng/tdg/clear-modifications-adopted-90.htm>).

#### Highway tank selection:

The CSA B620 committee has recommended that UN3494, PETROLEUM SOUR CRUDE OIL, FLAMMABLE, TOXIC be transported in TC 407 (25 psi) highway tanks, regardless of the packing group. TC supports this recommendation. In the interim, an exemption to Section 5.14 (1) (a) (ii) of the *Transportation of Dangerous Goods Regulations* specifying the exclusive use of a TC 407 highway tank (25 psi) would need to be introduced. The current standard requires a TC 407 highway tank (40 psi) for UN3494, PETROLEUM SOUR CRUDE OIL, FLAMMABLE, TOXIC of Packing Group I, but this tank is not currently available in sufficient numbers nor widely used by industry.