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Item 7 of the provisional agenda
Future work

Transport of ammonia solutions in IBCs

Transmitted by the Government of Belgium[1], [2]

Summary

Executive summary: to review	The aim of this proposal is to create an informal working group the transport of ammonia solutions in IBCs
Action to be taken:	Endorse the creation of an informal working group
Related documents:	Informal document INF.34 March 2009 (Portugal) Informal document INF.15 September 2009 (United Kingdom) ECE/TRANS/WP.15/AC.1/2010/24 (United Kingdom) Informal document INF.29 March 2010 (Belgium) Informal document INF.31 March 2010 (Portugal) Multilateral Agreement M256 Informal document INF.21 September 2013 (Belgium) Informal document INF.42 September 2013 (EuPC) ECE/TRANS/WP.15/AC.1/132, para. 113-114

[1] In accordance with the programme of work of the Inland Transport Committee for 2012–2016 (ECE/TRANS/224, para. 94, ECE/TRANS/2012/12, programme activity 02.7 (A1c)).
[2] Circulated by the Intergovernmental Organisation for International Carriage by Rail (OTIF) under the symbol OTIF/RID/RC/2014/2.

Background and history

1. In 1999, Norway and Sweden jointly proposed to the United Nations Sub-Committee of Experts on the Transport of Dangerous Goods that the special nature of ammonia (i.e. a PG III substance with a very high vapour pressure) should have special recognition to permit its carriage in IBCs. This was reflected in special packing provision B11 of Packing Instruction IBC03 in the United Nations Model Regulations which states:

"B11 Notwithstanding the provisions of 4.1.1.10, UN 2672 ammonia solution in concentrations not exceeding 25% may be transported in rigid or composite plastics IBCs (31H1, 31H2 and 31HZ1).".

It should also be noted that this provision has been adopted by the International Maritime Organization (IMO) in the IMDG Code.

2. It was because the Joint Meeting did not agree to incorporate this special packing provision into RID/ADR at that time that first Sweden (in its Multilateral Agreement M98) and then the United Kingdom (in its Multilateral Agreements M 138 and more recently M 256) took steps to permit such carriage between their countries and other Contracting Parties. The United Kingdom went further by proposing that the ammonia solution concentration permitted in IBCs could be increased to 35%.

3. The method used in the United Kingdom to ensure that no excessive pressures are generated, is to utilise a "pressure relief" vent in the headspace of the IBC, to allow over pressure to be relieved to atmosphere. The transport of these IBCs is also limited to open or curtain-sided vehicles.

4. In its informal document INF.34 of March 2009, Portugal referred to ADR provision 4.1.4.2 in the section on IBC packing instructions concerning the use of IBCs and further informed the Joint Meeting that solutions of ammonia in excess of 20% do not comply with 4.1.4.2. INF.31 by Portugal of the March 2010 session of the Joint Meeting further commented on the proposals set out in document 2010/24 by the United Kingdom, containing a tiered approach to allow up to 25% in sheeted vehicles and up to 35% in vented IBCs. In the arguments raised by Portugal, the ammonia toxicity and pressure resistance levels of the IBCs spoke strongly against the simple adoption of a special packing provision for concentrations up to 35%. Ultimately, the United Kingdom was invited to come back with a new proposal.

5. Currently, M 256, containing a derogation from section 4.1.1.10, IBC 03, permits ammonia solutions up to 35% in rigid or composite plastics IBCs of types 31H1, 31H2 and 31HZ1 but requires the fulfilment of 4.1.1.8. It is signed by the United Kingdom, Ireland and … Portugal.

***NOTE**: Sub-Section 4.1.1.8 allows packages, including IBCs, to be fitted with a vent where pressure may develop by the emission of gas from the contents. It also requires that the gas emitted will not cause danger on account of its toxicity, flammability or quantity released.*

Property analysis of ammonia solutions

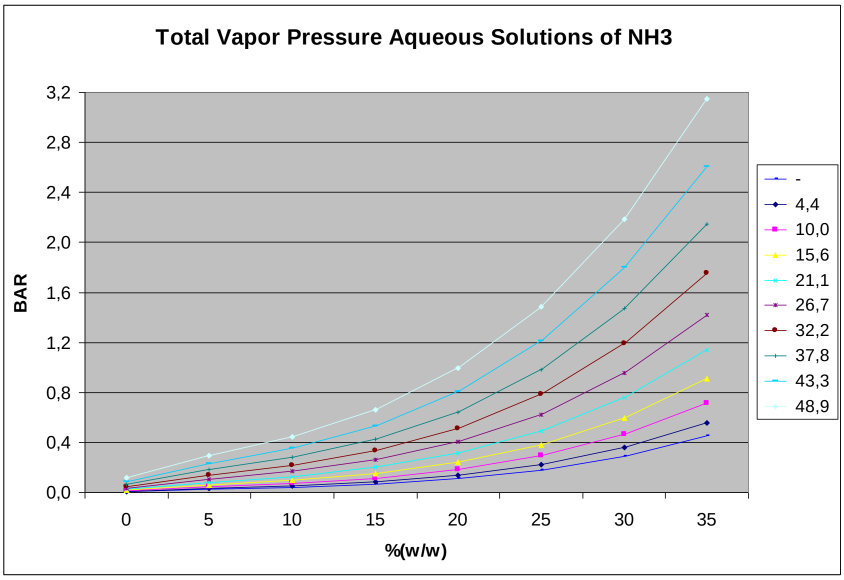
6. The current requirements in 6.5.6.8.4.2 regarding the hydraulic pressure test for commonly used composite IBCs (31H1, 31H2, 31HZ1, 31HZ2) define a test pressure equal to the substance vapour pressure taken at a reference temperature of 50°C or 55°C and multiplied by a safety factor of 1.75 or 1.5 respectively or twice the static pressure of the substance depending on which is the highest value. From these requirements we choose to evaluate the properties of various concentrations of ammonia solutions at 50°C, which also represents a realistic maximum surface temperature under sunny conditions (e.g. sun

impacting on metal container). The obtained partial and total vapour pressures via linear interpolation of the data shown in the graphs below, yield the following results:

NH_3%	NH_3 Vapour Pressure at 50°C
25%	154 kPa (1.54 bar)
35%	325 kPa (3.25 bar)

7. As a general remark it can be noted that the partial vapour pressure of water can be neglected in comparison with the ammonia vapour pressure at the considered temperatures up to 50°C. From the graphical and numerical analysis of the shown vapour pressure curves it is shown that ammonia solutions show a vapour pressure at 50°C which is higher then atmospheric pressure starting from concentrations between 18% and 20% depending on the data source and which "atmospheric pressure" was used (e.g. 1 atm = 101,325 kPa at sea level, 100 kPa IUPAC standard pressure,…). In the experimental data below, a concentration of 19,6% was calculated to give rise to a pressure exceeding 1 atm at 50°C.At the proposed concentrations of 25% or 35%, the vapour pressures exceed 1.5 bar and 3.2 bar respectively.

8. In further analysis, the experimentally obtained values for the ammonia-water solutions, contributed by an industrial partner, shown below, are used. These results were validated by comparison to commonly used literature data (e.g. Kemira, Kirk-Othmer, Perry & Green).



Property analysis of investigated light-weight composite IBCs

9. Based on the property analysis described above and the requirements set out in 6.5.6.8.4.2, the hydraulic test pressure of the referenced composite IBCs should be:

NH_3%	Hydraulic test pressure under 6.5.6.8.4.2 b) ii)
25%	154 kPa x 1.75 – 100 kPa = 170 kPa
35%	325 kPa x 1.75 – 100 kPa = 469 kPa

10. Sample IBCs from major European manufacturers currently used for aqueous ammonia solutions (up to 25%) were investigated. The investigated IBCs' approval certificates showed that the maximum allowed hydraulic pressures were assessed to be

around 115 kPa at 50°C, indicating that these IBCs may only be used for ammonia solution concentrations up to around 21%. The investigated IBCs were equipped with a venting device set at 110 kPa.

Scenario analysis

11. It is stated in document ECE/TRANS/WP.15/AC.1/2010/24 that “from assessments carried out in the United Kingdom, it has been concluded that the ammonia solution satisfies the requirement of 4.1.1.8”. How this assessment has been carried out however, is not detailed in the document. This section aims at describing a realistic transport scenario, indicating all of the assumptions made, to assess the fulfilment of 4.1.1.8 for two cases: a 25% and a 35% ammonia solution in the above investigated IBCs. The input data shown was taken from a real life scenario and provided by an industrial partner.

Boundary conditions

1. 40 ft container with volume 67,5 m³
2. 31 IBCs in container (maximum container load 26,68 ton)
3. 1m³ nominal capacity IBCs
4. IBC’s filled 88% (volume) at 15°C (maximum gross mass/IBC = 860 kg)
5. container is hermetically closed
6. temperature inside container is 50°C
7. PRV blow-off pressure 110 kPa
8. neglect H_2O partial vapour pressures at $T \leq 50°C$
9. Ideal gas law applies to ammonia vapour

12. Assumption 5 signifies a worst-case scenario (e.g. current containerized maritime transport of 25% concentrations), assumption 8 simplifies calculations and does not change the order of magnitude of the results.

Analysis

13. Starting at a given temperature Tx < 50°C, the ammonia vapour pressure in the IBCs will surpass the PRV set pressure and blow-off will occur. This will continue until the concentration of ammonia has decreased sufficiently to reduce the vapour pressure in the head space of the IBCs. Between Tx and 50°C, a continued process will occur where the temperature increase gives rise in an increase in ammonia vapour pressure, which leads in turn to blow-off and reduction of the ammonia concentration in the IBC. The speed of this process depends on the rate of heat input which augments the temperature inside the container. This speed was not calculated as the analysis is carried out between 2 steady state situations, one where T =15°C (< Tx) and one where T = 50°C (the speed could be modelled by using solar heat gain values from literature and calculating the thermal mass of the container).

14. At 50°C, an NH_3 concentration of 20,9% gives a vapour pressure of 110 kPa. Between steady state 1 and 2, the NH_3 concentration in the IBC will decrease from its initial value to this 20,9%, yielding the following results per IBC:

	25% NH3 solution	35% NH3 solution
Tx (°C)	40,6	20,1
density (15°C) (kg/m³)	910,8	880,0
net mass/IBC (15°C) (kg)	801,5	774,4
net mass NH_3/IBC (kg)	200,4	271,0
Δmass (x->20,9%) (50°C) (kg)	42,8	138,0

(density 20,9% NH_3 solution (50°C) = 847,9 kg/m³)

15. Considering that 31 IBCs occupy the container and that the container is assumed to be hermetically closed, the total quantity of released ammonia gas greatly (by several orders of magnitude) exceeds any referenced toxicity threshold (e.g. NIOSH IDLH level 300 ppm, AEGL-3 (10min lethal) level 2700 ppm). This effect is even more pronounced for 35% solutions, where the sharp increase in ammonia vapour pressure at 50°C is observed compared to lower temperatures.

Discussion

16. The above (worst case) analysis indicates that any ammonia solution with a concentration above 20,9% does not respect the requirements set out in 4.1.4.2, and without specific measures (e.g. mechanical ventilation) it is difficult to meet the criteria of 4.1.1.8. In addition, none of the investigated IBCs respected the hydraulic pressure requirements of 6.5.6.8.4.2 (and related requirements such as 4.1.1.21.2). According to 6.5.6.8.2, a PRV does not allow for a reduction of the hydraulic test pressure as all PRV must be removed and all openings closed prior to this test. The current multilateral agreement M 256 however, only gives a derogation from 4.1.1.10 for the use of these IBCs for certain liquids and not the testing requirements, nor does it describe any measures of how to fulfil 4.1.1.8 in practice (4.1.1.8 does not contain minimum quantities but contains a general safety requirement).

17. The multilateral agreement in question has been renewed several times. Paragraph 1.5.1.1 contains the idea that multilateral agreements are temporary in nature and do not compromise safety. At the same time, multilateral agreements should not create possible distortion in competition between industry players based on local justifications (e.g. standing practice or different climate conditions) since the ADR/RID is based on a common set of safety cut-off values which were the subject of a compromise.

18. Finally, the United Kingdom Chemical Business Association (CBA) mentions in its 2012 justification paper (see annex I in informal document INF.21 submitted at the autumn 2013 session).

"Clearly the three countries who are MLA signatories are working within the requirements but CBA are convinced in many other countries they apply the MLA without being a signatory, with or without the consent of their competent authorities."

19. Belgium has for this reason conducted the investigation as set out in this document, together with its concerned national industry. Discussions and differing interpretations will still exist among competent authorities and industry how best to proceed forward towards a long term solution. For this reason Belgium welcomes the work launched by CBA to form a specific working group, as announced in its spring 2013 Outlook publication (see annex II in informal document INF.21 submitted at the autumn 2013 session), but considers this as work to be undertaken jointly with competent authorities.

20. As a consequence, at the autumn 2013 session, Belgium proposed in informal document INF.21 to establish an informal working group. This proposal was supported by the European Plastics Converters (EuPC) in informal document INF.42 as follows:

> "EuPC studied INF 21 very carefully and wishes to thank Belgium for the detailed information about this issue. Of particular interest is the accurate description of the history since 1999 together with the conclusion that after almost 15 years there is no satisfactory solution for the transport of ammonia solutions in IBCs.
>
> EuPC supports the proposal by Belgium to create a special Working Group within the Joint Meeting and to give the Working Group the mandate to investigate all

questions referring to this issue with the aim to develop proposals for a fundamental solution.

EuPC as representative of the manufacturers of rigid plastics and composite IBCs with plastics inner receptacle in Europe would like to contribute to a long-term result by giving its input to the Working Group and herewith asks to be invited to the meetings of the Working Group.”.

21. During the session, it was recalled that special provision B11 to packing instruction IBC 03 allowing the carriage of ammonia solution in concentrations not exceeding 25% in rigid or composite IBCs contained in the United Nations Model Regulations was not included in RID/ADR/ADN and that such transport was permitted only by road under ADR multilateral agreement M256 on the territory of three countries. Some delegations were not in favour of reopening the discussion on that subject.

22. The representative of Belgium said that the proposal to set up an informal working group was aimed not at drawing up an amendment, but rather at investigating the issue and checking current practices in the industry. He was asked to formulate his proposal for an informal working group in an official document for the next session so that delegations would have time to consult the parties concerned (see ECE/TRANS/WP.15/AC.1/132, paras. 113-114). Therefore the Government of Belgium reiterates its proposal below.

Proposal

23. Support the creation of a specific working group within the Joint Meeting to investigate the use of IBCs for higher concentrations of ammonia solutions with at least the following items in its mandate:

(1) Investigate ammonia solutions in rigid plastic and composite IBCs up to 25%.

(2) Investigate ammonia solutions in rigid plastic and composite IBCs up to 35%.

(3) Evaluate current requirements and requirements in M 256 with regards to 4.1.1.8, 4.1.1.10, general packing provisions and (rigid plastic and composite) IBC construction and test requirements.

(4) Review current industrial best practices in various countries.

(5) Report findings back to the Joint Meeting and formulate proposals for amendment to the regulations if deemed appropriate.