Economic Commission for Europe

Inland Transport Committee

Working Party on the Transport of Dangerous Goods **30 August 2013**

Joint Meeting of the RID Committee of Experts and the Working Party on the Transport of Dangerous Goods

Geneva, 17-27 September 2013
Item 9 of the provisional agenda
Future work

Transport of ammonia solutions in IBCs

Transmitted by the Government of Belgium

Summary

Executive summary:	The aim of this proposal is to create a working group to review the transport of ammonia solutions in IBCs
Action to be taken:	Endorse the creation of a working group
Related documents:	INF.34 March 2009 (Portugal) INF.15 September 2009 (UK) ECE/TRANS/WP.15/AC.1/2010/24 (UK) INF.29 March 2010 (Belgium) INF.31 March 2010 (Portugal) Multilateral Agreement M256

Background and history

1. In 1999, Norway and Sweden jointly proposed to the UN 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 UN 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 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 UK, 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 UK 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 UK, 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

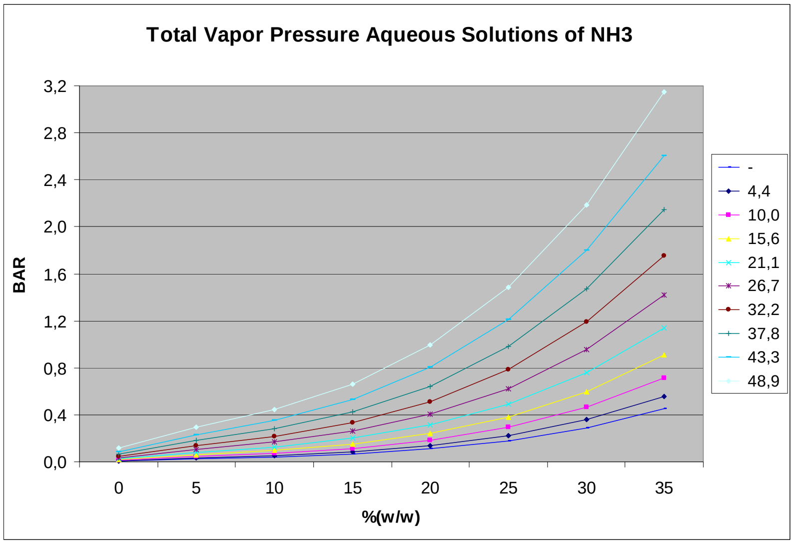
6. The current requirements in 6.5.6.8.4.2 regarding the hydraulic pressure test for commonly used composite IBCs (31H1, 31H2, 31HZ1, 31HZ2) define a test pressure equal to the substance vapour pressure taken at a reference temperature of 50°C or 55°C and multiplied by a safety factor of 1.75 or 1.5 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).



Experimental data (P,x) measured at different temperatures

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≤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 UK Chemical Business Association (CBA) mentions in its 2012 justification paper (see annex I)

"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), but considers this as work to be undertaken jointly with competent authorities.

Proposal

20. 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.

Annex 1: CBA justification paper (2012) - background

Transport of ammonia solution in Intermediate Bulk Containers (IBCs)

1. Introduction

The transport of ammonia solution (UN 2672) in IBCs has been the subject of several multilateral agreements since the year 2000 when agreement M98 was signed, followed by agreement M138 signed in the year 2003 and afterwards by agreement M193, presently in force and valid till 31.01.2013 (signed by United Kingdom, Sweden and Czech Republic).

Ammonia solution has been transported within the UK in excess of three decades with the commercial concentrations required by industry being predominately 20% - 35%. A significant number of customers require the higher concentration solutions (33.5%) to ensure their reaction products achieve the correct chemical species; this cannot be achieved using the lower concentrations. The predominant user of these grades is the pharmaceutical industry.
The data collected from the CBA membership involved in the carriage of ammonia solution indicates that there are in the region of 4,800 IBC deliveries of ammonia solutions per annum, which equates to over 20 IBCs per working day (based on 220 working days). The grades of ammonia solution supplied in the UK are in excess of 20% concentration, predominately 33.5%.
The UK distribution industry is aware that above 20% concentration, the transport of ammonia solution does not respect 4.1.4.2 (packaging instructions concerning the use of IBC's). UK industry approached the UK competent authority in the 1990s, following the decision to align the UK domestic regulations with the provisions of ADR, when this point was raised. The discussions centred on the industry practice that had been performed within the existing UK transport framework for over twenty years, to transport ammonia solutions in excess of 20%.

2. Justification:

The method used within the UK to ensure that IBCs do not generate excessive pressures is two-fold:

I. All IBCs are fitted with a "pressure relief" vent in the headspace of the IBC to allow over pressure to be relieved. ADR 4.1.1.8 allows packages, where pressure may develop by the emission of gas from the contents, to be fitted with a vent. It also requires that the gas emitted will not cause danger on account of its toxicity, flammability or quantity released.

II. The transport of these IBCs is then limited to open or curtain-sided vehicles. To allow any vapour released to dissipate easily, companies routinely install 'spinner vents' into the roof of curtainsided vehicles to increase the airflow during transport and reduce the risks.

Ammonia vapour has:

- an odour threshold of 3 - 5ppm (parts per million);
- an occupational exposure limit of 25ppm TWA (Time Weighted Average); and
- a LDLo (Lethal Dose Low) by inhalation for Humans of 5000ppm.

"The National Institute of Occupational Safety and Health (NIOSH) in America have set an IDLH (Immediately Dangerous to Life or Health) level of 300ppm. Experience has shown that the NIOSH level is not attained utilising UK carriage methodology."

The lower explosive limit (LEL) for ammonia vapour is 16%, (the flammable range of ammonia is 16 to 27% in air) which is also not achievable in practice.
The highest recorded ambient temperature within the UK is 38.5^{o}C, whereas we are aware that Portugal's highest recorded temperature is 46.5^{o}C. The fact that the UK's ambient temperature is below 40^{o}C reduces the vapour pressures actually achieved in comparison to those that might be achieved in southern Europe.
As stated earlier the UK has been using this method in excess of three decades and there have been no recorded incidents using this methodology in that time period.

3. Costs:

Limiting the transportation of ammonia solution greater than 20% to pressure vessels only, would have severe cost implications for the distribution sector and its downstream customers. To purchase suitable IBCs of a pressure rating (200-kPa and 400-kPa) to handle ammonia solutions would be in excess of four (4) million British Pounds. This would be achieved by purchasing two differently rated IBCs each specific to certain grades of ammonia solution.
The cost is derived from the number of IBCs currently in circulation, in the UK, at any one time being:

- 390 IBCs to handle the ammonia solutions 20-25% concentration
  - Quoted cost of approximately £2500 per IBC (2 bar).
- 775 IBCs to handle the ammonia solutions over 25% concentration
  - Quoted cost of approximately £5000 per IBC (4 bar).

Currently some composite IBCs used for ammonia carriage in the UK have an operating company self imposed 2½-year lifespan, after which they are transferred onto "non Hazardous" duty or returned for reconditioning/refurbishment, so these distributors do not currently undertake the periodic ADR testing on these IBCs. Other distributors use more robust IBC designs for the transport of ammonia and undertake the periodic ADR testing requirement to the maximum 5 year life span.
There are also cost implications within the UK relating to the Pressure Systems Safety Regulations (PSSR) 2000. These regulations only apply within the UK and would require these IBCs to be inspected as part of a "written Scheme of Examination" in addition to ADR requirements for periodic testing.

> "The cost of a PSSR inspection is £30 per unit so on the number of IBCs envisaged (1165) this would add another £34,950 to the distribution of ammonia solution in the UK, if tested annually."

The use of the higher ammonia concentrations in downstream customer's production processes is necessary to reduce the need to transport then utilise the potentially more hazardous anhydrous form of ammonia. Many of these industrial sites would need to upgrade storage facilities, install new equipment and implement additional Safety, Health, Environmental and Security requirements. There would be implications, both financial and procedural relating to:

- New or upgraded equipment
- Chapter 1.10 HCDG security plans
  - Customers and distributors
- Seveso II Major Hazards
  - Safe storage and off-site potentials
- Staff training
  - Customers and distributors

4. Existing practice:

CBA is aware that Ammonia solutions are currently being sold in composite IBCs in other European countries, in addition to the three signatories to the existing MLA – Czech Republic, Sweden and the UK;
IBCs of Ammonia solution above 18% are also routinely available in composite IBCs in: Belgium, Germany, France, Hungary, Ireland, Italy, Netherlands, Norway, Poland, Slovakia, Spain and Switzerland.
Over the past three years, volume purchases of the following strengths of solution have been made in the indicated countries:

- Belgium – 24.5%
- France – 20.5%, 25%, 32.5%
- Italy – 20%, 28%, 31%
- Ireland – 33%
- Spain – 25%
- Sweden – 25% (this is within scope of the existing MLA).

The types of IBC used vary significantly, most European countries are using light blow-moulded IBCs – usually with a vented bung fitted into the lid. The UK and Ireland normally use heavier rotationally-moulded composite IBCs or stainless steel IBCs, both fitted with vents in the headspace.
Indicative sales volumes from one organisation are as follows:

Country	2012 Kg	2012 No. of IBCs	2011 Kg	2011 No. of IBCs
France	454,240	497	826,700	904
Ireland	6,020	7	8,600	10
Italy	149,216	164	349,814	384
Netherlands	73,570	104	209,685	290
Norway	0	0	728	1
Spain	24,630	27	16,770	18
Sweden	44,408	61	104,104	143
UK	651,016	723	1,299,569	1,450

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.
There are significant volumes of sales currently throughout the EU, to major downstream using industries such as pharmaceuticals, where the cost of reformulation to use lower strength solutions and / or replacing packaging with pressure rated metallic IBCs will prove burdensome if not prohibitive and for no tangible safety benefit.

Annex II: CBA Outlook publication (Spring 2013 edition) - background

CBA SECURES NEW MULTILATERAL AGREEMENT FOR AMONIA SOLUTION IN IBCs

CBA has secured a new Multilateral Special Agreement (MLA) covering the carriage of ammonia solution (between 18%-35% concentration) in rigid and composite IBCs.

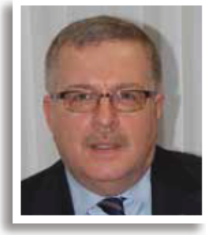
The previous MLA expired on 1 February this year and, without a new agreement in place, this method of delivery – used in the UK for the last 30 years – would have come to an end. In higher concentrations, typically 33.5%, ammonia solution is predominantly used by the pharmaceutical industry.

Data collected by CBA showed that about 4,800 IBC deliveries of ammonia solutions are made each year. Ammonia solution is a high volume product that is important for several CBA member companies.

Under the terms of the ADR Agreement, MLAs have to be agreed by two or more signatory states.

CBA therefore began to work with the UK Department for Transport (DfT) to secure a new MLA and prepared a justification for a new agreement. Once this justification was agreed, DfT officials approached potential signatories for the new MLA. In the event, the Irish Government agreed to be the second signatory and the new MLA was countersigned by the Health and Safety Authority in Ireland.

CBA's Chief Executive, Peter Newport, said, "The new MLA is only valid for five years and will expire in 2018. This may seem to be some time in the future but, as far as international agreements are concerned, it is a relatively short time horizon. CBA is therefore forming an Ammonia in IBCs Working Group reporting to the Association's Logistics Committee to review the overall needs of CBA member companies and develop a strategy for 2018."



Peter Newport