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Economic Commission for Europe

Inland Transport Committee

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Working Party on the Transport of Dangerous Goods

Joint Meeting of Experts on the Regulations annexed to the European Agreement concerning the International Carriage of Dangerous Goods by Inland Waterways (ADN)

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Item 4 (b) of the provisional agenda
Proposals for amendments to the Regulations annexed to ADN: other proposals

Request for discussion on entries in Table C containing more than 10% benzene and those identified by a star

Transmitted by CEFIC and FuelsEurope

Summary

Executive Summary:	The * positions for substances containing more than 10% Benzene as well as those which have a reference to the IBP in Column (2), Table C under UN 1203, 1267, 1268, 1863, 1993, 3295 can be simplified.
Action to be taken:	Start a discussion within the informal working group on substances.
Related documents:	Multilateral Agreement ADN/M 021 ECE/ADN/45 – Chapter 3.2, Table C: p.49-69 ECE/TRANS/WP.15/AC.2/2018/68, IV, A, item 14
Attached:	VNCI paper (link)

I. Introduction

1. Effective ADN 2017, substances containing more than 10% Benzene were specific positions with a specific barge type in Table C, as a result of which many of these products would have to be transported in C-1-1 tankers which are not available. This change with unintended side effects was fixed with Multilateral Agreement ADN/M 021, which ended 30.06.2019.

2. With the introduction of the * positions for substances containing more than 10 % Benzene and the introduction of the 3rd indent under 3.2.3.1 effective 1.1.2019, the minimum tanker requirement can now be established by means of the flowcharts, schemes and criteria in 3.2.3.3. Those positions with a Benzene content of more than 10% having a reference to the IBP in Column (2) of Table C remain unchanged.

3. Whereas first ADN/M 021 and later ADN 2019 solved the issues which arose as a result of ADN 2017, Table C has become very complicated as a result of these changes. It also appears that introduction of the 3rd indent under 3.2.3.1 goes against the classification hierarchy as described in Ch. 2.1 of ADN.

4. ADN 3.2.3.1, third indent indicates that:

> *"If a cell contains an asterisk, "*", the applicable requirements should be determined by applying 3.2.3.3. The determination of the applicable requirements by applying 3.2.3.3 should take precedence over using the entries for mixtures for which no sufficient data is available."*

II Topics for discussion

5. CEFIC and FuelsEurope see possibilities for a simplification of Table C by:

(a) Introducing specific entries to replace the star positions for those entries with more than 10 %;

(b) Considering the deletion of those entries with more than 10 % Benzene having a reference to the IBP in Column (2).

III. Rationale

6. The classification hierarchy as described in ADN 2.1 would be restored.

7. The entries with more than 10% Benzene having a reference to the IBP are in practice a duplication of what is reported in ADN 3.2.3.3, Scheme A.

8. In fact, starting from an entry where a * is assigned, one can use the flow chart of ADN 3.2.3.3 and Scheme A and end up with exactly the same barge requirements as for the entries in Table C, where an IBP is mentioned.

9. The attached industry guidance document, issued by the Royal Association of the Dutch Chemical Industry (VNCI) demonstrates that the formula of ADN 3.2.3.3 leads to a cargo pressure at liquid temperature of 30 °C higher than 50 kPa only if the vapor pressure of the substance at 50 °C is equal to or higher than 175 kPa. The document concludes that as long as the vapor pressure of a substance is lower than 175 kPa at 50 °C a C 2 2 barge with sprinklers, and a relief valve set pressure of 50 kPa can be conservatively selected.

IV. Request to the ADN Safety Committee

10. CEFIC and FuelsEurope invite the ADN Safety Committee to take note of the above as well as the attached VNCI guidance document, and to give its opinion;

11. The Safety Committee is then invited to submit the matter to the informal working group on “Substances”.

Guidance on barge selection for ADN (*) positions

Version : july 2019

1. Purpose

To assure compliance with ADN 2019 for a number of products classified as (*) positions in Table C, aligned with the responsibilities of a filler and a consignor.

The following entries with at least an asterisk (*) in Column (10) are in scope:

UN 1202, UN 1203; UN 1224, UN 1265, UN 1267, UN 1268, UN 1719; UN 1760, UN 1863, UN 1986, UN 1987, UN 1989, UN 1992, UN 1993, UN 2735, UN 2810, UN 2922, UN 2924, UN 2927, UN 2929, UN 3082, UN 3256, UN 3257, UN 3264, UN 3265, UN 3266, UN 3267, UN 3271, UN 3272, UN 3286, UN 3287, UN 3289, UN 3295, UN 3494, ID 9001, ID 9002, ID 9003, ID 9005, ID 9006

2. Scope

Selection of correct barge for specific and general N.O.S. UN entries, according to ADN 2019.

3. Approach

3.1. Introduction

For products which are classified within ADN 2019 as (*) positions (example below)

1268	PETROLEUM DISTILLATES, N.O.S. or PETROLEUM PRODUCTS, N.O.S. WITH MORE THAN 10% BENZENE	3	F1	I	3+CMR+F+ (N1, N2, N3)	C	*	*	*	*	*		*	yes	T4 [3]	II B[4] (II B3)	yes	*	1	27; 44 *see 3.2.3.3

the provision of chapter 3.2.3.3 are applicable for those columns which contain an asterisk (*)

In particular, the type of tank vessel, cargo tank design, cargo tank type and opening pressure of the pressure relief valve/high velocity vent-valve as referred to in Columns (6), (7), (8), (9) and (10) need to be selected based on Scheme A or Schema B of 3.2.3.3.

Note that in some entries, columns (6), and/or (7) and/or (8) already contains a value in which case ADN 3.2.3.3 refers to those columns which contain a * **and** the determination of the applicable requirements by applying 3.2.3.3 should take precedence over using the entries of mixtures for which no sufficient data is available (ADN 3.2.3.1)

Scheme A: Criteria for cargo tank equipment in vessels of type C

Cargo tank equipment	Cargo tank internal pressure at liquid temperature of 30 °C and gaseous phase temperature of 37.8 °C > 50 kPa	Cargo tank internal pressure at liquid temperature of 30 °C and gaseous phase temperature of 37.8 °C ≯≦ 50 kPa	Cargo tank internal pressure unknown, owing to absence of certain data
With refrigeration (No. 1 in column (9))	Refrigerated		
Pressure tank (400 kPa)	Non-refrigerated	Cargo tank internal pressure at 50 °C > 50 kPa without water spraying	Boiling point ≤ 60°C
Pressure relief valve/high velocity vent valve opening pressure: 50 kPa, with water-spraying system (No. 3 in column (9))		Cargo tank internal pressure at 50 °C > 50 kPa with water spraying	60 °C < boiling point ≤ 85°C
Pressure relief valve/high velocity vent valve opening pressure as calculated, but at least 10 kPa		Cargo tank internal pressure at 50 °C ≤ 50 kPa	
Pressure relief valve/high velocity vent valve opening pressure: 50 kPa			85 °C < boiling point ≤ 115°C
Pressure relief valve/high velocity vent valve opening pressure: 35 kPa			Boiling point > 115°C

Scheme B: Criteria for equipment of vessels of type N with closed cargo tanks

Cargo tank equipment	Class 3, flash-point < 23°C				Corrosive substances	CMR substances
Pressure tank (400 kPa)	175 kPa ≤ $P_{d\,50}$ < 300 kPa without refrigeration					
Pressure relief valve/high velocity vent valve opening pressure: 50 kPa	175 kPa ≤ $P_{d\,50}$ < 300 kPa, with refrigeration (No. 1 in column (9))	110 kPa ≤ $P_{d\,50}$ < 175 kPa without water spraying				
Pressure relief valve/high velocity vent valve opening pressure: 10 kPa			110 kPa ≤ $P_{d\,50}$ < 150 kPa with water spraying (No. 3 in column (9))	$P_{d\,50}$ < 110 kPa	Packing group I or II with $P_{d\,50}$ > 12.5 kPa or reacting dangerously with water or with gases in solution	Pressure relief valve/high velocity vent valve opening pressure: 10 kPa; with water spraying when vapour pressure > 10 kPa (calculation of the vapour pressure according to the formula for column 10, except that v_a = 0.03)

In both schemes the cargo tank internal pressure at various liquid temperatures and gaseous phase temperature of 37.8 °C is estimated according to ADN 3.2.3.3:

Column (10): Determination of opening pressure of high-velocity vent valve in kPa

For vessels of type C, the opening pressure of the high-velocity vent valve shall be determined on the basis of the internal pressure of the tanks, rounded up to the nearest 5 kPa

To calculate the internal pressure, the following formula shall be used:

$$P_{max} = P_{Obmax} + \frac{k \cdot v_a (P_0 - P_{Da})}{v_a - \alpha \cdot \delta_t + \alpha \cdot \delta_t \cdot v_a} - P_0$$

$$k = \frac{T_{Dmax}}{T_a}$$

In this formula:

P_{max}	:	Maximum internal pressure in kPa
P_{Obmax}	:	Absolute vapour pressure at maximum liquid surface temperature in kPa
P_{Da}	:	Absolute vapour pressure at filling temperature in kPa
P_0	:	Atmospheric pressure in kPa
v_a	:	Free relative volume at filling temperature compared with cargo tank volume
α	:	Cubic expansion coefficient in K^{-1}
δ_t	:	Average temperature increase of the liquid due to heating in K
T_{Dmax}	:	Maximum gaseous phase temperature in K
T_a	:	Filling temperature in K
k	:	Temperature correction factor
t_{Ob}	:	Maximum liquid surface temperature in °C

In the formula, the following basic data are used:

P_{Obmax}	:	At 50 °C and 30 °C
P_{Da}	:	At 15 °C
P_0	:	101.3 kPa
v_a	:	5% = 0.05
δ_t	:	5 K
T_{Dmax}	:	323 K and 310.8 K
T_a	:	288 K
t_{Ob}	:	50 °C and 30 °C

3.2. Scheme A

In the event of a C type tanker, the following applies:

For all (*) positions the industry is in state of estimating or measuring vapor pressure, so the column on the right of Schema A is not applicable.

If the vapor pressure is known at two different temperatures, it is possible to calculate the Antoine coefficients A and B:

$$Ln(P_V(T)) = A - \frac{B}{T+273}$$

and extrapolate the vapor pressure at 15 °C, 30 °C and 50 °C.

Assuming conservatively a cubic coefficient of 0.00125 1/K (for pure benzene), one can calculate through the formula in ADN 3.2.3.3 the cargo tank internal pressure at liquid temperature of 30 °C and with gaseous phase temperature of 37.8 °C.

The below matrix shows the cargo pressure at liquid temperature of 30 °C calculated from various couples of vapor pressures at 25 °C and 50 °C.

P_v (kPa) @ 25 °C \ P_v (kPa) @ 50 °C	50	75	100	110	125	150	175	180	190	200	225	250	275	300	325	350	400	500
10	31	33	35	35	36	37	38	38	38	38	39	40	40	41	41	42	42	44
20	31	36	39	40	42	44	45	46	46	47	48	49	50	51				
30	27	35	40	42	44	47	50	50	51	52	54	56	57					
40	20	32	39	41	44	49	52											
50	12	26	36	39	43	49												
60		19	31	35	40	47												
70			25	30	36	44												
80			18	23	31													

It is clear that the formula of ADN 3.2.3.3 leads to a cargo pressure at liquid temperature of 30 °C higher than 50 kPa *only if the vapor pressure of the substance at 50 °C is higher than or equal to 175 kPa*. It should be noticed that this is inherent with the application of the formula.

It can be concluded that as long as:

$$P_V(50℃) < 175\ kPa$$

The third column of Schema A is applicable.

A similar exercise can be done to estimate the cargo tank internal pressure at liquid temperature of 50 °C and with gaseous phase temperature of 37.8 °C. The use of the formula of ADN 3.2.3.3 leads to the below matrix.

P_v (kPa) @ 25 °C \ P_v (kPa) @ 50 °C	50	75	100	110	125
5	33	44	55	65	75
10		38	50	61	71
15		31	44	55	66
20			36	49	61
25					54
30					47

From this analysis it can be observed that the pressure estimated tends to decrease by increasing the vapor pressure at the lower temperature and at constant vapor pressure at high temperature. This is counterintuitive and derives from the fact that the thermal expansion term of the pressure formula becomes prevalent. In this case the conservative assumption on the thermal expansion coefficient is not useful anymore and the exact value needs to be used, and the pressure needs to be calculated without any short cut.

In this case an estimate of the vapor pressure at two temperatures, together with an estimate of the thermal expansion coefficient should be handed over to the consignor by the product manufacturer.

The consignor will then estimate vapor pressures at 50 °C and the cargo pressure at 50 °C and decide if water sprinklers are needed or not, based on Scheme A.

In any case the consignor can decide to conservatively choose barges with sprinklers if no reliable data for the thermal expansion coefficient is available.

3.3. Scheme B

In the event of an N-x-x tanker, the following applies.

In case of CMR products, for which the transport is allowed in N tankers, Scheme B may require to use the formula for column 10 to determine the opening pressure, and hence to determine if water spraying is needed (column 6, last one). The cut off point is a cargo tank internal pressure of 10 kPa.

For products with low vapor pressure the formula of ADN 3.2.3.3 shows that a cargo pressure lower than 10 kPa is hardly calculated. In fact, also setting vapor pressures to zero kPa, in the pressure equation of ADN 3.2.3.3, in order for P_{max} to be greater than 10 kPa a value for α of 0.0001 or lower is necessary, which is one order of magnitude lower than the typical values for hydrocarbons[1].

Hence if column 6 of Scheme B is applicable, the formula leads in practice to choosing cargoes with set pressure of 10 kPa and equipped with water spraying.

In all other cases the knowledge of the vapor pressures at 50 °C is sufficient to choose the barge following Scheme B and no special calculation is necessary.

4. Conclusion

Scheme A

If the vapor pressure of a substance is lower than 175 kPa at 50 °C, a C 2 2 barge with water spraying, and a relief valve set pressure of 50 kPa can be conservatively selected.

Scheme B

In case of CMR substances where column 6 of Scheme B is applicable, a barge with water spraying, and a relief valve set pressure of 10 kPa can be selected.

In all other cases the vapor pressure at 50 °C should be used to verify the choice of the barge.

This data should be provided by the product manufacturer to the consignor.

5. Retention of data

Data relative to the vapor pressure of the product at 50 °C shall be provided by the manufacturer. A method of providing this information is adding the data to the SDS, section 9.

[1] https://www.engineeringtoolbox.com/cubical-expansion-coefficients-d_1262.html

The data mentioned in paragraph 4 can be retained in various form, but it is recommended that it accompanies the transport document. Whether this information is part of the transport document or not is responsibility of the consignor.

The following sentence could be used to account for the choice of barge according to schema A:

Cargo tank internal pressure at liquid temperature of 30 °C and gaseous phase temperature of 37.8 °C is calculated to be lower than 50 kPa.

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