INF.20

Economic Commission for Europe

Inland Transport Committee

21 January 2022

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) (ADN Safety Committee)

English

Thirty-ninth session
Geneva, 24–28 January 2022
Item 5 (b) of the provisional agenda
Proposals for amendments to the Regulations annexed to ADN: other proposals

Dangerous goods which are not detectable with a toximeter

Submitted by the European Chemical Industry Council (CEFIC), the European Barge Union (EBU) and the European Skippers Organisation (ESO)

1. Referring to INF-Document 14 from EBU / ESO of 17 January 2020 and Working Document 2020/31 of 29 May 2020 we would like to draw attention to the following.

Introduction

- Some transports of dangerous goods require a toximeter, but cannot be measured with a toximeter
- An example is TiCl4, for which some alternative solutions could be found
- Cefic and EBU/ESO request the ADN Safety Committee to mandate the informal working group substance to investigate and propose solutions for dangerous goods which cannot be measured with a toximeter.

2. Dangerous goods for which a toximeter is required in ADN 3.2.1 Table A column 9 and 3.2.3 ADN Table C column 18, but which cannot be measured with a toximeter, may not be transported by inland waterway.

3. It should be noted that, for these reasons, a “reverse modal shift” has taken place. Transports carried out in the past by barges, will again take place by road (from water to road). This is not in line with the EU ambitions for modal shift from road to rail and inland waterways.

4. This problem could be solved by extending the requirements of the ADN so that a substance must not only be measured directly, but also the determination of secondary products would be allowed with the help of measuring devices approved for the secondary products.

5. A practical example is the transport of titanium tetrachloride TiCl4, which was transported in tank containers on barges, is now being moved again by road (about 8000 tons / year). No toximeters are required for road transport (ADR/RID).

6. This particular product cannot be measured with the toximeters required by ADN because no corresponding toximeter is available for this substance.

7. Since titanium tetrachloride hydrolyzes in the presence of water (humidity) and forms hydrogen chloride, a detection of titanium tetrachloride is possible indirectly via the hydrogen chloride formed by using a measuring device that detects HCl.

Example: $TiCl_4 (l) + 2 H_2O (l) \rightarrow TiO_2 (s) + 4 HCl (aq)$

Molar mass $TiCl_4$ = 189,69 g/mol

Molar mass HCl = 36.46 g/mol

Measured 50ppm HCl = 50 x 189,69 / 36.46 = 260ppm $TiCl_4$

8. This would be an actionable solution for detecting leaks and the presence of a hazardous concentration of the leaking substance.

9. The measurement of the secondary product could be used as a possible solution for the products listed below (see table). We would like to ask the informal working group "Substances" to examine the implementation of this idea.

Proposal

Proposal 1:

10. Insert SV804 in table A column 6:

> For substances (see Annex to ECE/TRANS/WP.15/AC.2/2020/31) that cannot be measured with a toximeter via direct measurement (e.B. $TiCl_4$), it is permitted to use an equivalent indirect measurement method (in this case Cl-) and to calculate the content of $TiCl_4$ mathematically. These measuring devices must be approved for the indirect measurement method of the specific substance. National exposure limit values have to be respected during transport.

Proposal 2: alternative to 1

11. In Table A column 11 insert IN04:

> For substances (see Annex to ECE/TRANS/WP.15/AC.2/2020/31) that **cannot** be measured with a toximeter via direct measurement (e.B. $TiCl_4$), it is permitted to use an equivalent indirect measurement method (in this case Cl-) and to calculate the content of $TiCl_4$ mathematically. These measuring devices must be approved for the indirect measurement method of the specific substance. National exposure limit values have to be respected during transport.

Proposal 3: alternative to 1 and 2

12. Insert a remark in table A, column 13:

> Note 46 in ADN 3.2.3 Table C has to be followed.

Proposal 4:

13. Use the following wording as a basis for the definition of Note 46:

> For substances (see Annex to ECE/TRANS/WP.15/AC.2/2020/31) that cannot be measured with a toximeter via direct measurement (e.B. $TiCl_4$), it is permitted to use an equivalent indirect measurement method (in this case Cl-) and to calculate the content of $TiCl_4$ mathematically. These measuring devices must be approved for the indirect measurement method of the specific substance. National exposure limit values have to be respected during transport.

Proposal 5:

14. Insert definition in 1.2.1: (first approach)

Other measuring devices: All approved measuring instruments for the determination of the nationally permissible exposure limit values when handling hazardous substances.

Proposal 6:

15. Expand Chapter 8.2.1:

The training of the experts is to be extended to include these procedures.

Examples of substances which cannot me measured with a toximeter - provisionally inventory EBU/ESO

UN nr	Procuct Name or description	Remarks
1026	CYANOGEN	
1069	NITROSYL CHLORIDE	
1381	PHOSPHORUS, WHITE or YELLOW, UNDER WATER or IN SOLUTION	Substance itself isunmeasurable, but vapours coming from this subsance are measurable with short term tubes for phosphorhydrogen
1182	ETHYL CHLOROFORMATE	
1541	ACETONE CYANOHYDRIN, STABILIZED	
1664	NITROTOLUENES, LIQUID	
1750	CHLOROACETIC ACID SOLUTION	
1790	HYDROFLUORIC ACID with % (3 positions!) hydrofluoric acid	
2013	STRONTIUM PHOSPHIDE	
2205	ADIPONITRILE	
2078	TOLUENE DIISOCYANATE (and isomeric mixtures) (2,4- TOLUENE DIISOCYANATE)	
2281	HEXAMETHYLENE DIISOCYANATE	
2290	ISOPHORONE DIISOCYANATE	
2295	METHYL CHLOROACETATE	
2438	TRIMETHYLACETYLCHLORID	
2748	2-ETHYLHEXYL CHLOROFORMATE	
2754	N-Ethyltoluidinen	
2927	TOXIC LIQUID, CORROSIVE, ORGANIC, N.O.S. (2 positions)	4- Chlorobutyryl chloride can be detecte with short term tube Phosgen 0.02a Other substances under UN 2927 are not measurable with elektronic (PID) meter or short term tubes.
2929	TOXIC LIQUID, FLAMMABLE, ORGANIC, N.O.S.	
2966	THIOGLYCOL (mercaptoethanol)	
3276	NITRILES, LIQUID, TOXIC, N.O.S. (3 positions)	
3302	2-DIMETHYLAMINOETHYLACRYLAAT, STABILIZED	
3381	TOXIC BY INHALATION LIQUID, N.O.S.	
3382	TOXIC BY INHALATION LIQUID, N.O.S.	
3383	TOXIC BY INHALATION LIQUID, FLAMMABLE, N.O.S.	
3384	TOXIC BY INHALATION LIQUID, FLAMMABLE, N.O.S.	
3385	TOXIC BY INHALATION LIQUID, FLAMMABLE, N.O.S.	
3386	TOXIC BY INHALATION LIQUID, WATERREACTIVE, N.O.S.	
3387	TOXIC BY INHALATION LIQUID, OXIDIZING, N.O.S.	
3388	TOXIC BY INHALATION LIQUID, OXIDIZING, N.O.S.	
3389	TOXIC BY INHALATION LIQUID, CORROSIVE, N.O.S.	
3390	TOXIC BY INHALATION LIQUID, CORROSIVE, N.O.S.	Diphosgene (ook UN 3390) is meetbaar met het proefbuisje Chloropircin 0.1a (zie bijlage). Andere stoffen onder UN 3390 zijn niet meetbaar met een elektronische (PID) meter of korte-duur-buisjes.
3455	CRESOLS, SOLID, MOLTEN	In tank barge liquid, TOX required, in dry cargo solide; no TOX required