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**COMMITTEE OF EXPERTS ON THE
TRANSPORT OF DANGEROUS GOODS**

**Sub-Committee of Experts on the
Transport of Dangerous Goods**
(Thirteenth session,
Geneva, 7-17 July 1997,
agenda item (3 (d)))

**DRAFT AMENDMENTS TO THE MODEL REGULATIONS
ON THE TRANSPORT OF DANGEROUS GOODS**

Other draft amendments

Toxic by inhalation substances

Transmitted by the Expert from the United States of America

Introduction

1. During the nineteenth session of the Committee, it was agreed on the basis of ST/SG/AC.10/R.530 to consider additional requirements for the transport of substances that either meet the criteria of Division 6.1 on the basis of toxicity by vapour inhalation or are classified in Division 2.3. The expert from the United States believes that these substances pose a higher degree of risk than other liquids and gases and warrant special consideration beyond that currently provided in the Recommendations. Hereafter these substances are referred to as “toxic by inhalation substances” or “TIH substances”.
2. This proposal seeks to improve hazard communication of these substances for purposes of transport acceptance and emergency services personnel, and improve the packaging of such materials to reduce the likelihood of release in transport. While TIH substances are either Division 6.1 substances or Division 2.3 substances, the primary focus of the proposal is on Division 6.1 substances.

3. The Expert from the United States recommends that a general discussion on this topic be held at the thirteenth session of the Sub-Committee. Depending on the outcome of these discussions, more detailed proposals could be considered at subsequent Sub-Committee sessions. The intent of this document is to provide a justification on why additional requirements should be applied to TIH substances and to identify the scope of classification, packaging, and hazard communication requirements considered necessary in order to adequately address this topic. The previous document ST/SG/AC.10/C.3/R.591 by the expert from the United States provides a list of TIH substances specifically listed in the Recommendations.

Degree of risk posed by TIH substances

4. Toxic by inhalation substances are already recognized as presenting a greater degree of danger than many other substances covered by the Recommendations in that the precedence of hazard provisions rank the inhalation hazard of Division 6.1, Packing Group I as always taking precedence, including over Division 6.1 substances that are toxic by oral or dermal exposure. Similarly Division 2.3 always takes precedence in the case of Class 2.

5. Unlike substances with acute oral toxicity which must be ingested or substances with acute dermal toxicity which require skin contact to cause injury, TIH substances do not require direct contact to cause injury. Substances are classified as Division 6.1, Packing Group I if the substance has an LC_{50} inhalation toxicity less than 1000 ml/m^3 and has a vapour pressure at 20°C more than 10 times the LC_{50} . As such these substances give off vapours at ambient conditions ten times more concentrated than the concentration expected to kill fifty percent of a test population when exposed for one hour. Furthermore, while substances are classified as being toxic by inhalation on the basis of an acute test, much lower concentrations pose risks in accident situations where any irreversible health effect is unacceptable and where members of the public with varying health conditions may be exposed. As such, when released in a spill, TIH substance evacuation distances can extend in some cases in excess of 11 kilometres from the spill site.

Significance of TIH Spills

6. The degree of danger posed by TIH substances can perhaps best be appreciated when one considers a hypothetical accident scenario.

7. The North American Emergency Response Guidebook (NAERG) provides evacuation distances for small and large spills of TIH substances and serves to illustrate their degree of danger. For the NAERG, evacuation distances were generated using validated computer models assuming 90 percentile weather conditions (i.e., only 10 percent of the possible weather conditions would produce more severe plume dispersals). For purposes of emergency response, the American Industrial Hygiene Association provides Emergency Response Planning Guidelines (ERPG) which are defined as airborne concentrations of substances that nearly all individuals could be exposed to for 1 hour without experiencing or developing irreversible or other serious health effects, or symptoms which could impair an individual's ability to take protective action.

8. For a small spill (i.e., less than 210 litres) of UN 1092, Acrolein (Div. 6.1, PG I, LC_{50} of 25 ml/m^3 and vapour pressure of $289,000 \text{ ml/m}^3 \text{ ppm}$), the recommended isolation distance (i.e., the radial distance from a spill where the concentration will be below the ERPG (the ERPG for acrolein is 0.5 ml/m^3)) is 125 metres. In addition for such a spill, people as far as 500 metres downwind of the spill location are at risk of harmful exposure. Because vapour plumes tend not to rise to the same extent at night, the same spill could put people at risk of harmful exposure as far as 2300 metres from the spill location. For a large spill of acrolein, the recommended isolation distance is 305 metres and the distances downwind of the spill where people are at risk of harmful exposure are 1900 metres (daytime) and 8400 metres (nighttime).

Current Transportation Regulations Affecting TIH Substances

9. Regulatory systems apply special requirements to TIH substances to varying degrees. The ICAO Technical Instructions on the Safe Transport of Dangerous Goods by Air forbid substances that meet the TIH criteria from being transported on passenger and cargo aircraft. Current US requirements include additional packaging and hazard communication requirements for all TIH substances. The IMDG Code and the European ADR and RID include special packaging requirements for some TIH substances but do not apply requirements to these substances systematically.

10. For example, for TIH substances UN 1051 Hydrogen Cyanide, stabilized, UN 1613 Hydrogen Cyanide, aqueous solution, UN 1259 Nickel Carbonyl, UN 1994 Iron Pentacarbonyl, UN 1185 Ethyleneimine, inhibited, and UN 2480 Methyl Isocyanate, the ADR/RID include special packaging requirements. However, comparable or higher hazard TIH substances such as UN 1092 Acrolein, UN 2484 tert-Butyl Isocyanate, UN 1238 Methyl Chloroformate, UN 1239 Methyl Chloromethyl Ether, UN 1244 Methylhydrazine, UN 1251 Methyl Vinyl Ketone, UN 1380 Pentaborane, and UN 2482 n-Propyl Isocyanate are allowed to be transported under general packaging provisions as could TIH substances not specifically listed by name which may be transported under an NOS entry. A solution of Aldicarb and Dichloromethane (LC_{50} 22ml/m³, SVC 346000 ml/m³) could be transported under such an entry. The treatment of TIH substances in the IMDG Code is similar.

11. Similarly, the IMDG Code prohibits well known TIH substances such as UN 1051 Hydrogen Cyanide, stabilized from being transported on passenger vessels (more than 25 passengers) and limits stowage to “on deck only” on other vessels. However, for other named TIH substances and TIH substances transported under NOS proper shipping names with similar levels of toxicity, less stringent stowage requirements apply.

Improvements in Emergency Response by Better Identification of TIH Substances

12. The emergency response procedures for responding to substances that are toxic by inhalation differ significantly from those required for responding to substances that are toxic by ingestion and skin contact. For TIH substances, emergency responders require breathing apparatus and must consider extensive and perhaps costly evacuation in order to adequately protect the public. For substances that are toxic by oral and dermal exposure, limited respiratory protection and minimal evacuation are necessary.

13. The currently provided NOS proper shipping names for toxic substances do not distinguish between substances that are toxic by inhalation and substances that are toxic by oral or dermal toxicity. Consequently, emergency responders acting on the basis of a substance’s UN number must assume that any toxic substance transported under a Division 6.1 NOS description is a substance that is toxic by inhalation and must take appropriate steps to protect themselves with breathing apparatus and protect the public through evacuation even though such actions may be unnecessary when the toxic substance involved is not toxic by inhalation.

14. Unnecessary disruption of the public activity through evacuation could be avoided if these TIH liquid substances were clearly distinguished from other Division 6.1 substances.

General Description of the US Proposal on TIH Substances

15. The purpose of this proposal is to:

- systematically address TIH substances so that comparable requirements are applied to all substances of comparable risk;

- through improved packaging, reduce the risk that TIH substances are released in accident situations in order to provide greater protection to the public and to avoid potentially costly public evacuations; and
- distinguish TIH substances from other substances of Division 6.1 through hazard communication to enhance emergency response effectiveness.

16. The expert from the United States proposes to address requirements for TIH substances comprehensively by introducing new requirements affecting classification criteria, proper shipping names, labels, and packaging requirements, including requirements for portable tanks. A discussion of each area follows.

Classification Criteria

17. As the Sub-Committee has discussed previously, the current criteria for inhalation toxicity in the UN Recommendations will at some time in the future need to be amended in order to be alligned with internationally harmonized criteria being developed in accordance with Chapter 21 of Agenda 19 of the UN Conference on the Environment and Development under the leadership of the OECD. The current UN criteria are in some respects inconsistent with OECD proposed internationally harmonized inhalation toxicity criteria for liquids and gases. While some issues such as the units of measure and whether classification should be affected by vapour pressure remain outstanding, the new toxicity levels being proposed by OECD are not at issue. It is proposed that the criteria for inhalation toxicity be amended consistent with the proposed OECD toxicity levels at this time while retaining the existing approach of using vapour pressure as part of the criteria and using ml/m^3 as the unit of measure.

18. The OECD values for inhalation toxicity are 250 ml/m^3 , 1000 ml/m^3 and 5000 ml/m^3 (1 hour LC_{50} test) as compared to current values of 1000, 3000 and 5000 ml/m^3 in the Recommendations. The values differ from the Division 6.1 packing group I and II inhalation toxicity limits of 1000 ml/m^3 and 3000 ml/m^3 .

19. In order to adjust to the new OECD criteria, it is proposed that the packing group I and II criteria be shifted so that packing group I would include substances with acute inhalation toxicities of less than or equal to 250 ml/m^3 and packing group II would include substances with toxicities in the range of more than 250 ml/m^3 to less than or equal to 1000 ml/m^3 .

20. From a precedence of hazard standpoint, a toxicity of less than 1000 should still be considered as always taking precedence. The precedence of hazard provisions would have to be revised accordingly (i.e., inhalation hazard at the packing group I or II levels always takes precedence).

Vapor pressure criteria

21. In order to distinguish the more highly toxic in the new Packing Group I substances from the new Packing Group II substances, it is also proposed that the vapour pressure criteria for the Packing Group I substances be set at $V \geq 500\text{LC}_{50}$ and the current $V \geq 10\text{LC}_{50}$ be retained for Packing Group II substances.

Proper shipping names

22. The Recommendations generally provide different proper shipping names for substances that illicit different emergency response actions. As discussed above, TIH substances clearly illicit different emergency response actions than substances that are orally or dermally toxic. On this basis it is proposed that new NOS entries be added to the Recommendations for substances toxic by inhalation. An example entry would be:

UN XXXX, Toxic By Inhalation, Liquid, NOS.

23. To prevent existing liquid toxic substance NOS entries from being used to transport TIH substances, a special provision indicating that they should not be used if the substance meets the TIH criteria should be placed against each toxic NOS entry which would no longer be appropriate for TIH substances.

Labeling and Placarding

24. To convey the special dangers that TIH substances pose, it is also proposed that TIH substances be identified through a special label and placard. The expert from the United States considers that a new label is necessary in order to effectively communicate the risk of TIH substances to emergency response personnel. Labels for TIH substances and gases required under new regulations in the United States are shown in Annex 1. It is recognized that wordless labels and placards would have to be developed for the Recommendations.

Packaging

25. It is proposed that the packaging required for TIH substances be more stringent than packaging that is normally prescribed for substances in packing groups I and II. A two tiered system is proposed. The highest integrity packaging requirements would apply to Packing Group I TIH substances and a somewhat lower level of packaging integrity be applied to Packing Group II TIH substances. These packaging requirements could be included in packing instructions. Proposed packing instructions are set out in Annex 2 to this proposal.

Portable Tanks

26. Requirements for TIH substances transported in tanks were originally proposed in document ST/SG/AC.10/C.3/R.591 by the expert from the United States. Requirements for new Packing Group I and II TIH substances in Division 6.1 are proposed as two new portable tank instructions and a new portable tank special provision in Annex 3 to this proposal.

ANNEX 1

LABEL



ANNEX 2**Packing Instructions for Division 6.1 TIH Substances**

P60X	PACKING INSTRUCTION	P60X
	<p>This packing instruction applies to substances toxic by inhalation, Packing Group I. Except for compressed gas cylinders each packaging shall conform to the general packaging requirements in Chapter 4.1 and the requirements of Chapter 6.1. The following packagings are permitted:</p> <p>(a) Compressed gas cylinders and gas receptacles in conformance with the construction, testing and filling requirements approved by the competent authority. Each cylinder with a wall thickness less than 2 mm must be overpacked in a strong outer packaging and secured or cushioned so as to prevent significant movement within the outer packaging during normal conditions of transport.</p> <p>(b) 1A1, 1B1, 1H1, 1N1 drums or 6HA1 composite packagings; further packed in a 1A2 or 1H2 drums. The inner drum or composite packaging shall meet the following requirements:</p> <p>(1) it shall conform to the performance test requirements prescribed in Chapter 6.1 at the PG I performance level for liquids except that:</p> <p>(i) the hydrostatic pressure test shall be carried out at a pressure of at least 550 kPa; and</p> <p>(ii) the design and production leakproofness tests shall be carried out at a test pressure of at least the greater of two times the vapor pressure of the substance to be carried at 55°C and 0.30 bar.</p> <p>(2) the capacity shall not exceed 220 litres;</p> <p>(3) closures shall be of a screw cap type that are :</p> <p>(i) physically held in place by any means capable of preventing back-off or loosening of the closure by impact or vibration during transport; and</p> <p>(ii) provided with a cap seal that is capable of withstanding an internal pressure of at least 100 kPa.</p> <p>(4) when the capacity is less than or equal to 120 litres have a minimum thickness of:</p> <p>(i) for 1A1 and 1N1 drums 1.3 mm;</p> <p>(ii) for 1B1 drums 3.9 mm;</p> <p>(iii) for 1H1 drums 3.2 mm; and</p> <p>(iv) for 6HA1 composite packagings, 1.6 mm for the inner plastic receptacle and 1.1 mm for the outer steel drum;</p> <p>(5) when the capacity is greater than 120 litres have a minimum thickness of:</p> <p>(i) for 1A1 and 1N1 drums 1.7 mm;</p> <p>(ii) for 1B1 drums 4.7 mm;</p> <p>(iii) for 1H1 drums 3.2 mm; and</p> <p>(iv) for 6HA1 composite packagings, 1.6 mm for the inner plastic receptacle and 1.1 mm for the outer steel drum;</p> <p>(6) be so packed inside the outer drum using an inert cushioning material so that its ability to withstand the prescribed performance tests is not adversely affected by the use of the outer drum.</p> <p>The outer drum shall:</p> <p>(1) conform to the performance test requirements for solids;</p> <p>(2) shall withstand a hydrostatic pressure test in accordance with Chapter 6.1 at a pressure of at least 100 kPa; and</p> <p>(3) have a minimum thickness of 1.35 mm for a 1A2 drum and 6.3 mm for a 1H2 plastic drum.</p> <p>(c) In combination packagings, consisting of an inner packaging system and one of the following outer packagings:</p> <p>Drums: 1A2, 1B2, 1N2, 1D, 1G and 1H2</p> <p>Jerricans: 3A2, 3H2</p> <p>Boxes: 4A, 4B, 4C1, 4C2, 4D, 4F, 4G, 4H1 and 4H2</p> <p>The inner packaging system shall consist of impact-resistant receptacles of glass, earthenware, plastic or metal securely cushioned with an inert absorbent material inside in a leakproof packaging of metal or plastic. The capacity of each inner receptacle shall not exceed 4 litres. The closure of each inner receptacle shall be physically held in place by any means capable of preventing back-off or loosening of the closure by impact or vibration during transport. The inner packaging system shall conform to the performance test requirements of Chapter 6.1 at the PG I performance level without the benefit of the outer packaging. The outer packaging shall also conform to the performance test requirements of Chapter 6.1 at the PG I performance level as a single packaging suitable for solids. The amount of liquid contained in the outer packaging may not exceed 16 litres.</p>	

60Y**PACKING INSTRUCTION****60Y**

This packing instruction applies to substances toxic by inhalation, Packing Group II. Except for compressed gas cylinders each packaging shall conform to the general packaging requirements in Chapter 4.1 and the requirements of Chapter 6.1. The following packagings are permitted:

(a) Packagings that are authorized in packing instruction P60X.

(b) In 1A1, 1B1, 1H1, 1N1 drums or 6HA1 composite packagings; further packed in a 1A2 or 1H2 drum. The inner drum or composite packaging shall meet the following requirements:

(1) it shall conform to the performance test requirements prescribed in Chapter 6.1 at the PG I performance level for liquids except that the design and production leakproofness tests shall be carried out at a test pressure of at least the greater of two times the vapor pressure of the substance to be carried at 55°C and 0.30 bar.

(2) the capacity shall not exceed 220 litres;

(3) have screw-type closures that are:

(i) physically held in place by any means capable of preventing back-off or loosening of the closure by impact or vibration during transportation; and

(ii) provided with a cap seal that is capable of withstanding an internal pressure of at least 100 kPa.

(4) when the capacity is less than or equal to 30 litres have a minimum thickness of:

(i) for 1A1 and 1N1 drums 0.69 mm;

(ii) for 1B1 drums 2.8 mm;

(iii) for 1H1 drums 1.1 mm; and

(iv) for 6HA1 composite packagings, 1.6 mm for the inner plastic receptacle and 0.7 mm for the outer steel drum;

(5) when the capacity is greater than 30 litres but less than or equal to 120 litres have a minimum thickness of:

(i) for 1A1 and 1N1 drums 1.1 mm;

(ii) for 1B1 drums 3.9 mm;

(iii) for 1H1 drums 3.2 mm; and

(iv) for 6HA1 composite packagings, 1.6 mm for the inner plastic receptacle and 1.0 mm for the outer steel drum; and

(6) when the capacity is greater than 120 litres have a minimum thickness of:

(i) for 1A1 and 1N1 drums 1.4 mm;

(ii) for 1B1 drums 4.7 mm;

(iii) for 1H1 drums 3.2 mm; and

(iv) for 6HA1 composite packagings, 1.6 mm for the inner plastic receptacle and 1.1 mm for the outer steel drum;

(7) be so packed inside the outer drum using an inert cushioning material so that its ability to withstand the prescribed performance tests is not adversely affected by the use of the outer drum.

The outer drum shall:

(1) conform to the performance test requirements for solids;

(2) withstand a hydrostatic pressure test in accordance with Chapter 6.1 at a pressure of at least 100 kPa; and

(3) have a minimum thickness of 1.35 mm for a 1A2 drum and 6.3 mm for a 1H2 plastic drum.

(c) 1A1, 1B1, 1H1, 1N1 drums or 6HA1 composite packagings described in paragraph (b) of this packing instruction may be used without being further packed in a 1A2 or 1H2 drum if the shipper loads the material, blocks and braces the packagings within the transport unit and also seals the unit. Packagings so loaded may not be stacked within the transport unit. Shipments must be from one origin to one destination only without any intermediate pickup or delivery.

ANNEX 3**Portable Tank Instructions for Division 6.1 TIH Substances**

T35 T35 <i>This portable tank instruction applies to substances toxic by inhalation, Packing Group I. The general requirements of Section 4.2.1 and the requirements of Section 6.6.2 shall be met.</i>				
Portable tank instruction	Minimum test pressure (bar)	Minimum shell thickness (in mm-reference steel) (see 6.2.4)	Bottom opening requirements (see 6.6.2.6)	Pressure relief requirements (see 6.6.2.8)
T35	9	10 mm	Not allowed	See 6.6.2.8.3

T36 T36 <i>This portable tank instruction applies to substances toxic by inhalation, Packing Group II. The general requirements of Section 4.2.1 and the requirements of Section 6.6.2 shall be met.</i>				
Portable tank instruction	Minimum test pressure (bar)	Minimum shell thickness (in mm-reference steel) (see 6.2.4)	Bottom opening requirements (see 6.6.2.6)	Pressure relief requirements (see 6.6.2.8)
T36	9	8 mm	Not allowed	See 6.6.2.8.3

New Portable Tank Special Provision:

TP 25 - Portable tanks shall be insulated. The insulation material shall be of sufficient thickness that the overall thermal conductance at 15.5 °C is not more than 1.533 kilojoules per hour per square meter per degree celsius temperature differential. The insulation material should be protected with a jacket made of steel, austenitic steel or a material with similar fire resistance and melting point characteristics.
