



Secretariat

Distr.
GENERAL

ST/SG/AC.10/C.3/1999/81
20 September 1999

Original: ENGLISH

COMMITTEE OF EXPERTS ON THE
TRANSPORT OF DANGEROUS GOODS
Sub-Committee of Experts on the
Transport of Dangerous Goods
(Seventeenth session,
Geneva, 6-17 December 1999,
agenda item 5 (a))

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

Listing and classification

Transport of materials capable of undergoing uncontrolled polymerization
Stabilization by means of temperature control

Transmitted by the expert from the United Kingdom

Introduction

1. At the twentieth session of the Committee of Experts on the Transport of Dangerous Goods (Geneva, 7 - 16 December 1998) it was agreed, in principle, to use the term "stabilized" in English instead of "inhibited", where this appears in the proper shipping name of monomers in the Dangerous Goods List in Chapter 3.2 of the Recommendations (Document ST/SG/AC.10/25, paragraph 87 and ST/SG/AC.10/25/Add.1). The purpose of this change was to clarify that temperature control is also an acceptable means of preventing uncontrolled polymerization of these materials.

2. The substances listed in ST/SG/AC.10/1998/10 includes many different types of monomer, gases of Class 2 Divisions 2.1 and 2.3, and liquids of Class 3, Class 6 Division 6.1 and Class 8. These substances, when stabilized by a chemical inhibitor, are currently allowed for transport in packages, IBCs and / or tanks, depending upon the particular material.

3. Whilst cooling is an effective means of preventing potentially dangerous polymerization, the proposal in paper ST/SG/AC.10/1998/10 made no reference to control and emergency temperatures that are essential requirements for safe transport under temperature control particularly when transported in IBC's or tanks. This point was raised by the Expert from the United Kingdom at the twentieth session of the Committee of Experts and supported by a number of the other Experts.

4. Subsequently, at its sixteenth session (Geneva, 5 - 16 July 1999), the Sub-Committee also agreed to the proposal from the Expert from Austria to insert, with slight amendments, a new paragraph 3.1.2.6 into the Model Regulations for substances to which the word "STABILIZED" is added to the proper shipping name (see ST/SG/AC.10/C.3/32 paragraph 36).

5. The Model Regulations already contain specific requirements for (other) substances that, because they are thermally unstable at temperatures likely to be encountered during transport, can be transported only under conditions of temperature control. These requirements apply specifically to some self-reactive substances of Division 4.1 and some organic peroxides of Division 5.2 that contain the words "TEMPERATURE CONTROLLED" in their (generic) proper shipping name.

6. It is not the purpose of this paper to change the current classification of any substance for which the proper shipping name is affected by replacing "INHIBITED" by "STABILIZED", or to which "STABILIZED" is added. It is intended only to ensure that appropriate safety requirements are applied to these substances if, during transport, their temperature has to be maintained below 55°C by means of cooling.

Proposals

Proposal 1

7. In Chapter 3.1, insert at the end of new paragraph 3.1.2.6 (see ST/SG/AC.10/C.3/32 paragraph 36):

"When temperature control is used to stabilize such substances to prevent the development of any dangerous excess pressure then, for gases, special provision "xxx" shall apply, and for liquids special provisions "yyy" and for transport in IBC's or tanks "zzz" shall apply (see Chapter 3.3)."

Proposal 2

8. In the Dangerous Goods List:

In column (6) add the number of a new special provision "xxx" for the entries for gases given in the Annex 1.

In column (6) add the number of a new special provision "yyy" for the entries for liquids given in the Annex 2.

In Column (9) and (11) add the number of a new special provision "zzz" for entries for those substances transported in an IBC or tank.

Proposal 3

9. In Chapter 3.3 of the Model Regulations add the following special provisions:

"xxx When stabilized by means of temperature control, this substance shall only be transported under conditions authorized by the competent authority."

"yyy When this substance is stabilized by means of temperature control the provisions of 7.1.4 shall apply."

"zzz When this substance is stabilized by means of temperature control and transport is in an IBC or tank, the IBC shall meet the requirements of Packing Instruction 522 and the tank shall meet Portable Tank Instruction T34. The control and emergency temperatures shall be approved by the competent authority of the country of origin."

Proposal 4

10. In Chapter 4.2:

Insert after 4.2.1.10.1 a new paragraph 4.2.1.10.2 as follows:

"4.2.1.10.2 For additional general provisions for liquid reactive monomers of Class 3 that are stabilized by temperature control, see 4.2.1.13."

At the end of **4.1.13 Additional general provisions applicable to the transport of Division 5.2 substances in portable tanks**" add "*/" and, at the bottom of the page, the following footnote:

"/ These requirements also apply to stabilized substances when, during transport, stabilization is by means of temperature control."*

Proposal 5

11. Insert in 4.2.1.14 a new paragraph 4.2.1.14.1 as follows:

"4.2.1.14.1 For additional general provisions for liquid reactive monomers of Division 6.1 that are stabilized by temperature control, see 4.2.1.13."

Proposal 6

12. Insert in 4.2.1.16 a new paragraph 4.2.1.16.2 as follows:

"4.2.1.16.2 For additional general provisions for liquid reactive monomers of Class 8 that are stabilized by temperature control, see 4.2.1.13."

Proposal 7

13. In Chapter 5.4, insert a new paragraph 5.4.1.1.5 as follows:

"5.4.1.1.5 *Special provisions for temperature stabilized substances*

If the proper shipping name of a substance that is transported or is offered for transport includes the word "STABILIZED", or "STABILIZED" is added to the proper shipping name (see 3.1.2.6), when stabilization is by means of temperature control, the control and emergency temperatures (see 7.1.4.3.1) shall be indicated in the transport document."

Renumber the current paragraph 5.4.1.1.5 as 5.4.1.1.6 and subsequent paragraphs accordingly.

Proposal 8

14. In Chapter 7, at the end of "**7.1.4 Special provisions applicable to the carriage of self-reactive substances of Division 4.1 and organic peroxides of Division 5.2**" add "*/" and, at the bottom of the page, add the footnote:

"/ These requirements also apply to stabilized substances when, during transport, stabilization is by means of temperature control."*

Justification

15. The proposed additions to the Model Regulations are required to ensure that when temperature control is used as the means of stabilizing reactive monomers during transport, appropriate measures are taken to ensure an appropriate level of safety is maintained.

16. *Liquid reactive monomers that are stabilized by temperature control can, under transport conditions, present dangers similar to self-reactive liquids and similar provisions are necessary:* If a reactive monomer that is not chemically stabilized is maintained at a suitably low temperature, dangerous polymerization is prevented however, if the temperature rises, polymerization can develop into an uncontrolled thermal runaway reaction. Uncontrolled polymerization of such a monomer can generate a dangerous amount of heat and pressure, which may give rise to explosive rupture of the containment with the consequent release of hot flammable and / or toxic vapour. In effect, a reactive monomer in the liquid phase may exhibit the properties of a self-reactive liquid.

17. There is currently an unstabilized reactive monomer, DIETHYLENEGLYCOL BIS(ALLYL CARBONATE) + DI-ISOPROPYLPEROXY DICARBONATE, UN 3237, in the list of currently assigned self-reactive substances (see Model Regulations Table 2.4.2.3.2.4). Because of the danger of (free radical induced) uncontrolled polymerization of the allyl group, this mixture requires to be transported under temperature control.

18. The incident to which reference is made the paper from the Expert from Austria (ST/SG/AC.10/1998/42) involved cyanamide. Cyanamide, when not chemically stabilized, is known to be "thermally unstable" and to undergo "sudden violent exothermic polymerization" leading to an explosive event (L Bretherick, Bretherick's Handbook of Reactive Chemical Hazards, 4th Edition, p 144; ISBN-0-408-04983-9).

19. *Determination of the temperature at which uncontrolled reaction occurs (liquids):* Test Series H in Section 28 of the Recommendations in the Transport of Dangerous Goods, Manual of Tests and Criteria gives procedures suitable for determining the self-accelerating decomposition temperature (SADT) of a self-reactive liquid of Division 4.1. Control and emergency temperatures are derived from the SADT using the relationships in Table 7.1.4.3.1.2 in the Model Regulations. These procedures are equally valid for assessing the risk of both decomposition and polymerization reactions at a specific temperature. New special provision "yyy" is therefore applied to the liquids in Annex 2 .

20. *Current general provisions for reactive substances transported under temperature control:*

- The transport documents must include the control and emergency temperatures (Model Regulations paragraph 5.4.1.1.5.1).
- Specific provisions and general guidance (Model Regulations Paragraphs 7.1.4.3.1 and 7.1.4.3.2).

21. *Current provisions for reactive substances transported under temperature control in IBCs and tanks:* There are specific packing instructions and portable tank requirements with special venting requirements when reactive substances are transported in IBCs and tanks.

- Competent Authority approval is required for transport of TYPE F self-reactive substances in IBCs (Paragraph 4.1.5.2) and the IBC must meet the requirements of Packing Instruction 522.
- There are no special provision for the transport of self-reactive substances in tanks (Paragraph 4.2.1.11), because at this time such materials may not be considered for tank transport (Fig 2.1(b)). Any requirements that may in the future be included in the Model Regulations are likely to be similar to those for organic peroxides of Division 5.2; Portable Tank Instruction T34 and the additional general provisions given in 4.2.1.13 are likely to apply and Competent authority approval will be required.

22. *Gases cannot be treated in the same way as liquids:* The substances listed in ST/SG/AC.10/1998/10 are gases and liquids. The procedures given in Section 28 of Part II of the Manual of Tests and Criteria are suitable for measuring the temperature at which uncontrolled polymerization can occur in a liquid, but they may not be applicable to some or all of the gases. For this reason, for the (gaseous) substances listed in Annex 1, transport under temperature control should be undertaken only under conditions laid down by the competent authority, as specified in special provision 'xxx'.

Annex 1

List of entries in Chapter 3.2 of the Model Regulations to which Special Provision 'xxx' should be added in Column (6).

| UN No (1) | Name and Description (2) | UN No (1) | Name and Description (2) |
|--------------------------|---------------------------------------|--------------------------|-------------------------------------|
| 1010 | BUTADIENES, STABILIZED | 1087 | VINYL METHYL ETHER, STABILIZED |
| 1081 | TETRAFLUOROETHYLENE, STABILIZED | 1860 | VINYL FLUORIDE, STABILIZED |
| 1082 | TRIFLUOROCHLORETHYLENE, STABILIZED | 2200 | PROPADIENE, STABILIZED |
| 1085 | VINYL BROMIDE, STABILIZED | 2452 | ETHYLACETYLENE, STABILIZED |
| 1086 | VINYL CHLORIDE, STABILIZED | | |

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Annex 2

List of entries in Chapter 3.2 of the Model Regulations to which Special Provisions 'yyy' and 'zzz' should be added in Column (6).

| UN No (1) | Name and Description (2) |
|----------------------|--|
| 1051 | HYDROGEN CYANIDE, STABILISED containing less than 3% water |
| 1092 | ACROLEIN, STABILIZED |
| 1093 | ACRYLONITRILE, STABILIZED |
| 1143 | CROTONALDEHYDE, STABILIZED |
| 1167 | DIVINYL ETHER, STABILIZED |
| 1185 | ETHYLENEIMINE, STABILIZED |
| 1218 | ISOPRENE, STABILIZED |
| 1246 | METHYL ISOPROPENYL KETONE, STABILIZED |
| 1247 | METHYL METHACRYLATE MONOMER, STABILIZED |
| 1251 | METHYL VINYL KETONE, STABILIZED |
| 1301 | VINYL ACETATE, STABILIZED |
| 1302 | VINYL ETHYL ETHER, STABILIZED |
| 1303 | VINYLDENE CHLORIDE, STABILIZED |
| 1304 | VINYL ISOBUTYL ETHER, STABILIZED |
| 1305 | VINYLTRICHLOROSILANE, STABILIZED |
| 1541 | ACETONE CYANOHYDRIN, STABILIZED |
| 1545 | ALLYL ISOTHIOCYANATE, STABILIZED |
| 1695 | CHLOROACETONE, STABILIZED |
| 1724 | ALLYLTRICHLOROSILANE, STABILIZED |
| 1917 | ETHYL ACRYLATE, STABILIZED |
| 1919 | METHYL ACRYLATE, STABILIZED |

| UN No (1) | Name and Description (2) |
|----------------------|--|
| 1921 | PROPYLENEIMINE, STABILIZED |
| 1991 | CHLOROPRENE, STABILIZED |
| 2055 | STYRENE MONOMER, STABILIZED |
| 2075 | CHLORAL, ANHYDROUS, STABILIZED |
| 2218 | ACRYLIC ACID, STABILIZED |
| 2227 | n-BUTYL METHACRYLATE, STABILIZED |
| 2251 | BICYCLO[2.2.1]HEPTA-2,5-DIENE, STABILIZED(2,5-NORBORNADIENE, STABILIZED) |
| 2283 | ISOBUTYL METHACRYLATE, STABILIZED |
| 2348 | BUTYL ACRYLATES, STABILIZED |
| 2352 | BUTYL VINYL ETHER, STABILIZED |
| 2396 | METHACRYLALDEHYDE, STABILIZED |
| 2521 | DIKETENE, STABILIZED |
| 2527 | ISOBUTYL ACRYLATE, STABILIZED |
| 2531 | METHACRYLIC ACID, STABILIZED |
| 2607 | ACROLEIN DIMER |
| 2618 | VINYLTOLUENES, STABILIZED |
| 2838 | VINYL BUTYRATE, STABILIZED |
| 3022 | 1,2-BUTYLENE OXIDE, STABILIZED |
| 3073 | VINYLPYRIDINES, STABILIZED |
| 3079 | METHACRYLONITRILE, STABILIZED |