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COMMITTEE OF EXPERTS ON THE TRANSPORT OF DANGEROUS GOODS AND ON THE GLOBALLY HARMONIZED SYSTEM OF CLASSIFICATION AND LABELLING OF CHEMICALS

Sub-Committee of Experts on the Transport of Dangerous Goods (Twenty-first session, 1-10 July 2002, agenda item 8 (d))

#### LISTING AND CLASSIFICATION

<u>Criteria for the corrosiveness of liquids and solids belonging to Class 8,</u>

Packing Group III, for steel and aluminium

Testing of liquid and solid substances as dangerous goods of class 8, packing group III,

according to their corrosive properties on steel or aluminium

Specification of the Test regulations (miscellaneous draft amendments to the

Model Regulations and the Manual of Tests and Criteria

on the Transport of Dangerous Goods)

**Submitted by the expert from Germany** 

## **Background**

- 1. At the twenty-first session of the Committee of Experts, the expert from Germany reiterated the request he had made at the last session of the Sub-Committee for comments on his proposal "Testing of liquid and solid substances as dangerous goods of class 8, packing group III, according to their corrosive properties on steel or aluminium Specification of the Test regulations" and asked that this topic should be placed on the Committee's programme of work for 2001 2002; his request was accepted (see ST/SG/AC.10/27, para. 23). Furthermore he invited interested experts to an informal working group to be convened in Germany.
- 2. At the nineteenth 19th session of the Sub-Committee of Experts on the Transport of Dangerous Goods the expert from Germany stated that he would submit an informal document regarding the outcome of the international meetings in Germany.

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- 3. At the twentieth session of the Sub-Committee of Experts on the Transport of Dangerous Goods, the expert from Germany submitted an informal document (UN/SCETDG/20/INF.27) regarding the outcome of two international meetings in Germany.
- 4. As reflected in the report of the Sub-Committee of Experts on its twentieth session (see ST/SG/AC.10/C.3/40, paras. 71 to 72) the expert from Germany was invited to submit a complete proposal to amend the Model Regulations and the Manual of Tests and Criteria on the Transport of Dangerous Goods.
- 5. This document includes new provisions for testing substances of class 8, packing group III with regard to their corrosive properties on steel or aluminium. Test criteria, material, reaction receptacle, volume/surface relation, preparation of metal samples, test temperature, operation period, test evaluation, test evaluation at local corrosion, test of corrosive properties of liquids which react corrosive under the influence of water, test of corrosive properties of solids and test of corrosive properties of substances being chemically unstable are proposed.

The purpose of this document is not to mandate re-testing of all materials that have been classified under the existing metal-corrosion criteria.

## Reasoning

6. Detailed reasons concerning the necessity of the implementation of a new test procedure including new reference materials are given in the German documents ST/SG/AC.10/C.3/2000/24 and UN/SCETDG/20/INF.27.

## **Proposal**

- 7. Proposals related to the "Recommendations on the Transport of Dangerous Goods, Model Regulations, Twelfth revised edition" and the "Manual of Tests and Criteria, Third revised edition" concerning new reference materials and new provisions for the "Test on corrosion", class 8, are considered below.
- 8. <u>Amendments to the "Recommendations on the Transport of Dangerous Goods, Model</u> Regulations, Twelfth revised edition"

In Chapter 2.8, No. 2.8.2.5, (c) (ii) the second and third sentence should be amended as follows:

"For the purposes of testing steel, type S235JR+CR (1.0037 resp. St 37-2), S275J2G3+CR (1.0144 resp. St 44-3) or a similar type, and for testing aluminium, non-clad, types 7075–T6 or AZ5GU-T6 shall be used. An acceptable test is prescribed in the Manual of Tests and Criteria, Part III, Section 37".

9. Amendments to the "Manual of Tests and Criteria, Third revised edition"

In "GENERAL TABLE OF CONTENTS", page v, the heading of "PART III" should be amended as follows: "PART III: CLASSIFICATION PROCEDURES, TEST METHODS AND CRITERIA RELATING TO CLASS 3, CLASS 4, DIVISION 5.1, CLASS 8 AND CLASS 9".

Section 37 should be amended as follows:

"CLASSIFICATION PROCEDURES, TEST METHODS AND CRITERIA RELATING TO CLASS 8"

#### 10. Amendment to contents of Part III

In the heading of Part III, page 301 "CLASS 8" should be added.

Section 37, page 303, should be amended as follows:

# 37. CLASSIFICATION PROCEDURES, TEST METHODS AND CRITERIA RELATING TO SUBSTANCES OF CLASS 8

- 37.1 PURPOSE
- 37.2 SCOPE
- 37.3 CLASSIFICATION PROCEDURES
- 37.4 TEST METHODS FOR CORROSIVE SUBSTANCES (CORROSION)
- 37.4.1 Test C.1 Test for determining corrosive properties of liquid substances, solid substances liquifying during transport or being hygroscopic in terms of requirements for classification as dangerous goods of class 8, packing group III (UNO)

## 11. Amendments to Section 30.1.1 and 30.1.2, page 305

In 30.1.1 new (f) should be added as follows:

# "(f) Corrosion of corrosive substances of class 8 (see section 37 of this Manual and chapter 2.8 of the Model Regulations);"

The existing letters (f) and (g) should be amended into (g) and (h)

In 30.1.2 the reference to Section 37 and Class 8 should be deleted.

# 12. Addition of "Classification procedures, test methods and criteria relating to substances of Class 8"

From page 353 the new Section 37 should be added; the reference in brackets should be deleted.

The new Section 37 should read as follows:

## "SECTION 37

## CLASSIFICATION PROCEDURES, TEST METHODS AND CRITERIA RELATING TO SUBSTANCES OF CLASS 8

## 37.1 Purpose

37.1.1 This section presents the United Nations scheme for the classification of the corrosion of corrosive substances of Class 8 (see paragraph 2.8.1 and 2.8.2 of the Model Regulations). A flowchart for the classification is given in figure 37.3.1 and the test prescriptions are given in section 37.4.

## **37.2** Scope

New products offered for transport should be subjected to the classification procedures as set out in paragraph 2.8.2.5, (c) (ii) of the Model Regulations unless it is impracticable (e.g. because of the physical properties) to perform the tests. Substances which cannot be tested should be classified by analogy with existing entries. The classification procedure

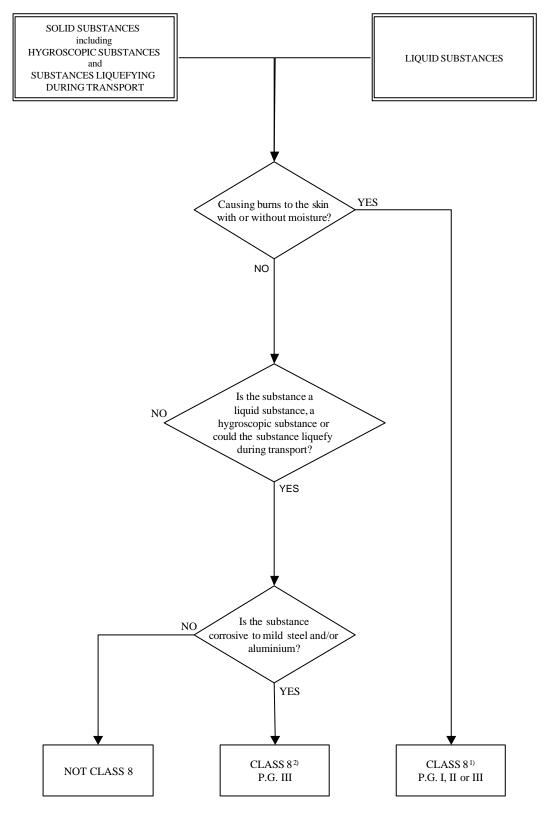
should be undertaken before a new product is offered for transport.

# 37.3 Classification procedure

The test procedures outlined here adequately assess the relative corrosion hazard of corrosive substances so that an appropriate classification for transport can be made.

37.3.1 Flowchart for the classification of corrosive substances of class 8

Figure 37.3.1 FLOW CHART FOR CLASSIFICATION OF CORROSIVE SUBSTANCES OF CLASS 8



<sup>&</sup>lt;sup>1</sup>) Dangerous to humans/animals due to corrosion to living tissue (OECD 404).

<sup>&</sup>lt;sup>2</sup>) Dangerous due to corrosion to mild steel/aluminium monitored over a period of one year.

## 37.4 Test methods for corrosive substances (corrosion)

37.4.1 Test C.1: Test for determining corrosive properties of liquid substances, solid substances liquefying during transport or being hygroscopic in terms of requirements for classification as dangerous goods of class 8, packing group III (UNO)

### 37.4.1.1 Introduction

This test is used to determine the corrosive properties of liquid substances, solid substances liquefying during transport or being hygroscopic in terms of requirements for classification as dangerous goods of class 8, packing group III (UNO)

## 37.4.1.2 Apparatus and material

For the purposes of testing steel, type **S235JR+CR** (1.0037 resp. St 37-2), S275J2G3+CR (1.0144 resp. St 44-3) or a similar type, and for testing aluminium, non-clad, types 7075–T6 or AZ5GU-T6 shall be used.

For exposure to medium being classified specimen of 2 mm thick plates shall be made of the following materials:

- Aluminium, non-clad types 7075-T6 or AZ5GU-T6 and
- Steel, S235JR+CR (1.0037 resp. St 37-2), S275J2G3+CR (1.0144 resp. St 44-3) or a similar type (Fig. 1)

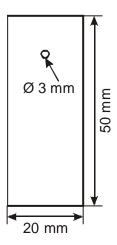


Fig. 1: specimen

At least 3 sets (9 specimens) of each material shall be used.

3 l cup-like reaction receptacles with face cut top and three necks NS 29/32 as well as one neck NS 14 made of glass or PTFE shall be used. The entrance of air, however, into the receptacle has to be guaranteed. Aluminium- and steel-samples have to be tested in different reaction receptacles. To prevent liquid loss a reflux condenser should be attached (Fig. 2).



Fig. 2: Exposure receptacle with reflux condenser

In order to carry out the corrosion test, corrosive medium shall have a minimum volume of 1.5 l to ensure enough reactive agent during the whole exposure time. This is even more important if the corrosion is not caused by the material to be tested but by its quantitatively small amount of impurities.

#### *37.4.1.3 Procedure*

Metal sheets shall be polished with grinding paper of 120 grid. After removal of grinding remainings with alcohol in the ultrasound bath and the degreasing with acetone the metal specimens shall be weighed out to ? 0.0002 g. No chemical surface preparation (pickling, etching etc.) shall be performed to prevent surface "irritations" (inhibition, passivation). Sheets shall be fixed inside the receptacle by non extruded PTFE-threads. Metal wire shall not be used. The test with the so prepared metals shall be initiated the same day to prevent reformation of oxide layer (especially on Al-samples). For each set one metal specimen has completely to be dipped into the solution, another one only half way and a third one shall hang in the gas phase. The distance between the upper edge of the completely inserted specimen and the surface of the liquid is supposed to be 10 mm. Losses of liquid shall be avoided.

The test temperature of 55 °C? 1 should be maintained constant and should be reached in the vapour phase as well.

Sheets shall be exposed at these stable conditions for at least one week (168? 1 hour).

After finishing the test the metal specimens shall be rinsed off and cleaned with a brush with synthetic or natural bristles (no metal). Only in case of not mechanically removable remainings (adherent corrosion product or depositions) inhibited pickling solutions should be used. In those cases a not exposed reference specimen needs to be treated in the same manner (time, temperature, concentration, surface preparation) to determine the weight loss caused by pickling solution. This value needs to be subtracted before evaluating the corrosion rate. After the final cleaning with alcohol and acetone in the ultrasound bath and drying the metal samples are going to be weighed. The resulting weight under consideration of the specific weight of the metal leads to the corrosion rate.

## 37.4.1.4 Test criteria and method of assessing results

Based on different corrosion behaviour 2 types of attack needs to be distinguished.

## 37.4.1.5 Test evaluation at uniform corrosion

In case of uniform corrosion attack weight loss of strongest attacked sample shall be used. Solution passes the test if weight loss on  $50 \times 20 \times 2$  mm sheet is less than amount stated in the following table

Table 1: Maximum weight loss of specimens after different exposure times

| exposure time | weight loss |
|---------------|-------------|
| 7 days        | 13.5 %      |
| 14 days       | 26.5 %      |
| 21 days       | 39.2 %      |
| 28 days       | 51.5 %      |

Those values are calculated based on a 6.25 mm/year corrosion rate. So within exposure time sample size decreases to following dimensions

Table 2: Threshold dimensions of specimens after different exposure times

| exposure time |          | specimen dimensions |          |   |         |
|---------------|----------|---------------------|----------|---|---------|
| 7 days        | 49.76 mm | X                   | 19.76 mm | X | 1.76 mm |
| 14 days       | 49.52 mm | X                   | 19.52 mm | X | 1.52 mm |
| 21 days       | 49.28 mm | X                   | 19.28 mm | X | 1.28 mm |
| 28 days       | 49.04 mm | X                   | 19.04 mm | X | 1.04 mm |

#### 37.4.1.6 Test evaluation at localised corrosion

In case of localised corrosion besides or instead of uniform corrosion attack of surface, the depth of the deepest hole respectively the strongest thickness reduction will be added or only be used to determine the intrusion. Deepest intrusion (to be determined metallographically) shall not exceed values shown in following table.

Table 3: Maximum intrusion depths after exposure time

| exposure time | max. intrusion depth |
|---------------|----------------------|
| 7 days        | 120 μm               |
| 14 days       | 240 μm               |
| 21 days       | 360 μm               |
| 28 days       | 480 μm               |

## 37.4.1.7 Test of corrosive properties of liquids which react corrosive under the influence of water

Substances reacting corrosive with water have to be tested according to their corrosive properties in water. The aqueous solution with the highest corrosion rate which mostly is in the middle concentration range, has to be determined by a test (see test of corrosive properties of solid substances liquefying during transport or being hygroscopic).

# 37.4.1.8 Test of corrosive properties of solid substances liquefying during transport or being hygroscopic

To evaluate solids which do not react corrosive in dry state on the above mentioned materials but may become corrosive while consuming humidity the aqueous solution with the highest possible corrosive effect on metals has to be determined.

Established by experiences, aqueous solutions in the middle concentration range have the highest corrosive effect on metallic materials. In case the most aggressive concentration is not known by the tester, he has to approach the concentration with the highest corrosiveness in steps of 10%. Therefore two or three tests have to be carried out at the same time.

## 37.4.1.9 *Test of the corrosive properties of substances being chemically unstable*

In case of chemically unstable products the substance as well as the reaction product(s) have to be tested in the same manner as described above. The corrosion test has to be carried out with the necessary safety precautions.

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