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COMMITTEE OF EXPERTS ON THE TRANSPORT OF DANGEROUS GOODS

Sub-Committee of Experts on the Transport of Dangerous Goods
(Fourteenth session,
Geneva, 8-18 December l997,
agenda item 2 (d))

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

Other draft amendments

Additional screening procedures

Transmitted by the European Chemical Industry Council (CEFIC)

Introduction

1. It is common practice in classification that full classification tests are not performed on all the substances which are candidates for classification. Technical decisions are made on the need for particular test programmes on the basis of the physical and chemical nature of the substance, together with supplementary information from small scale screening tests. CEFIC considers that provision of example screening procedures has considerable benefits since:

- smaller quantities of materials are required for testing reducing hazards to the test personnel and impact on the environment;
- it avoids unnecessary testing with consequent reduction in costs; and
- by providing consensus example procedures, a benchmark is given.

Accordingly, CEFIC submitted draft amendments to the Manual of Tests and Criteria on additional screening procedures (see document ST/SG/AC.10/C.3/1997/4) for consideration at the 13 th session of the Sub-committee.

2. The report of the Sub-Committee of experts on its thirteenth session recognizes that it is helpful to publish a voluntary guideline on screening procedures as an appendix to the Manual of Tests and Criteria:

> "The proposal to include additional screening procedures in the Manual of Tests and Criteria to enable an adequate hazard evaluation to be carried out without the need for larger scale classification tests was widely supported in principle. The representative of CEFIC was invited to collect detailed comments from all interested delegations and to submit a revised proposal for the next session which would take account of all these comments." [paragraph 112]

3. CEFIC considered all handed in comments. Comments that helped clarifying the screening procedures were gratefully accepted. Some comments stressed the responsibility of the test authority. This was taken into account by adding a reference to paragraph 1.1.2 of the general introduction in section 1 of the Manual on Tests and Criteria in the proposed text.

One comment received concerned screening procedures for mixtures which may be flammable liquids (calculation of flash point). This comment has been taken into account by clarifying the criteria under which the procedure can be used.

Proposals

4. CEFIC proposes screening procedures for:

(a) Substances which may have explosive properties (Class 1);

(b) Mixtures which may be flammable liquids (Class 3);

(c) Substances which may be flammable solids (Class 4);

(d) Substances which may be oxidizing substances and organic peroxides (Class 5).

5. Proposed text for a new Appendix 6 to the Manual of Tests and Criteria is given in the annex to this document together with consequential amendments.

Annex

PROPOSED AMENDMENTS TO THE MANUAL OF TESTS AND CRITERIA (ST/SG/AC.10/11.REV.2)

GENERAL TABLE OF CONTENTS

Appendices *Insert a new entry to read:*

"Appendix 6 SCREENING PROCEDURES"

GENERAL INTRODUCTION

1.1.2 *Append a new sentence to read*:

"In some cases, a small scale screening procedure may be used to decide whether or not it is necessary to perform larger scale classification tests. Suitable examples of procedures are given in the introductions to some test series and in Appendix 6."

1.2.1 *Amend the last sentence to read*:

"... Test Details, on an example method for emergency relief vent sizing of portable tanks for the transport of organic peroxides and on screening procedures."

INTRODUCTION TO PART II

20.3.3.3 *Amend the last indent and append a new sentence to read*:

"using rapid heating rates (differential scanning calorimetry, heating rates should normally be in the range 2 to 5 K/min.)

If differential scanning calorimetry is used, the extrapolated onset temperature is defined as being the point of intersection of the tangent drawn at the point of greatest slope on the leading edge of the peak with the extrapolated baseline."

CONTENTS OF APPENDICES

Insert a new entry to read:

"6 SCREENING PROCEDURES"

NEW APPENDIX 6

Insert a new Appendix 6 to read:

APPENDIX 6

SCREENING PROCEDURES

1. Purpose

1.1 Industry uses screening procedures to identify the hazard potential of raw materials, reactive mixtures and intermediates, products and by-products. The use of such procedures is essential to ensure safety during research and development and to ensure that new products and processes are as safe as possible. These procedures usually consist of a combination of a theoretical appraisal and small-scale tests and, in many cases, enable an adequate hazard evaluation to be carried out without the need for larger scale classification tests. This reduces the quantity of material required, lessens any detrimental effect on the environment and minimizes the amount of unnecessary testing.

1.2 The purpose of this appendix is to present example screening procedures. It should be used in conjunction with any screening procedures given in the introductions to the relevant test series. With the specified safety margin, the results from the screening procedures adequately predict when it is not necessary to perform the classification test as a negative result would be obtained. They are presented for guidance and their use is not compulsory. Other screening procedures may be used provided that adequate correlation has been obtained with the classification tests on a representative range of substances and there is a suitable safety margin.

2. Scope

2.1 A hazard evaluation for a new substance should be undertaken before it is offered for transport. Initially this evaluation can use the screening procedures given in this Appendix. If the screening procedure indicates that there is a hazard, the full classification procedure should be applied.

2.2 The screening procedures are only applicable to substances and stable, homogeneous mixtures of substances. If a mixture can separate out during transport, the screening procedure should also be performed on each reactive component of the mixture in addition to the mixture.

2.3 The remarks 1.1.2 from section 1 „general introduction“ are emphasized that competence on the part of the testing authority is assumed and responsibility for classification is left with them.

3. Screening procedures for substances which may have explosive properties (Class 1)

3.1 The screening procedure may be used for new substances which are suspected of having explosive properties. When considering the explosive properties of self-reactive substances of Division 4.1 or organic peroxides of Division 5.2, refer to Part II of this manual and section 5.1 of this appendix. It should not be used for substances manufactured with the intention of producing a practical explosive or pyrotechnic effect.

3.2 Explosive properties are associated with the presence of certain chemical groups in a molecule which can react to produce very rapid increases in temperature or pressure. The screening procedure is aimed at identifying the presence of such reactive groups and the potential for rapid energy release. If the screening procedure identifies the material to be a potential explosive, the Class 1 Acceptance Procedure (see 10.3) should be applied.

Note: Neither a Series 1 type (a) propagation of detonation test nor a Series 2 type (a) test of sensitivity to detonative shock is required if the exothermic decomposition energy of organic materials is less than 800 J/g.

3.3 The acceptance procedure for Class 1 explosives need not be applied:

(a) When there are no chemical groups associated with explosive properties present in the molecule. Examples of groups which may indicate explosive properties are given in Table A6.1

Table A6.1 EXAMPLES OF CHEMICAL GROUPS INDICATING EXPLOSIVE PROPERTIES IN ORGANIC MATERIALS

Structural feature	Examples
C-C unsaturation	Acetylenes, acetylides, 1,2-dienes
C-Metal, N-Metal	Grignard reagents, organo-lithium compounds
Contiguous nitrogen atoms	Azides, aliphatic azo compounds, diazonium salts, hydrazines, sulphonylhydrazides
Contiguous oxygen atoms	Peroxides, ozonides
N-O	Hydroxylamines, nitrates, nitro compounds, nitroso compounds, N-oxides, 1,2-oxazoles
N-halogen	Chloramines, fluoroamines
O-halogen	Chlorates, perchlorates, iodosyl compounds

or

(b) When the substance contains chemical groups associated with explosive properties which include oxygen and the calculated oxygen balance is less than -200.

The oxygen balance is calculated for the chemical reaction:

$$C_xH_yO_z + [x + (y/4)-(z/2)].\ O_2 \rightarrow x.\ CO_2 + (y/2).\ H_2O$$

using the formula:

$$\text{oxygen balance} = -1600.[2.x +(y/2) -z]/\text{molecular weight}$$

or

(c) When the organic substance or a homogenous mixture of organic substances contain chemical groups associated with explosive properties but the exothermic decomposition energy is less than 500 J/g and the onset of exothermic decomposition is below 500 ºC. (The temperature limit is to prevent the procedure being applied to a large number of organic materials which are not explosive but which will decompose slowly above 500 ºC to release more than 500 J/g.) The exothermic decomposition energy may be determined using a suitable calorimetric technique (see 20.3.3.3).

or

(d) For mixtures of inorganic oxidizing substances of Division 5.1 with organic material(s), the concentration of the inorganic oxidizing substance is:

less than 15 %, by mass, if assigned to Packing Group I (high hazard) or II (medium hazard);
less than 30 %, by mass, if assigned to Packing Group III (low hazard).

3.4 When the substance is a mixture containing any known explosives, the class 1 acceptance procedure should be applied.

4. Screening procedures for mixtures which may be flammable liquids (Class 3)

4.1 The procedure only applies to possible flammable mixtures containing known flammable liquids in defined concentrations although it may contain non-volatile components e.g. polymers, additives etc. The flash point of these mixtures need not be determined experimentally if the calculated flash point of the mixture, using the method given in 4.2, is at least 5 °C greater than the relevant classification criterion and provided that:

(a) The composition of the mixture is accurately known (if the material has a specified range of composition the composition with the lowest calculated flash point should be selected for assessment);

(b) The flash point (closed cup as given in 2.3.3 of the Recommendations) of each component is known (an appropriate correlation has to be applied when these data are extrapolated to other temperatures than test conditions);

(c) The activity coefficient is known for each component as present in the mixture including the temperature dependence;

(d) The liquid phase is homogeneous.

4.2 A suitable method is described by Gmehling and Rasmussen (Ind. Eng. Chem. Fundament, **21**, 186, (1982)). For a mixture containing non-volatile components, e.g. polymers or additives, the flash point is calculated from the volatile components. It is considered that a non-volatile component only slightly decreases the partial pressure of the solvents and the calculated flash point is only slightly below the measured value.

5. Screening procedures for substances which may be flammable solids (Class 4)

5.1 *Substances which may be self-reactive substances (Division 4.1)*

The classification procedures (see section 20.4) for self-reactive substances need not be applied if:

(a) There are no chemical groups present in the molecule associated with explosive or self-heating properties; examples of such groups are given in Tables A6.1 and A6.2.

Table A6.2 EXAMPLES OF CHEMICAL GROUPS INDICATING SELF-REACTIVE PROPERTIES IN ORGANIC MATERIALS

Structural feature	Examples
Mutually reactive groups	Aminonitriles, haloanilines, organic salts of oxidizing acids
S=O	Sulphonyl halides, sulphonyl cyanides, sulphonyl hydrazides
P-O	Phosphites
Strained rings	Epoxides, aziridines
Unsaturation	Olefins, cyanates

or

(b) For a single organic substance or a homogeneous mixture of organic substances, the onset of exothermic decomposition is greater than 175 °C or the exothermic decomposition energy is less than 300 J/g. The onset temperature and isothermal decomposition energy may be estimated using a suitable calorimetric technique (see 20.3.3.3).

5.2 *Substances which may be liable to spontaneous combustion (Division 4.2)*

5.2.1 The classification procedure for *pyrophoric solids and liquids* need not be applied when experience, in production or handling, shows that the substance do not ignite spontaneously on coming into contact with air at normal temperatures (i.e. the substance is known to be stable at room temperature for prolonged periods of time (days)).

5.2.2 The classification procedure for *self-heating substances* need not be applied if the results of a screening test can be adequately correlated with the classification test and an appropriate safety margin is applied. Examples of screening tests are:

(a) The Grewer Oven test (VDI guideline 2263, part 1, 1990, *Test methods for the Determination of the Safety Characteristics of Dusts*) with an onset temperature 80 K above the reference temperature for a volume of 1 *l* (33.3.1.6).

(b) The Bulk Powder Screening Test (Gibson, N. Harper, D. J. Rogers, R. *Evaluation of the fire and explosion risks in drying powders,* Plant Operations Progress, **4** (3), 181 - 189, 1985) with an onset temperature 60 K above the reference temperature for a volume of 1.l (33.3.1.6).

5.3 *Substances which in contact with water may react to emit flammable gases (Division 4.3)*

The classification procedure for substances which may react with water to emit flammable gases need not be applied if:

(a) The chemical structure of the substance does not contain metals or metalloids; or

(b) Experience in production or handling shows that the substance does not react with water, e.g. the substance is manufactured in water or washed with water; or

(c) The substance is known to be soluble in water to form a stable mixture.

6. Screening procedures for substances which may be oxidizing substances and organic peroxides (Class 5)

6.1 *Substances which may be oxidizing substances (Division 5.1)*

6.1.1 For *organic compounds*, the classification procedure for oxidizing substances of Division 5.1 need not be applied if:

(a) The compound does not contain oxygen, fluorine or chlorine; or

(b) The compound contains oxygen, fluorine or chlorine and these elements are chemically bonded only to carbon or hydrogen.

6.1.2 For *inorganic substances*, the test procedure in Section 34 need not be applied if the substance does not contain any oxygen or halogen atoms.

6.2 *Substances which may be organic peroxides (division 5.2)*

6.2.1 Organic peroxides are classified by definition based on their chemical structure and on the available oxygen and hydrogen peroxide content of formulations (see 20.2.2).