

Economic and Social Council

Distr. GENERAL

TRANS/WP.15/AC.1/2003/20/Add.1 2 January 2003

ENGLISH ONLY

ECONOMIC COMMISSION FOR EUROPE

INLAND TRANSPORT COMMITTEE

Working Party on the Transport of Dangerous Goods

<u>Joint Meeting of the RID Safety Committee and the</u> <u>Working Party on the Transport of Dangerous Goods</u> (Bern, 24-28 March 2003)

REVISION OF THE PROOF OF THE CHEMICAL COMPATIBILITY WITH LIQUIDS FOR PLASTICS DRUMS AND JERRICANS, COMPOSITE PACKAGINGS (PLASTICS MATERIAL), RIGID PLASTICS IBCS AND COMPOSITE IBCS

Addendum 1

Informal Working Group "Assimilation list" to the Joint ADR/RID Meeting

Report on the meeting in Bad Homburg, Germany (17 June 2002)

Transmitted by the Government of Germany */

1. During its meeting in March 2002, the Joint Meeting had agreed to accept Germany's offer to invite an informal working group to address the outcome of the discussion on revised requirements for the chemical compatibility tests for plastics packagings and IBCs (see items 38-34 of the report OCTI/RID/GT-III/2002-A-TRANS/WP.15/AC.1/88).

2. The informal working group "Assimilation list" met in Bad Homburg on 17-18 June with the attendance of experts from Germany, Sweden, EUPC and CEN.

<u>*/</u> Circulated by the Central Office for International Carriage by Rail (OCTI) under the symbol OCTI/RID/GT-III/2003/20/Add.1.

3. The following papers were considered: Document OCTI/RID/GT-III/2002/1 (Germany) and informal documents INF. 26, INF. 32 and INF. 35 (Germany).

4. Compared with the earlier suggestions put forward by Germany on the subject, some additional changes were discussed. In particular, it was realized that the assimilation of filling substances to standard liquids is usually subject to decisions taken by the filler/user of packagings and IBCs, based on the performance tests with standard liquids during the design type test procedure (see current 6.1.5.2.6: When a packaging design-type has satisfied the approval tests with a standard liquid, the comparable filling substances listed in 6.1.6.2 may be accepted for carriage without further testing, subject to ...). Therefore, it was deemed logic to allocate the revised assimilation procedure to Part 4 of the ADR/RID. Requirements, related to the application of the laboratory tests and the approval tests with standard liquids, were kept in Part 6.

5. On background and traceability, it was confirmed by the German experts that the principles applied for the selection of entries of the assimilation list and its allocation to standard liquids were the same as for the current list: it is based on the results of numerous compatibility tests for packaging and IBC design types, neutralized and combined with chemical basic knowledge. However, due to its private character, tracing back to the test reports will only be possible for the competent authorities. Since the draft of the new list has been published, some amendments have been put forward and been considered. This includes the outcome of the discussions within the CEN/ISO standard project on that issue, including the outcome of the internal inquiry.

6. Among others, the English term "average" molecular mass polyethylene, which was a wrong translation of the German term, was changed into "medium" molecular mass polyethylene throughout the text.

7. With respect to the numbering of the amended and new paragraphs, the general principle to preserve the structure of the UN Model Regulations was taken into account.

8. The working group did not decide on the inclusion of several examples, which were part of the previous German proposals, and deemed it necessary to support the understanding of this difficult matter. They were put in square brackets, which requires a decision by the Joint Meeting.

9. The working group agreed on the need for an additional document to be provided for the users in order to make them aware of the significant changes made in the assimilation list, particularly with respect to restrictions compared with the current version. Germany would be prepared to provide such a document, once the Joint Meeting has decided on the final contents.

10. The flow-charts as part of the assimilation procedures are proposed to be named "schemes".

11. Some modifications to the assimilation list were agreed upon as follows:

11.1 According to general principles, all substances defined on the basis of national standards should be cancelled. That applies to the following entries:

- 1136 Solvent naphtha heavy DIN 51633 C10-Ar
- 1136 Solvent naphtha light DIN 51633 C9-Ar
- 1203 Motor spirit, Super DIN 51600-S-leaded
- 1268 FAM-normal benzine, DIN 51635-A
- 1268 Safety lamp petroleum spirit, DIN 51634-A
- 1268 Special boiling point spirits, DIN 51631°-1-A
- 1268 Special boiling point spirits, DIN 51631°-1-B
- 1268 Special boiling point, DIN 51631°-2-A
- 1268 Special boiling point, DIN 51631°-2-B
- 1268 Special boiling point spirits, DIN 51631°-3
- 3082 Fuel oil, DIN 51603-S-K-04
- 3082 Fuel oil M, DIN 51603
- 3082 Heating oil, heavy, DIN 51603-S-03
- 3082 Solvent naphtha heavy, DIN 51633 C10-Ar.

11.2. All entries of UN No. 2571, 2584 and UN No. 2586 assimilated to the combination of standard liquids "n-Butyl acetate/n-butyl acetate-saturated wetting solution and Water" should be amended. Those entries should indicate the standard liquid "n-Butyl acetate/n-butyl acetate-saturated wetting solution" only.

Substitute in column 7 "n-Butyl acetate/n-butyl acetate-saturated wetting solution and Water" by

"n-Butyl acetate/n-butyl acetate-saturated wetting solution" for:

- 2571 Ethylsulphuric acid
- 2584 Alkylsulphonic acids, liquid, with more than 5% free sulphuric acid
- 2584 Dodecylbenzene sulphonic acid, liquid, with more than 5% free sulphuric acid
- 2584 Arylsulphonic acids, liquid, with more than 5% free sulphuric acid
- 2586 Alkylsulphonic acids, liquid, with not more than 5% free sulphuric acid
- 2586 Dodecylbenzene sulphonic acid, liquid, with not more than 5% free sulphuric acid
- 2586 Arylsulphonic acids, liquid, with not more than 5% free sulphuric.

11.3 Based on performed laboratory tests, there is evidence that (1-Methoxy-2-propyl) acetate can be assimilated to the standard liquid "n-Butyl acetate/n-butyl acetate-saturated wetting solution". Therefore, a new line was inserted after "1993 Flammable liquid, n.o.s., vapour pressure at 50°C not more than 110 kPa", reading:

- "UN No.: 1993, Name: (1-Methoxy-2-propyl) acetate, Class: 3, Classificaton code: F1, Packing group: III, Standard liquid: n-Butyl acetate/n-butyl acetate-saturated wetting solution".

As a result of the meeting, the following amendments are proposed:

3. Amendments to Part 4

Add a new sub section before 4.1.2 with the title and paragraphs as outlined below:

4.1.1.19 Verification of the chemical compatibility of plastics packagings and IBCs by assimilation of filling substances to standard liquids

4.1.1.19.1 Scope

For high and medium molecular mass polyethylene packagings as specified in 6.1.5.2.6 and for high molecular mass polyethylene IBCs as specified in 6.5.4.3.6, the chemical compatibility with filling substances may be verified without further testing by assimilation to standard liquids following the procedures as set out in 4.1.1.19.3 to 4.1.1.19.5 and using the list in 4.1.1.19.6, provided that the particular design types have been tested with these standard liquids in accordance with 6.1.5 or 6.5.4, respectively, and that the conditions in 4.1.1.19.2 are met. When assimilation in accordance with this sub section is not possible, the chemical compatibility needs to be proved in another way. This may be done by additional design type testing or by laboratory tests in accordance with 6.1.5.2.7.

[Note: Independent from the provisions of this section the use of packagings and

IBCs for a specific filling substance is subject to the limitations of chapter 3.2, Table

A and the packing instructions in chapter 4.1]

4.1.1.19.2 Conditions

The relative densities of the filling substances shall not exceed that used to determine the height for the drop test and the mass for the stacking test with the assimilated standard liquid. The vapour pressures of the filling substances at 50 °C or 55 °C shall not exceed that used to determine the pressure for the internal pressure test with the assimilated standard liquid. In case that filling substances are assimilated to a combination of standard liquids, the minimum values of the drop heights, stacking masses and internal test pressures of all of those standard liquids shall be considered. [Example: UN 1736 Benzoyl chloride is assimilated to the combination of standard liquids "Mixture of hydrocarbons and wetting solution". Benzovl chloride has a vapour pressure of 0.34 kPa at 50 °C and a density of approximately 1.2 kg/litres. Design type tests were frequently performed at the minimum required test level. In practice this means that the stacking test is performed with stacking loads considering a density of 1.0 for the mixture of hydrocarbons and a density of 1.2 for the wetting solution. As a consequence chemical compatibility of such tested design types would not be proved for benzoyl chloride by reason of the inadequate test level of the design type with the standard liquid "mixture of hydrocarbons. (Due to the fact that the inner hydraulic test pressure in the most cases is 100 kPa at the minimum, the vapour pressure of benzoyl chloride would be covered by such test level.]

All components of the filling substance, which may be a solution, mixture or preparation, such as wetting agents in detergents and disinfectants, irrespective whether dangerous or non-dangerous, shall be included in the assimilation procedure.

4.1.1.19.3 Assimilation procedure

The following steps shall be taken to assign filling substances to listed substances or groups of substances (see also scheme in **Figure 4.1.1.19-1**).

- a) Classify the filling substance in accordance with the procedures and criteria of Part 2 (determination of the UN Number and packing group).
- b) Go to the UN number in column 1 of the assimilation list.
- c) Select the line that most corresponds to this UN Number in terms of packing group, concentration, flashpoint etc. by means of the information given in columns 2, 3 and 6, if there is more than one entry for this UN number.
- d) If there is no line under this UN Number and packing group where the substance or group of substances is mentioned by name, the correct line of the corresponding single entry or collective entry may be selected, if available.

[Example: 3-Methyl-1-heptene is not indicated as a specific isomer mentioned by name among the entries of UN Number 1216 in the assimilation list. In such case the line with the name Isooctene may be selected, if the properties of the isomer are in accordance with the criteria of class 3. classification code F1 and packing group II even if the entry "isomeric mixture" is indicated in cell of the column "Description".]

e) Apply the "Rule for collective entries" if this is indicated in column 7 of the selected line as described in 4.1.1.19.5.

4.1.1.19.4 Aqueous solutions

Aqueous solutions of substances and groups of substances assimilated to specific standard liquid(s) in accordance with 4.1.1.19.3 may also be assimilated to that/those standard liquid(s) provided the following conditions are met:

- the aqueous solution can be assigned to the same UN number as the listed substance in accordance with the criteria of 2.1.3.3, and
- the aqueous solution is not specifically mentioned by name otherwise in the assimilation list in 4.1.1.19.3, and
- no chemical reaction is taking place between the dangerous substance and the solvent water.

[Example: Aqueous solutions of UN 1120 tert-Butanol may be assigned to the standard liquid acetic acid.

- Reasons:
- Pure tert-Butanol itself is assigned to the standard liquid acetic acid in the assimilation list.
- Aqueous solutions of tert-Butanol can be classified under the entry UN 1120 BUTANOLS in accordance with 2.1.3.3. Because the aqueous solution of tert-Butanol does not differ from the entries of the pure substances relating to the class, the packing group(s) and the physical state. Furthermore, the entry 1120 BUTANOLS is not explicitly limited to the pure substances, and aqueous solutions of these substances are not specifically mentioned by name otherwise in chapter 3.2, Table A.
- UN 1120 BUTANOLS do not react with water under normal conditions of transport.]
- 4.1.1.19.5 Rule for collective entries:

For the assimilation of filling substances for which "Rule for collective entries" is indicated in column 7, the following steps shall be taken and conditions be met (see also scheme in **Figure 4.1.1.19-2**):

- a) Perform the assimilation procedure for each component of the solution, mixture or preparation in accordance with 4.1.1.19.3 taking into account the conditions in 4.1.1.19.2. In the case of generic entries, components may be neglected, that are known to have no damaging effect on PE-HD (e.g. solid pigments in UN 1263 PAINT or PAINT RELATED MATERIAL).
- b) A solution, mixture or preparation cannot be assimilated to a standard liquid, if
 - the UN Number and packing group of one or more of the dangerous components does not appear in the list or
 - "Rule for collective entries" is indicated for one or more of the components, or
 - (with exemption of UN 2059 NITROCELLULOSE SOLUTION; FLAMMABLE) the classification code of one or more of its dangerous components differs from that of the solution, mixture or preparation.
- c) If all dangerous components are listed in the assimilation list, and its classification codes are in accordance with the classification code of the solution, mixture or preparation itself, and all dangerous components are assimilated to the same standard liquid or combination of standard liquids in column 7, the chemical compatibility of the solution, mixture or preparation may be regarded as proven taking into account 4.1.1.19.1.
- d) If all dangerous components are listed in the assimilation list and its classification codes are in accordance with the classification code of the

solution, mixture or preparation itself, but different standard liquids are indicated in column 7, the chemical compatibility may only be regarded as proven for the following combinations of standard liquids taking into account 4.1.1.19.1:

- water/nitric acid 55 %; with exemption of inorganic acids with the classification code C1, which are assigned to standard liquid water
- water/wetting solution;
- water/acetic acid;
- water/mixture of hydrocarbons
- water/n-butyl acetate n-butyl acetate-saturated wetting solution.

[Example 1: Mixture of UN 1940 THIOGLYCIC ACID (50%) and UN 2531 METHACRYLIC ACID; STABILIZED (50%); classification of the mixture: UN 3265 CORROSIVE LIQUID, ACIDIC, ORGANIC, N.O.S.

- Both the UN Numbers of the components and the UN Number of the mixture are included in the assimilation list.
- Both the components and the mixture have the same classification code: C3.
- UN 1940 THIOGLYCIC ACID is assimilated to standard liquid "acetic acid", and UN 2531 METHACRYLIC ACID; STABILIZED is assimilated to standard liquid "n-butyl acetate/n-butyl acetate-sat. wetting solution". According to paragraph d) this is **not** an acceptable combination of standard liquids. The chemical compatibility of the mixture has to be proved by another way.

Example 2: Mixture of UN 1793 ISOPROPYL ACID PHOSPHATE (50%) and UN 1803 PHENOLSULPHONIC ACID, LIQUID (50%); classification of the mixture: :UN 3265 CORROSIVE LIQUID, ACIDIC, ORGANIC, N.O.S.

- Both the UN Numbers of the components and the UN Number of the mixture are included in the assimilation list.
- Both the components and the mixture have the same classification code: C3.
- UN 1793 ISOPROPYL ACID PHOSPHATE is assimilated to standard liquid "wetting solution", and UN 1803 PHENOLSULPHONIC ACID, LIQUID is assimilated to standard liquid "water". According to paragraph d) this is one of the acceptable combinations of standard liquids As a consequence the proof of the chemical compatibility may be regarded as given for this mixture, provided the packaging design type is approved for the standard liquids wetting solution and water.]

4.1.1.19.5 Assimilation list

In the following table (assimilation list) dangerous substances are sorted in the order of their UN Numbers. As a rule, each line deals with a dangerous substance, single entry or collective entry covered by a specific UN number. However, several consecutive lines may be used for the same UN number, if substances belonging to the same UN Number have different names (e.g. individual isomers of a group of substances), different chemical properties, different physical properties and/or different transport conditions. In such cases the single entry or collective entry within the particular packing group is the last one of such consecutive lines.

Columns 1 to 6 are used to identify the substance for the purpose of this sub section similar to the structure of the dangerous goods list in Chapter 3.2. The last column indicates the standard liquid(s) to which the substance can be assimilated.

In detail, the columns can be explained as follows:

Column 1	UN No. This column contains the UN number
	- of the dangerous substance if the substance has been assigned to its own specific UN Number, or
	- of the collective entry to which dangerous substances not listed by name have been assigned in accordance with the criteria ("decision trees") of Part 2.
Column 2	Name
	This column contains the name of the substance, the name of the single entry, which may cover various isomers, or the name of the collective entry itself.
	The indicated name can deviate from the applicable proper shipping name.
Column 3	Description
Column 3	Description This column contains a descriptive text to clarify the scope of the entry in those cases when the classification, the transport conditions and/or the chemical compatibility of the substance may be variable.
Column 3 Column 4	This column contains a descriptive text to clarify the scope of the entry in those cases when the classification, the transport conditions
	This column contains a descriptive text to clarify the scope of the entry in those cases when the classification, the transport conditions and/or the chemical compatibility of the substance may be variable.
	This column contains a descriptive text to clarify the scope of the entry in those cases when the classification, the transport conditions and/or the chemical compatibility of the substance may be variable. Class This column contains the number of the Class, whose heading covers the dangerous substance. This Class number is assigned in
Column 4	This column contains a descriptive text to clarify the scope of the entry in those cases when the classification, the transport conditions and/or the chemical compatibility of the substance may be variable. Class This column contains the number of the Class, whose heading covers the dangerous substance. This Class number is assigned in accordance with the procedures and criteria of Part 2.

This column contains the packing group number (I, II or III) assigned to the dangerous substance. These packing group numbers are assigned on the basis of the procedures and criteria of Part 2. Certain substances are not assigned to packing groups.

Column 7 Standard Liquid

This column indicates either a standard liquid or a combination of standard liquids to which the substance can be assimilated as definite information, or contains a reference to the rule for collective entries in 4.1.1.19.5.

(Assimilation list to be inserted here)

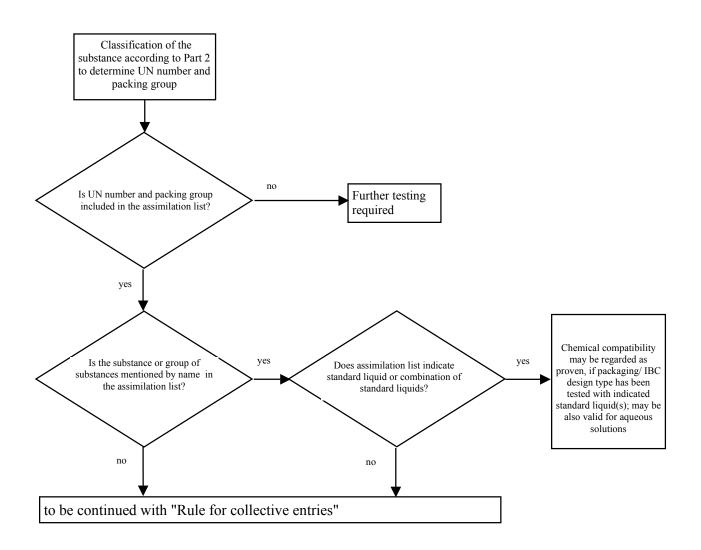
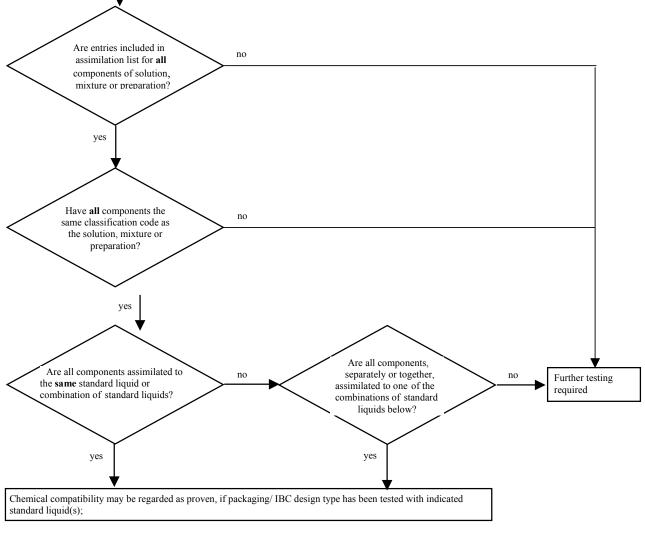


Figure 4.1.1.19-1: Scheme for the assimilation of filling substances to standard liquids

TRANS/WP.15/AC.1/2003/20/Add.1 page 11 Single entries, collective entries, solutions, mixtures, preparations with indication "Rule for collective entries" in



Acceptable combinations of standard liquids:

- water/nitric acid (55%), with exemption of inorganic acids of classification code C1 which are assigned to standard liquid water
- water/wetting solution
- water/acetic acid
- water/mixture of hydrocarbons
- water/n-butyl acetate n-butyl acetate saturated wetting solution

Figure 4.1.1.19-2: Scheme "Rule for collective entries"

assimilation list

4. <u>Amendments to Part 6</u>

2.1 Amendments to Section 6.1

Amend 6.1.5.2.6 as follows:

- 6.1.5.2.6 For high molecular mass polyethylene drums and jerricans in accordance with 6.1.4.8 and if necessary, composite packagings of high molecular mass polyethylene in accordance with 6.1.4.19, conforming to the following specifications:
 - relative density at 23° C after thermal conditioning for one hour at 100 C ≥ 0.940 , in accordance with ISO Standard 1183,
 - melt flow rate at 190° C/21.6 kg load ≤ 12 g/10 min, in accordance with ISO Standard 1133,

and for jerricans in accordance with 6.1.4.8 and, if necessary, for composite packagings in accordance with 6.1.4.19 of medium molecular mass polyethylene conforming to the following specifications:

- relative density at 23° C after thermal conditioning for one hour at 100° C ≥ 0.940 , in accordance with ISO Standard 1183,
- melt flow rate at 190° C/2.160 kg load ≤ 0.5 g/10 min and ≥ 0.1 g/10 min, in accordance with ISO Standard 1133,
- melt flow rate at 190°C/5 kg load \leq 3 g/10 min and \geq 0.5 g/10 min, in accordance with ISO Standard 1133,

the chemical compatibility may be verified by storage of the required test samples for three weeks at 40 °C with the appropriate standard liquid(s) as specified in 6.1.6.1, to which filling substances may be assimilated in accordance with the procedures set out in 4.1.1.19. The selection of the standard liquid(s) shall be related to the processes of deterioration on the samples, as there are softening through swelling, cracking under stress, molecular degradation and combinations thereof.

For the first and last 24 hours of storage, the test samples shall be placed with the closure downwards. However, packagings fitted with a vent shall be so placed on each occasion for five minutes only. After this storage, the test samples shall undergo the tests prescribed in 6.1.5.3 to 6.1.5.6.

Where this standard liquid is water, pre-storage in accordance with this procedure is not required.

The compatibility test for tert-Butyl hydroperoxide with more than 40% peroxide content and peroxyacetic acids of Class 5.2 shall not be carried out using standard liquids. For these substances, proof of sufficient chemical compatibility of the test

samples shall be provided during a storage period of six months at ambient temperature with the substances they are intended to carry.

Results of tests in accordance with this paragraph are also valid for packagings made from these materials, the surface of which is fluorinated.

Amend 6.1.5.2.7 as follows:

6.1.5.2.7 For packagings made of high or medium molecular mass polyethylene, as specified in 6.1.5.2.6 the chemical compatibility with filling substances may also be verified by laboratory tests¹ proving that the effect of such filling substances on the test specimens is less than that of the appropriate standard liquid(s) taking into account the relevant processes of deterioration. The same conditions as those set out in 4.1.1.19.2 shall apply with respect to relative density and vapour pressure.

Amend heading of 6.1.6 as follows:

<u>Chemical compatibility testing of high and medium molecular mass polyethylene</u> <u>packagings</u>

Text of 6.1.6.1 unchanged;

6.1.6.2 deleted (replaced by 4.1.1.19).

2.2 Amendments to 6.5

Add new Paragraphs after 6.5.4.3.5 as follows and renumber the subsequent paragraphs:

- 6.5.4.3.6 For high molecular mass polyethylene rigid plastics IBCs (types 31H1 and 31H2) in accordance with 6.5.3.3 and composite IBCs (types 31HZ1 and 31HZ2) in accordance with 6.5.3.4, conforming to the following specifications:
 - relative density at 23° C after thermal conditioning for one hour at 100° C ≥0.940, 0.940, in accordance with ISO Standard 1183,
 - melt flow rate at 190° C/21.6 kg load \geq 12 g/10 min, in accordance with ISO Standard 1133,

the chemical compatibility may be verified by storage of the required test samples for three weeks at 40 °C with the appropriate standard liquid(s) as specified in 6.1.6.1, to which filling substances may be assimilated in accordance with the procedures set out in 4.1.1.19. The selection of the standard liquid(s) shall be related to the processes of deterioration on the samples, as there are softening through swelling, cracking under stress, molecular degradation and combinations thereof.

Where this standard liquid is water, pre-storage in accordance with this procedure is not required.

¹ Laboratory tests for the proof of the chemical compatibility of high molecular mass polyethylene according to 6.1.5.2.6 proving that the effect of filling substances (substances, mixtures and preparations) is less than that of the standard liquids set out in 6.1.6.1 see guidelines in the non-legally binding part of the RID published by the Central Office for the International Carriage by Rail (printed at the end of Chapter 6.1)

The compatibility test for tert-Butyl hydroperoxide with more than 40% peroxide content and peroxyacetic acids of Class 5.2 shall not be carried out using standard liquids. For these substances, proof of sufficient chemical compatibility of the test samples shall be provided during a storage period of six months at ambient temperature with the substances they are intended to carry.

Results of tests in accordance with this paragraph are also valid for IBCs made from these materials, the surface of which is fluorinated.

6.5.4.3.7 For IBC design types, made of high molecular mass polyethylene, as specified in 6.1.5.2.6, the chemical compatibility with filling substances may also be verified by laboratory tests⁴ proving that the effect of such filling substances on the test specimens is less than that of the appropriate standard liquid(s) taking into account the relevant processes of deterioration. The same conditions as those set out in 4.1.1.19.2 shall apply with respect to relative density and vapour pressure.

⁴ Laboratory tests for the proof of the chemical compatibility of high molecular mass polyethylene according to 6.1.5.2.6 proving that the effect of filling substances (substances, mixtures and preparations) is less than that of the standard liquids set out in 6.1.6.1 see guidelines in the non-legally binding part of the RID published by the Central Office for the International Carriage by Rail (printed at the end of Chapter 6.1).