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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

Transmitted by the Government of Germany */

Summary

- 1. On the basis of document OCTI/RID/GT-III/2002/1 (TRANS/WP.15/AC.1/2002/1) and of the related informal documents INF. 26, INF. 32 and INF. 35 submitted at the March 2002 session, the Joint Meeting had agreed to accept the offer by the Government of Germany to host an informal working group to discuss revised requirements for the chemical compatibility tests for plastics packagings and IBCs (see OCTI/RID/GT-III/2002-A-TRANS/WP.15/AC.1/88, paras 30-34).
- 2. The informal working group "Assimilation list" met in Bad Homburg on 17 and 18 June 2002 with experts from Sweden, Germany, EUPC and CEN. The report is reproduced in addendum 1 to this document
- 3. This proposal of Germany is based on the text proposed by the informal working group with minor amendments clarifying the meaning of the text and elimination of errors.
- 4. No decision was made on the inclusion of several notes and examples, which were part of the previous German proposals and deemed necessary to support the understanding of this difficult matter. These notes and examples are placed between square brackets, for decision by the Joint Meeting.

^{*/} Circulated by the Central Office for International Carriage by Rail (OCTI) under the symbol OCTI/RID/GT-III/2003/20.

1. 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 6.5.4.3.5 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 taking into account 6.1.6 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 shall be done by design type testing or by laboratory tests in accordance with 6.1.5.2.5 or 6.1.5.2.7 for packagings and in accordance with 6.5.4.3.3 or 6.5.4.3.6 for IBCs.

[Note: Independent from the provisions of this sub-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 performed successfully according to 6.1.5.3.4 or 6.5.4.1.3 and the mass for the stacking test performed successfully according to 6.1.5.6 or where necessary according to 6.5.4.6 with the assimilated standard liquid(s). 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 (hydraulic) test performed successfully according to 6.1.5.5.4 or 6.5.4.8.4.2 with the assimilated standard liquid(s). In case that filling substances are assimilated to a combination of standard liquids, the minimum values derived from the applied drop heights, stacking masses and internal test pressures of all of those standard liquids shall be considered comparing these values with the corresponding values the filling substances.

[Example: UN 1736 Benzoyl chloride is assimilated to the combination of standard liquids "Mixture of hydrocarbons and wetting solution". Benzoyl chloride has a vapour pressure of 0.34 kPa at 50 °C and a density of approximately 1.2 kg/litres. Design type tests for plastics drums and jerricans were frequently performed at minimum required test levels. In practice this means that the stacking test is commonly performed with stacking loads considering only a density of 1.0 for the

"Mixture of hydrocarbons" and a density of 1.2 for the "Wetting solution" (see definition of standard liquids in 6.1.6). As a consequence chemical compatibility of such tested design types would <u>not be proved for benzoyl chloride</u> by reason of the inadequate test level of the design type with the standard liquid "mixture of hydrocarbons". (Due to the fact that in the majority of cases the applied internal hydraulic test pressure is not less than 100 kPa, the vapour pressure of benzoyl chloride would be covered by such test level according to 4.1.1.10.]

All components of a 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 in 4.1.1.19.6 (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 in 4.1.1.19.6.
- (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) If the UN number and packing group of the filling substance determined in accordance with (a) is not included in the assimilation list or if the filling substance cannot be assigned to a single entry or collective entry in accordance with (d), the chemical compatibility shall be proved in accordance with 6.1.5.2.5, 6.1.5.2.6 or 6.1.5.2.7 for packagings and in accordance with 6.5.4.3.2, 6.5.4.3.3, 6.5.4.3.4, 6.5.4.3.6 or 6.5.4.3.7 for IBCs"

- (f) 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.
- (g) The chemical compatibility of the substance mentioned by name may be regarded as proven taking into account 4.1.1.19.1 and 4.1.1.19.2, if a standard liquid or a combination of standard liquids is assimilated in column 7.

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 4.1.1.19.6, and
- no chemical reaction is taking place between the dangerous substance and the solvent water.

[Example: Aqueous solutions of UN 1120 tert-Butanol:

- 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 as well as in the assimilation list.
- UN 1120 BUTANOLS do not react with water under normal conditions of transport.

As a consequence aqueous solutions of UN 1120 tert-Butanol may be assigned to the standard liquid acetic acid.]

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 THIOGLYCOLIC 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 THIOGLYCOLIC 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.]

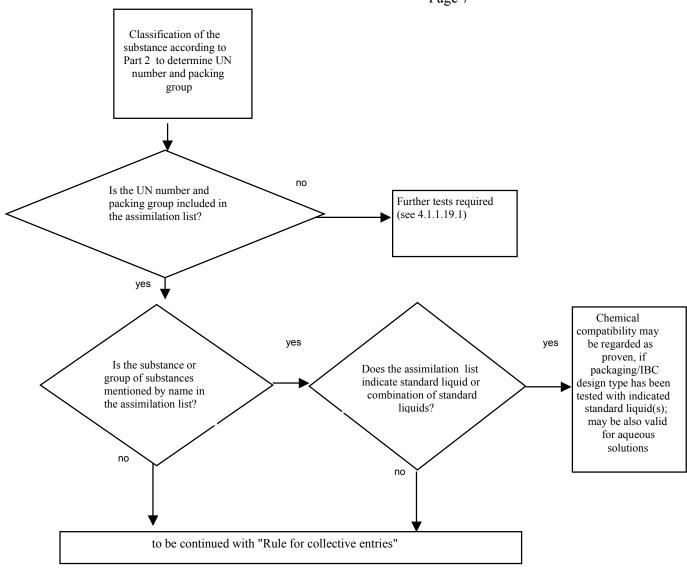
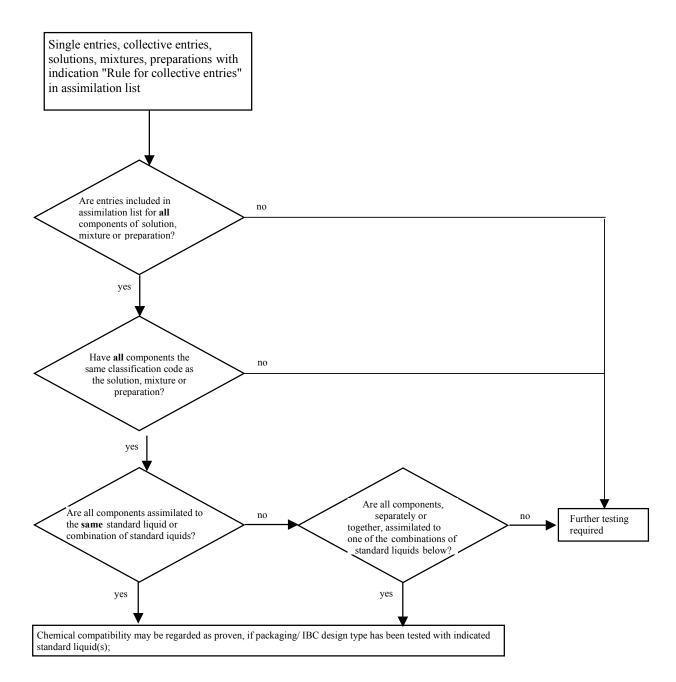


Figure 4.1.1.19-1: Scheme for the assimilation of filling substances to standard liquids



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"

4.1.1.19.6 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

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 4 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.

Column 5 Classification code

This column contains the classification code of the dangerous substance in accordance with the procedures and criteria of Part 2.

Column 6 Packing group

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.

[Note: the assimilation list is reproduced in addendum 2 to this document.]

2. Amendments to Part 6

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 in medium molecular mass polyethylene meeting 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/2.16 kg load \leq 0.5 g/10 min and \geq 0.1g/10 min, in accordance with ISO Standard 1133,
- melt flow rate at 190 °C/5 kg load \le 3 g/10 min and \ge 0.5 g/10 min, in accordance with ISO Standard 1133,

chemical compatibility with filling liquids assimilated in accordance with 4.1.1.19 may be verified as follows with standard liquids (see 6.1.6).

The standard liquids are representative for the processes of deterioration on high or medium molecular mass polyethylene, as there are softening through swelling, cracking under stress, molecular degradation and combinations thereof. The sufficient chemical compatibility of the packagings may be verified by storage of the required test samples for three weeks at 40 °C with the appropriate standard liquid(s); where this standard liquid is water, storage in accordance with this procedure is not required. 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.

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 the procedure in accordance with this paragraph from high density, high or medium mass polyethylene packagings can be approved for an equal design type, the internal 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, which have passed the test in 6.1.5.2.6, filling substances other than those assimilated in accordance with 4.1.1.19 may also be approved. Such approval shall be based on 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:

6.1.6 Standard liquids for verifying the chemical compatibility testing of high or medium molecular mass polyethylene packagings and IBCs in accordance with 6.1.5.2.6 and 6.5, respectively

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:

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 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)

- 6.5.4.3.5 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, 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,

chemical compatibility with filling liquids assimilated in accordance with 4.1.1.19 may be verified as follows with standard liquids (see 6.1.6).

The standard liquids are representative for the processes of deterioration on high or medium molecular mass polyethylene, as there are softening through swelling, cracking under stress, molecular degradation and combinations thereof. The sufficient chemical compatibility of the IBCs may be verified by storage of the required test samples for three weeks at 40 °C with the appropriate standard liquid(s); where this standard liquid is water, storage in accordance with this procedure is not required.

After this storage, the test samples shall undergo the tests prescribed in 6.5.4.4 to 6.5.4.9.

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 the procedure in accordance with this paragraph from high density, high mass polyethylene IBCs can be approved for an equal design type, the internal surface of which is fluorinated.

6.5.4.3.6 For IBC design types, made of high molecular mass polyethylene, as specified in 6.5.4.3.5, the chemical compatibility with filling substances may also be verified by laboratory tests² 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.

Add a new paragraph 6.5.4.2.2 as follows and renumber the subsequent paragraphs.

6.5.4.2.2 To prove there is sufficient chemical compatibility with the contained goods or standard liquids in accordance with 6.5.4.3.3 or 6.5.4.3.5 for rigid plastics IBCs of type 31H2 and for composite IBCs of types 31HH1 and 31HH2, a second IBC can be used when IBCs are designed to be stacked. In such case both IBCs shall be subjected to a preliminary storage.

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 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)

Amend 6.5.4.3.7 as follows:

Substitute "3rd" by "3rd^f" in line 5 and 7 of column "Stacking".

Add a new text:

The second IBC in accordance with 6.5.4.2.2 can be used out of the sequential order direct after the preliminary storage.

Amend 6.5.4.6.3 (a) as follows:

6.5.4.6.3 Method of testing

(a) The IBC shall be placed on its base on level hard ground and subjected to a uniformly distributed superimposed test load (see 6.5.4.6.4). For rigid plastics IBCs of type 31H2 and composite IBCs of types 31HH1 and 31HH2, a stacking test shall be carried out with the original filling substance or a standard liquid (see 6.1.6) in accordance with 6.5.4.3.3 or 6.5.4.3.5 using the second IBC in accordance with 6.5.4.2.2 after the preliminary storage. IBCs shall be subjected to the test load for a period of at least: