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Working Party on the Transport of Dangerous Goods

**Joint Meeting of the RID Safety Committee and the
Working Party on the Transport of Dangerous Goods**
(Bern, 18-22 March 2002)

**Sub-section 6.1.6.2: Revision of the "list of substances to which the standard liquids
may be regarded as equivalents for the purposes of 6.1.5.2.6"**

Transmitted by the Government of Germany */

Summary

1. A working group of German experts has checked the chemical compatibility of high or average molecular mass polyethylene (PE-HD) with additional substances in comparison with the existing substance list in 6.1.6.2. On the occasion the substances of the existing list were checked in detail in view of the actual knowledge of the experts, mistakes were found relating to the proof of the chemical compatibility and defects relating to the user friendliness of the substance list 6.1.6.2 of the restructured RID and ADR.
2. The Joint Meeting is asked for considerations whether some of the demonstrated mistakes are so severe for safety reasons that there should be immediate amendments. Furthermore, it seems to be necessary to adapt the existing substance list to the new structure of RID/ADR making it more user friendly. This could be done either by including additional codes in the packing provisions in the regulation itself or by accepting a substance list included in a future standard (at this stage there is a draft standard prCEN/ISO 16101 – compatibility testing of plastics packagings), in both cases completed by a new rule for collective entries.

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Introduction

According to 6.1.5.2.6 of the restructured RID/ADR the chemical compatibility with the liquids listed in 6.1.6.2 may be verified with standard liquids (see 6.1.6.1), which are representatives for the damaging effects of dangerous substances on plastics packagings manufactured by high or average molecular mass polyethylene (PE-HD) of a distinct specification. When design type tests have been successfully performed with these standard liquids, the comparable filling substances listed in 6.1.6.2 may be accepted for carriage without further testing, subject to two further conditions related to the density and the vapour pressure of the dangerous liquid. This list in 6.1.6.2 represents the state of the art around the year 1980. Therefore, a working group of German experts was established in order to gather and assess the results and experiences gained in the mean time by plastics manufacturers, plastics converters and plastics packagings users. For this assessment the following principles were applied:

- ?? Only such substances were included in a new assimilation list, from which real test results exist proving that the effect of such filling substances on test specimens is less than the effect of the standard liquids according to the established laboratory methods (softening through swelling, cracking under stress and molecular degradation).
- ?? Substances not tested or tested with differing test results were not included in the list.
- ?? Collective entries were included in the list on condition, that they either describe well-defined chemical groups of substances and there are no doubts that positive test results of specific members of this chemical group can be assigned to the whole group or can be subjected to a new assignment rule for collective entries.

The new list of substances gained under application of those principles and assigned to the established standard liquids was submitted to the Target Group Plastics of CEN TC 261 with the purpose of including it in the intended standard prCEN/ISO 16101 compatibility testing for plastics packagings.

Raising Problems

- a) Working on the assimilation list it was noticed that the existing list in 6.1.6.2 of the RID/ADR shows mistakes due to the assessment of the experts. The following examples seem to be obvious:
 - ?? According to the definition of 6.1.6.1 of the RID/ADR the standard liquid "mixture of hydrocarbons (white spirit)" has an aromatic content of 16 % to 21 %. Nevertheless, **all** hydrocarbons classified under class 3, packing group II or III and classification code F1 can be assigned to this standard liquid. By mistake the following pure aromatic hydrocarbons are regarded as covered by the standard liquid "mixture of hydrocarbons" relating to their damaging effects: e.g. UN 1114 BENZENE, UN 1175 ETHYLBENZENE, UN 1294 TOLUENE, UN 1307 XYLENES and UN 1918 ISOPROPYLBENZENE. These substances clearly have a higher damaging effect relating to the softening of the PE-HD through swelling than the standard liquid "mixture of hydrocarbons".

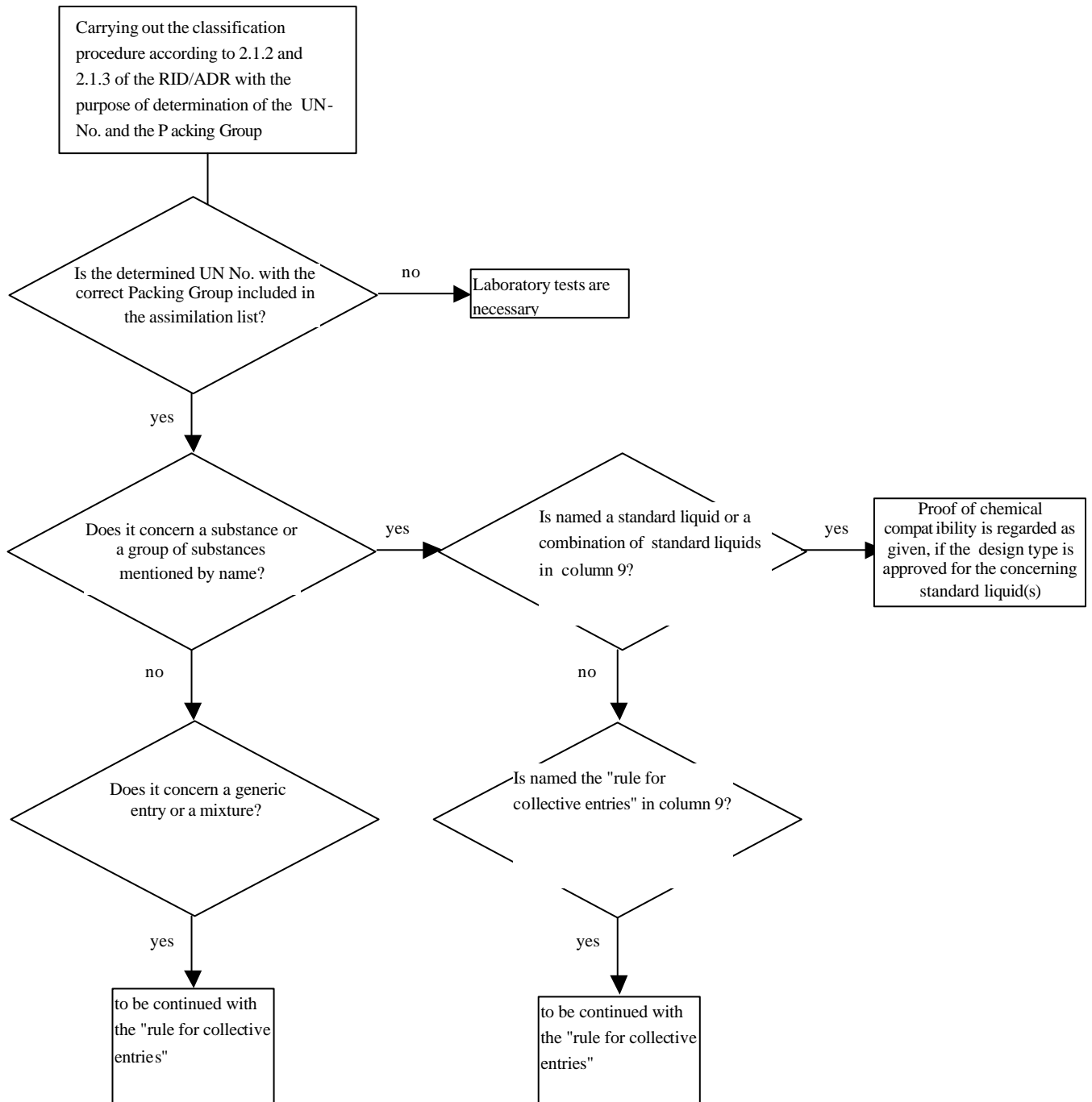
- ?? UN 2014 HYDROGEN PEROXIDE, AQUEOUS SOLUTION with not more than 60% hydrogen peroxide clearly leads to molecular degradation on PE-HD caused by the oxidation of the hydrogen peroxide. Therefore, this substance should not be assigned to the non damaging standard liquid “water” but to the standard liquid “nitric acid”.
- ?? There are no test results of the established laboratory methods for a number of chemical groups of substances named in the list 6.1.6.2, with the consequence that they could not be assigned to standard liquids following the principles mentioned above. For example, the permeation of most of the halogenated flammable substances through drums and jerricans made from PE-HD has such a high amount that there is no consignment in such packaging types for practical reasons. Therefore, there was no need for the proof of the chemical compatibility, and it is understandable that there are no test results. It seems not to be responsible to assign the “halogenated substances” of class 3 with classification code F1 as a whole to the standard liquid “mixture of hydrocarbons” as it is made in the list in 6.1.6.2.
- ?? In a similar way, the wholesale assignment of all alcohols of class 3 with classification code F1 to standard liquid “acetic acid” is dubious. The alcohols have more and more swelling effects on PE-HD with their growing chain length. In the case of alcohols causing PE-HD to swell more than acetic acid, those alcohols should be assigned to standard liquid “n-butyl acetate/n-butyl acetate-saturated wetting solution”.
- b) Users, who do not have specialized knowledge in chemistry, can be misled in the new RID/ADR, because they cannot find any more the single entries and generic entries which are related to the general chemical substance groups named in the list in 6.1.6.2. Furthermore, according to the new list, some generic entries cannot be assigned any more to standard liquids as it was possible in the old list of substances. The following examples seem to be obvious:
- ?? According to the new list “Viscous substances that meet the classification criteria of 2.2.3.1.4” being substances of class 3 with packing group II and classification code F1 are assigned to standard liquid “mixture of hydrocarbons”. All these descriptions and conditions could be covered e.g. by UN 1170 ETHANOL adding gelatine to meet the required viscous properties. In this case, it is obvious that the assignment to “mixture of hydrocarbons” would be a mistake.
- ?? Reading the above mentioned entry for viscous substances in a more restrictive way, thus raises a new problem: In the case that only such viscous substances are meant which include the wording “viscous” in their official description in table A of chapter 3.2 of the RID/ADR (e.g. UN 1133 *ADHESIVES containing flammable liquid (having flashpoint below 23 °C and viscous according to 2.2.3.1.4)(vapour pressure at 50 °C not more than 110 kPa)*), a new problem becomes evident, that all “viscous” entries of chapter 3.2 are packing group III entries, which are not named in the substance list of 6.1.6.2. As a result of such confusion no viscous substance can be assigned to a standard liquid.
- ?? In 6.1.6.2 “*Mixtures of above mentioned substances having a boiling point or initial boiling point exceeding 35 °C, containing not more than 55 % nitrocellulose with a nitrogen content not exceeding 12.6 % (UN No. 2059)*” are listed. The wording “above-mentioned” is applied to the chemical groups of substances mentioned above in this list. The assignment of specific substances to single entries or collective entries under the additional aspect of membership in chemical substance groups not defined in detail in the RID/ADR requires a very high specialized knowledge, which cannot be expected of a normal user.

?? Generally, the restriction of the assigned substances to packing groups and vapour pressures is a matter of classification and not a matter of chemical compatibility. These restrictions frequently seem to be unnecessary.

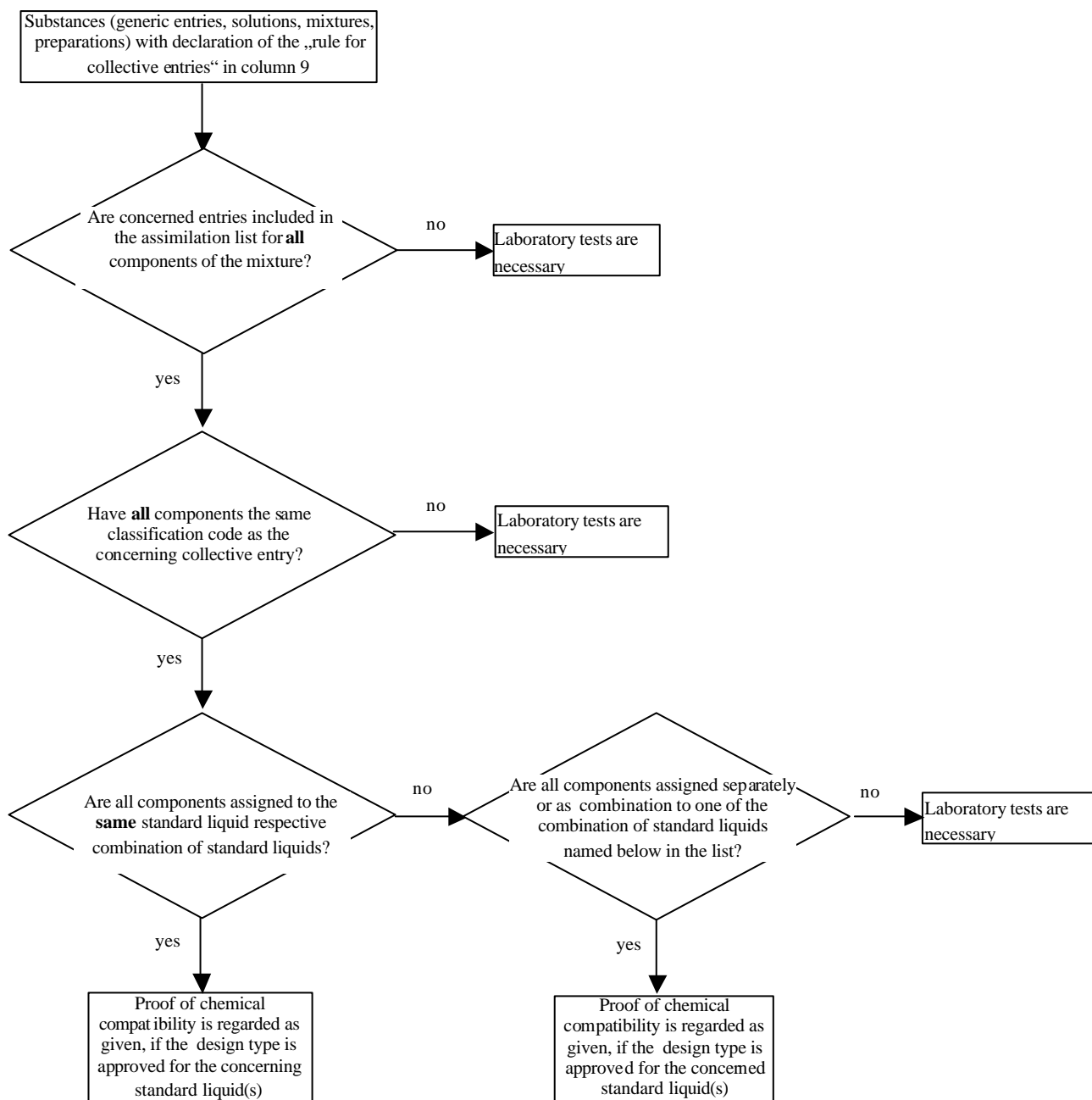
Possible solution of the problems

1. Some of the problems raised could be removed by editorial changes at this stage of the discussions.
2. The structural problems could be solved in the future adding new codes e.g. in column 9a of chapter 3.2 for each entry concerned.
3. The Joint Meeting could apply to a future standard (e.g. draft standard prCEN/ISO 16101 – compatibility testing for plastics packagings), which includes an appropriately structured assimilation list; the process of standardization could be controlled by the new working group of the Joint Meeting.
4. In both cases No 2 and 3 an additional rule for collective entries would be necessary as it was worked out in the German working group and as it is outlined below, either in the provisions or in the standard.

Scheme for the assignment of substances, solutions and mixtures to standard liquids



Rule for Collective Entries



- List of combinations of standard liquids:
?? water/nitric acid (55%)
?? water/wetting solution
?? water/acetic acid
?? water/mixture of hydrocarbons
?? water/n-butylacetate – n-butylacetate saturated wetting solution