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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

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Item 3 (c) of the provisional agenda
Listing, classification and packing: miscellaneous

Packing requirements for UN1873

Transmitted by the Council on Safe Transportation of Hazardous Articles (COSTHA)[1]

Introduction

1. High purity perchloric acid ($HClO_4$) is used to prepare samples for sub parts per billion (ppb) level elemental analyses that use analytical methods such as inductively coupled plasma mass spectrometry (ICP-MS). Used on its own perchloric acid <72% w/w is ineffective as it is not particularly aggressive, nor is it a strong oxidizer at normal temperatures. It is commonly added to acid digestion mixtures to increase their oxidizing power and digestions are performed at elevated temperatures and/or pressures. Common mixtures include combining perchloric acid with nitric, sulphuric and hydrofluoric acids. Primary examples are dissolution of samples for geochemical analyses and of quartz used in the semiconductor industry. Less commonly, perchloric acid is used to prepare organic matter for analysis.

2. Perchloric acid is regulated either as UN1873 as a 5.1(8) when in solutions with a concentration of more than 50% but not more than 72% perchloric acid, or as UN1802 as a 8(5.1) when in solutions with a concentration up to 50% perchloric acid.

3. UN1802 is required to be packed in accordance with P001 which authorizes glass, plastic, or metal inner containers. UN1873 is required to be packed in accordance with P502 and while P502 authorizes glass, plastic, and metal inner containers, special packing

[1] In accordance with the programme of work of the Sub-Committee for 2013-2014 approved by the Committee at its sixth session (refer to ST/SG/AC.10/C.3/84, para. 86 and ST/SG/AC.10/40, para. 14).

provision PP28 limits the construction of inner packagings and inner receptacles to glass for combination and composite packagings. Plastic 1H1 single packagings are permitted for UN1873 up to a maximum capacity of 250 *l*.

4. The availability of high quality, low reaction plastics has increased since adoption of PP28. In particular, the use of fluoropolymers has resulted in very stable, chemically resistant packaging which would technically fall under the definition of plastic packaging. The current language in PP28 prohibits the use of these chemically stable and safe packagings.

Fluorinated plastics

5. Fluoropolymers are fluorinated plastics. Most plastics are chains of carbon atoms with hydrogen or other atoms attached to them. In fluoropolymers, fluorine atoms replace all (type one fully fluorinated polymers) or some (type two partially fluorinated polymers) of the hydrogen atoms. This creates a high binding energy among atoms within the plastic molecules and makes these plastics highly stable. As a result fluoropolymers generally exhibit superior resistance to heat and chemical attack than other plastics. Type one fully fluorinated polymers such as fluorinated ethylene-propylene (FEP) and perfluoroalkoxy (PFA) generally emphasise these properties. Literature confirming the properties and chemical resistance of fluoropolymers is widely available.

6. Fluoropolymer inner packagings meet the construction requirements of 6.1.4. To support this assertion tests were conducted on FEP and PFA bottles that contained UN1873 perchloric acid in concentrations from 67%-72% w/w for periods ranging from almost six to greater than fourteen years. These tests included;

(a) 24 hr stack;

(b) 2.55 m drop;

(c) 95 kPa internal pressure;

(d) ASTM D2463 impact resistance drops up to 3.25 m.

The bottles used passed all tests. Testing results are included as annex in informal document INF.5.

Increased safety

7. Glass inner containers provide protection from chemical reactions for perchloric acid. However, physical hazards such as impacts and extreme temperatures can have a detrimental effect on glass. Plastic packaging provides greater flexibility in certain circumstances, being able to absorb hard impacts without shattering or cracking. Fluoropolymers in particular have been shown to provide long term flexibility without the embrittlement associated with other plastics. The results of the ASTM D2463 impact resistance drop tests for blow molded thermoplastic containers on the test report in informal document INF.5confirm these assertions.

Industry needs

8. UN1873 is used by industries such as geochemical and semiconductor for elemental analyses. Most elements in high purity perchloric acid used for elemental analyses are certified at concentrations as low as one part in 10^{12} (part per trillion). This level of purity

cannot be maintained unless chemically pre-cleaned fluoropolymer containers are used. Glass and metal containers are unsuitable as they are incapable of maintaining purity at ppt levels.

Discussion

9. Given the discussion above, COSTHA believes the special packing provision of PP28 is too restrictive and overly limits the use of safe and available packaging options. Although we do not propose in this paper to remove or modify PP28 in P502, COSTHA is interested in the opinion of the Subcommittee on the use of fluoropolymer packaging for UN1873. Current options as outlined in 6.1.1.2 are limited to competent approvals or exemptions which may require multilateral agreements for international or intermodal transport.

10. For discussion, COSTHA suggests the following changes to PP28.

> PP28 For UN 1873, only glass <u>and plastic</u> inner packagings and glass <u>and plastic</u> inner receptacles are authorized respectively for combination packagings and composite packagings. <u>Plastic inner packagings and receptacles must be constructed of fluoropolymers or other substances proven to be chemically stable with perchloric acid for greater than 5 years.</u>

11. Comments received will be used to generate a formal proposal for the forty-fourth session in December 2013.