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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 Globally Harmonized System of Classification and Labelling of Chemicals

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Item 3 (f) of the provisional agenda
Classification criteria and related hazard communication:
aspiration hazard

Aspiration hazard – viscosity criterion for classification of mixtures

Submitted by the International Paint and Printing Ink Council (IPPIC)*

Background

- 1. At the twentieth session of the Sub-Committee IPPIC presented informal document INF.28 regarding Chapter 3.10 of the GHS on aspiration hazard, and specifically the absence of viscosity criteria suitable for mixtures such as paints and printing inks, for which it is generally not practicable to measure kinematic viscosity at 40 °C.
- 2. IPPIC proposed to develop appropriate viscosity criteria determined at 23 °C, using a method such as flow cups according to ISO 2431, for inclusion in paragraph 3.10.3.3 of the GHS (with consequential changes to the Manual of Tests and Criteria as necessary). The Sub-Committee agreed to include this item in its programme for further work.
- 3. This issue remains of high importance for paint and printing ink manufacturers.
- 4. IPPIC has invited its members and third party organisations to deliver test data in order to substantiate the proposed amendment of the criteria.

^{*} In accordance with the programme of work of the Sub-Committee for 2017–2018 approved by the Committee at its eighth session (see ST/SG/AC.10/C.3/100, para. 98, and ST/SG/AC.10/44, para. 14).

Introduction

- 5. In the chapters for classification of physical hazards, appropriate test methods are included as described in the Manual of Tests and Criteria, in ISO or other standards. Whereas the GHS uses viscosity data as experimental basis for classification of the aspiration hazard in Category 1 or 2 (GHS Table 3.10.1), the Model Regulations on the Transport of Dangerous Goods (also the modal regulations ADR/RID), which do not include aspiration hazard, use viscosity data determined as an additional criterion for allocation of the Packing Group in Class 3 Flammable Liquids for certain products (e.g. paints, varnishes). These criteria are described in section 2.3.2.2 of the Model Regulations with reference to the Manual of Tests and Criteria Part III, sub-section 32.4.3, the flow-time method (ISO 2431).
- 6. Although the determination of viscosity is also a measurement of a physical parameter, there is no reference to test methods in GHS Chapter 3.10 Aspiration Hazard. Thus, it would be appropriate and consistent with the practice in the physical hazard classes to include suitable test methods also in GHS Chapter 3.10.

Discussion of issues

- 7. It is well known that the rheological properties (e.g. Newtonian versus non-Newtonian flow behaviour) are responsible for the choice of the appropriate test method(s) for viscosity measurements. Thus, different methods are suitable for different types of chemicals. These methods can be issued e.g. by ISO and ASTM.
- 8. In the European Union legislation before implementation of the GHS, the following product-specific test methods with corresponding assessment criteria were given for the former cut-off value for kinematic viscosity of ≤ 7 mm²/s (Annex VI of the European Union Dangerous Substances Directive 67/548/EEC; twentieth-eighth adaptation to technical progress, Directive 2001/59/EC, section 3.2.3):
 - Paints and varnishes: ISO 2431:2011 (March 2012); Paints and varnishes Determination of flow time of less than 30 s in a 3 mm ISO flow cup.
 - Petroleum products transparent and opaque liquids: ISO 3104 Determination of kinematic viscosity (at 40 °C) and calculation of dynamic viscosity; ISO 3105 Glass capillary kinematic viscometers
 - Polymers/resin: in the liquid state or as emulsions or dispersions: ISO 3219 using a rotational viscometer at 40 °C.

The same methods were also referenced in the former Australian criteria.

- 9. In contrast to other physicochemical data which are generally based on results from tests at a standard temperature of 20 °C or 25 °C, the criteria for aspiration hazard use viscosity data at 40 °C. The aforementioned flow-time test method ISO 2431 prescribes 23 \pm 0.5 °C as standard temperature. Thus, for paints/varnishes generally test data at 23 °C are available. The method allows in principle also other temperatures, e.g. 40°C, but problems potentially undermining correct performance of the test and validity of the results include possible decomposition, separation into different layers during testing, skinning of the paint and clogging of the cups. Thus it is often rather difficult to measure solvent-borne products at 40 °C or higher.
- 10. Paragraph 3.10.1.5.3 of GHS provides a formula for conversion between dynamic and kinematic viscosity (under equivalent conditions). However there is no simple equation permitting extrapolation of a kinematic viscosity criterion at 40 °C to one measured at 23 °C;

or the other way around from test data at 23 °C to values at 40 °C. The viscosity-temperature relationship must normally be derived by tests and calculation of the flow activation energy.

11. Suitable and validated test methods for viscosity measurement according to ISO, ASTM or other internationally recognised standards should ideally be included in Chapter 3.10 as for the physical hazards, in order to facilitate proper classification of substances and mixtures for aspiration hazard. These methods and criteria should be compatible with practices in those industries where there is a need to classify.

Basis of proposal

- 12. Section 3.10.3.3 should be amended to include an appropriate aspiration classification criterion for viscosity determined according to ISO 2431:2011 at 23 °C, thus enabling paint and printing ink manufacturers to classify in this hazard class without the change to worldwide industry practice which would otherwise be required, with associated costs.
- 13. For products for which valid data are available, i.e. from tests performed according to ISO 2341 at 40 °C where no decomposition, separation into layers or clogging of the cup occurred during the test, these data may be used directly for classification according to the criteria in Table 3.10.1 and sub-section 3.10.3.3 according to current practice.
- 14. If there are valid data from studies performed at the standard conditions for test method ISO 2431 (23 °C \pm 0.5 °C and atmospheric pressure of 101.3 kPa.), these test results may be used by applying an uncertainty factor of 10% after calculating the kinematic viscosity from the resulting flow-times and the dynamic viscosity. A similar procedure for taking uncertainties into consideration is used when calculating flash points of mixtures in the hazard class flammable liquids: the flashpoint values must be at least 5°C greater than the relevant classification criterion and in addition certain conditions have to be met (see GHS sub-section 2.6.4.2.2).
- 15. Thus when applying a 10% uncertainty factor, the criterion for classification in Category 1 and Category 2 would be \leq 22.5 mm²/s and \leq 15.5 mm²/s respectively for kinematic viscosity if the data result from a valid test performed at 23 °C.
- 16. Expert judgement is necessary in choosing the appropriate test conditions and assessment procedures.

Proposal

- 17. Amend GHS sections 3.10.3.3.2.1, 3.10.3.3.2.2, 3.10.3.3.3.1 and 3.10.3.3.3.3 as follows (additions shown <u>underlined</u>):
- "3.10.3.3.2.1 A mixture is classified as Category 1 when the sum of the concentrations of Category 1 ingredients is \geq 10%, and the mixture has a kinematic viscosity \leq 20.5 mm²/s, measured at 40 °C (or \leq 22.5 mm²/s using data from a valid test performed at 23 °C).
- 3.10.3.3.2.2 In the case of a mixture which separates into two or more distinct layers, the entire mixture is classified as Category 1 if in any distinct layer the sum of the concentrations of Category 1 ingredients is \geq 10%, and it has a kinematic viscosity \leq 20.5 mm²/s, measured at 40 °C (or \leq 22.5 mm²/s using data from a valid test performed at 23 °C)."

- "3.10.3.3.3.1 mixture is classified as Category 2 when the sum of the concentrations of Category 2 ingredients is $\geq 10\%$ and the mixture has a kinematic viscosity ≤ 14 mm²/s, measured at 40 °C (or ≤ 15.5 mm²/s using data from a valid test performed at 23 °C)."
- "3.10.3.3.3.3 In the case of classifying a mixture which separates into two or more distinct layers, the entire mixture is classified as Category 2 if in any distinct layer the sum of the concentrations of Category 2 ingredients is $\geq 10\%$, and it has a kinematic viscosity ≤ 14 mm²/s, measured at 40 °C (or ≤ 15.5 mm²/s using data from a valid test performed at 23 °C)."
- 18. A consequential change to Part III, sub-section 32.4.3 of the UN Manual of Tests and Criteria may be required, depending upon the solution identified.
- 19. Test data to substantiate this proposal, along with proposals for consequential amendments, will be presented in a subsequent informal document.