



**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****Forty-ninth session**

Geneva, 27 June – 6 July 2016

Item 2 (c) of the provisional agenda

Explosives and related matters:**Review of tests in parts I and II of the Manual of Tests and Criteria****Manual of Tests and Criteria
Proposal for replacing dibutyl phthalate(DBP) in Koenen
Test****Transmitted by the expert from France¹****Introduction**

1. Dibutyl phthalate (DBP) is used in the test for calibrating the heating rate which should be 3.3 ± 0.3 K/s from 135°C to 285°C. It holds for Koenen test descriptions in Part I of the Manual i.e. Test 1(b), Test 2(b), Test 8(c) and in Part II i.e. Test E.1.
2. DBP is forbidden for general use within the European Union because it has been identified as substance of very high concern within the EU's REACH regulation. For that reason France undertook a research for a suitable replacement for DBP, (see informal document INF.40), presented at the forty-seventh session of the Sub-Committee. Based on the comments made – see also section 6 of informal document INF.53 (47th session) and report ST/SG/AC.10/C.3/94, para.13 – France finalized its research taking into account the heat capacity as part of the specifications for the replacement substance.

¹ In accordance with the programme of work of the Sub-Committee for 2015–2016 approved by the Committee at its seventh session (see ST/SG/AC.10/C.3/92, paragraph 95 and ST/SG/AC.10/42, para. 15).

Discussion

3. As reported in informal document INF.53 (47th session), the Working Group on Explosives suggested that the use of synthetic oils rather than natural oils might be a viable solution to the problem described by France. As France previously identified one mineral oil and one silicone oil as synthetic oils suitable for replacing DBP, it was examined in the meantime which from the above two candidates would be the best option i.e. in the view of retaining a single specification.

4. The silicone oil tested which gave satisfactory results in terms of heating rate i.e. 3.47 ± 0.20 K/s between 135°C and 285°C, see informal document INF.40 (47th session, para.5), has the following chemical composition, properties and availability:

- Chemical composition: siloxanes and silicones, dimethyl (CAS-No 63148-62-9);
- Heat capacity (specific heat): 1.46 J/g.K at 25°C, to be compared to 1.71 J/g.K for DBP and to 2.13 J/g.K for mineral oils;
- Low flammability: flash point 300°C (572°F) determined in closed cup apparatus;
- Auto-ignition temperature: > 400°C (752°F);
- Melting point/freezing point: - 55°C (- 67°F);
- Relative density: 0.96 at 20°C (68°F);
- Worldwide available with open technical information.

5. This silicone oil appears an appropriate substance for replacing DBP especially due to its heat capacity lower than the heat capacity of mineral oils and to its thermal stability and low flammability.

6. Due to the restriction for use of DBP within the European Union, French laboratories e.g. from defence and industry areas are currently on the way to adopt temporarily the above silicone oil as replacement substance, before the final decision for replacement is taken.

7. The silicone oil could be specified by its apparent density and by its heat capacity, with appropriate tolerancies for taking into account possible regional variations in the manufacturing process and availability in various parts of the world.

Proposal

8. It is proposed to replace in the test descriptions in sections 11.5.1.2.2, 12.5.1.2.2, 18.6.1.2.2 and 24.4.1.2.2, the sentence:

"Calibration involves heating a tube (fitted with a 1.5 mm orifice plate) filled with 27 cm³ of dibutyl phthalate".

by:

"Calibration involves heating a tube (fitted with a 1.5 mm orifice plate) filled with 27 cm³ of silicone oil, apparent density 0.96 ± 0.02 at 20°C and heat capacity 1.46 ± 0.02 J/g.K at 25°C".
