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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

Thirty-third session
Geneva, 30 June-9 July (a.m) 2008
Item 2 of the provisional agenda

EXPLOSIVES AND RELATED MATTERS

Amendment to the Proper Shipping Name of UN 3474 for inclusion of 1-HOBt Monohydrate

Transmitted by the International Council of Chemical Associations (ICCA)*

Background

1. At its 31st session, the Sub-Committee considered a proposal from the United States of America for inclusion of 1-HOBt Monohydrate in UN 3474 (ST/SG/AC.10/C.3/ 2007/22, see also papers INF.33 and INF.37). However, discussions showed that additional information was necessary. Therefore, the decision about the proposal was postponed.
2. One of the key issues was the desensitizing effect of water in terms of thermal stability to demonstrate compliance with special provision 28.
3. ICCA has taken the concerns and opinions given at the 31st session of the Sub-Committee into account and decided to provide more insight into the special properties of this substance. The details of further testing will be given in an informal paper which will be submitted in due time before the session.

* In accordance with the programme of work of the Sub-Committee for 2007-2008 approved by the Committee at its third session (refer to ST/SG/AC.10/C.3/60, para. 100 and ST/SG/AC.10/34, para. 14).

Discussion

4. For reasons of readability, the anhydrous Hydroxybenzotriazole will be further referred to as HOBT and the Hydroxybenzotriazole monohydrate shortly as monohydrate.

5. HOBT and its monohydrate have very different crystal structures. This becomes evident in their X-ray diffraction spectra where an X-ray beam is deflected under different angles directly in relation to the structure of the crystallographic unit cell: see Figure 1 in the Annex.

6. The structure of the monohydrate crystal and its unit cell are displayed in the following graphs: see Figures 2 and 3 in the Annex.

7. The HOBT molecules are arranged in columns running parallel to the crystallographic c axis. Water molecules reside in small pockets between the columns, with each one forming three hydrogen bonds (two as donor, one as acceptor). Each hydrogen bond interaction is to a separate HOBT molecule in a separate column.

8. Since the water molecule is firmly bonded within the crystal, it cannot be easily removed. It is absolutely homogeneously distributed and does not form a separate layer or phase as in many other desensitized explosives where the organic molecules and water form a heterogeneous system of two microphases.

9. Under standard conditions (room temperature / atmospheric pressure), the monohydrate is the thermodynamically preferred form. In the presence of liquid water, anhydrous HOBT rapidly converts to the monohydrate. However, the reaction of HOBT in humid air – even at a relative humidity of 95 % - is very slow and may take a long time (i.e. at least several days). This behavior is easily explained by the different crystal structures of HOBT and its monohydrate. In the presence of liquid water, a hydrate jacket is formed which facilitates the necessary rearrangement of the crystal structure.

10. The rapid conversion of HOBT to the monohydrate can be demonstrated by X-ray diffraction studies: When water is added to HOBT, a partial conversion is seen immediately. Within 15 minutes, only the monohydrate can be detected which indicates a complete reaction. See Figure 4 in the Annex.

11. In DSC measurements, HOBT and the monohydrate can be also distinguished clearly: The anhydrous HOBT exhibits its melting peak above 150 °C with immediate transition into decomposition. The monohydrate, however, melts above 80 °C; the subsequent endothermic effects are due to the evaporation of water, again followed by the exothermic decomposition above 150 °C. See Figure 5 in the Annex.

12. The thermal stability of the monohydrate is confirmed in a heat accumulation storage test (UN H.4) at 80 °C. After nearly 240 hours at 80 °C, the material was unchanged, and a mass loss of only 0.6 % had occurred which is remarkably small in reference to the severe test conditions near the melting point. See Figure 6 in the Annex.

Conclusion

13. HOBt monohydrate is thermally stable and not too dangerous for transport in the form in which it was tested. Storage tests prove that HOBt monohydrate keeps its water under temperature conditions encountered in storage and transport over extended periods of time (details of further tests and the data sheet for amended classification will be submitted in a separate informal paper). This behaviour is in agreement with crystallographic studies which demonstrate that the water cannot escape easily from the crystal. ICCA comes to the conclusion that the requirements of special provision 28 are fulfilled. Based on the above findings, it appears proper to classify 1-HOBt Monohydrate as a Division 4.1 Desensitized Explosive substance.

Proposal

14. It is proposed that the proper shipping name for UN 3474 be amended to read as follows:

“1-HYDROXYBENZOTRIAZOLE, ANHYDROUS, WETTED with not less than 20% water, by mass or 1-HYDROXYBENZOTRIAZOLE, MONOHYDRATE”.

Annex

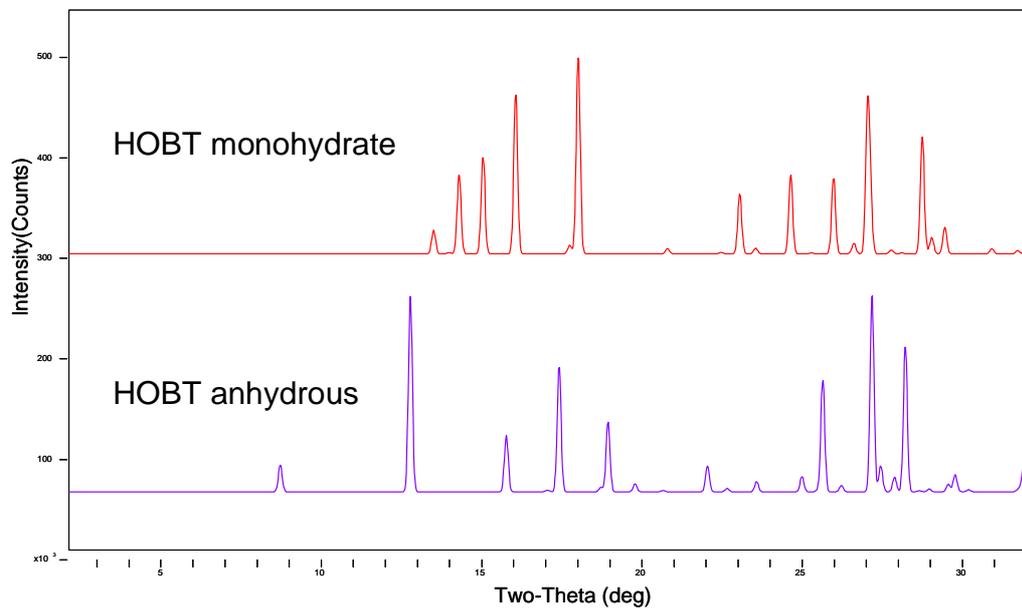


Figure 1: X-ray diffraction spectra of HOBT and its monohydrate

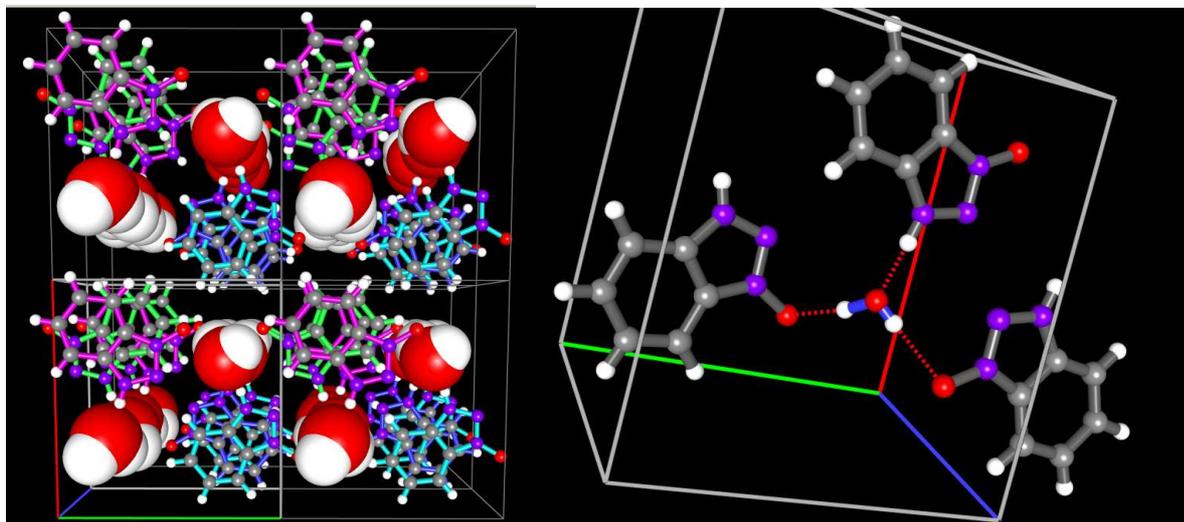


Figure 2: Crystal structure of HOBT monohydrate

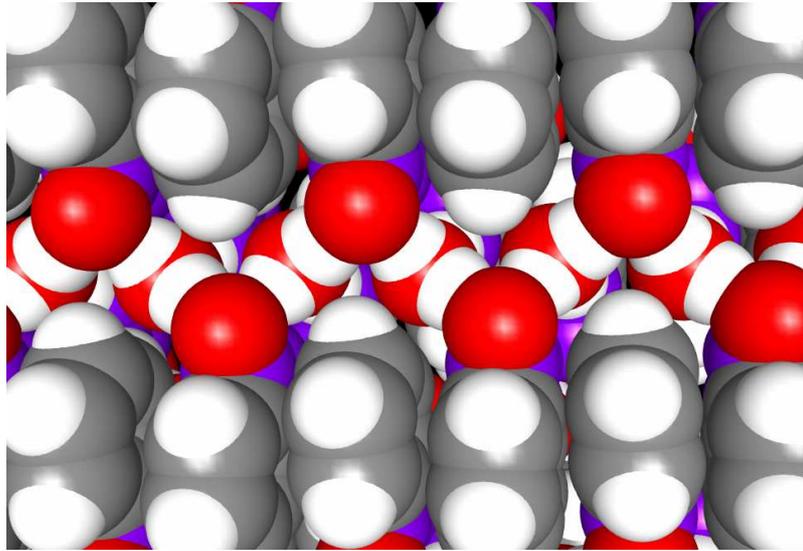


Figure 3: Water in pockets of HOBT monohydrate crystal

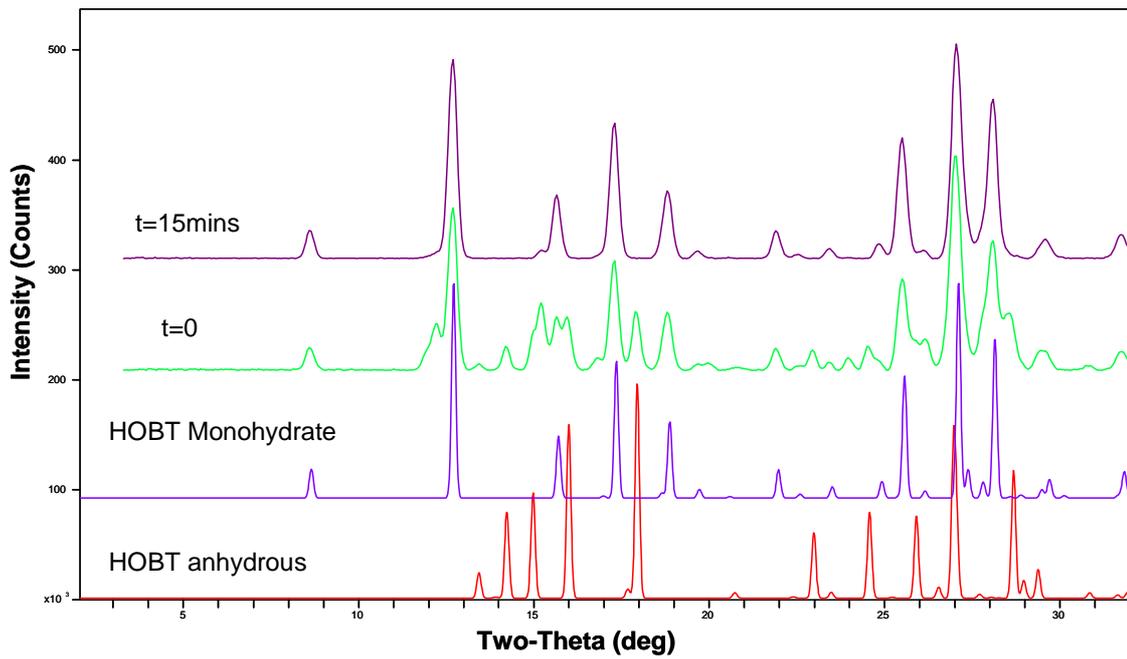
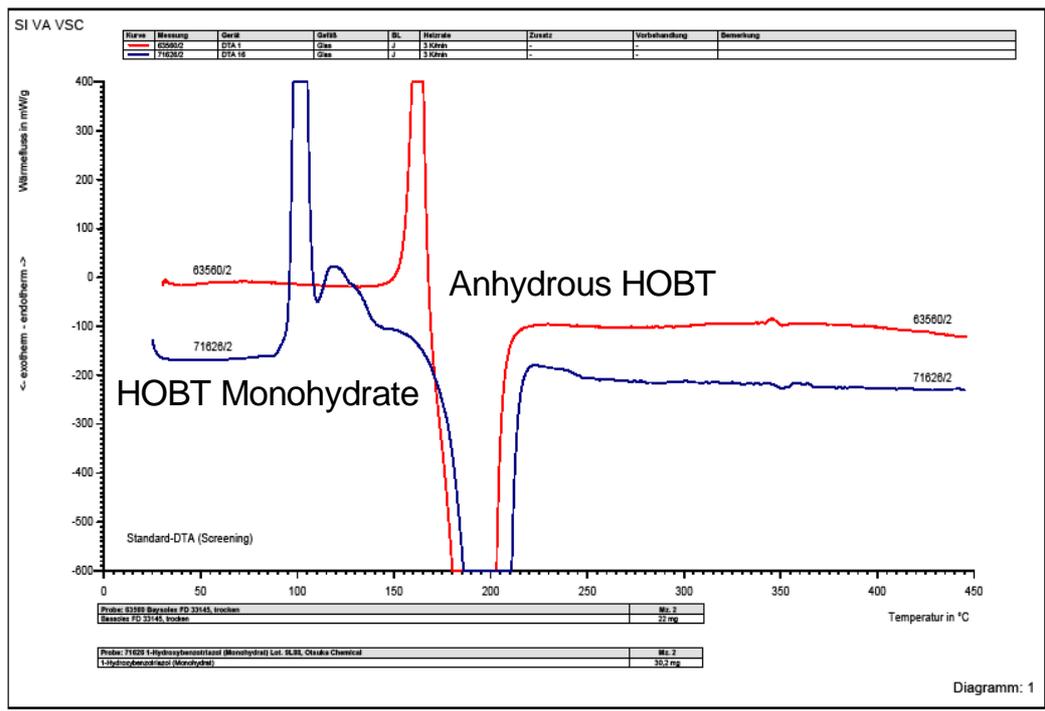


Figure 4: Reaction of HOBT with water (measured by X-ray diffraction)



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Figure 5: DSC diagrams of HOBT and its monohydrate

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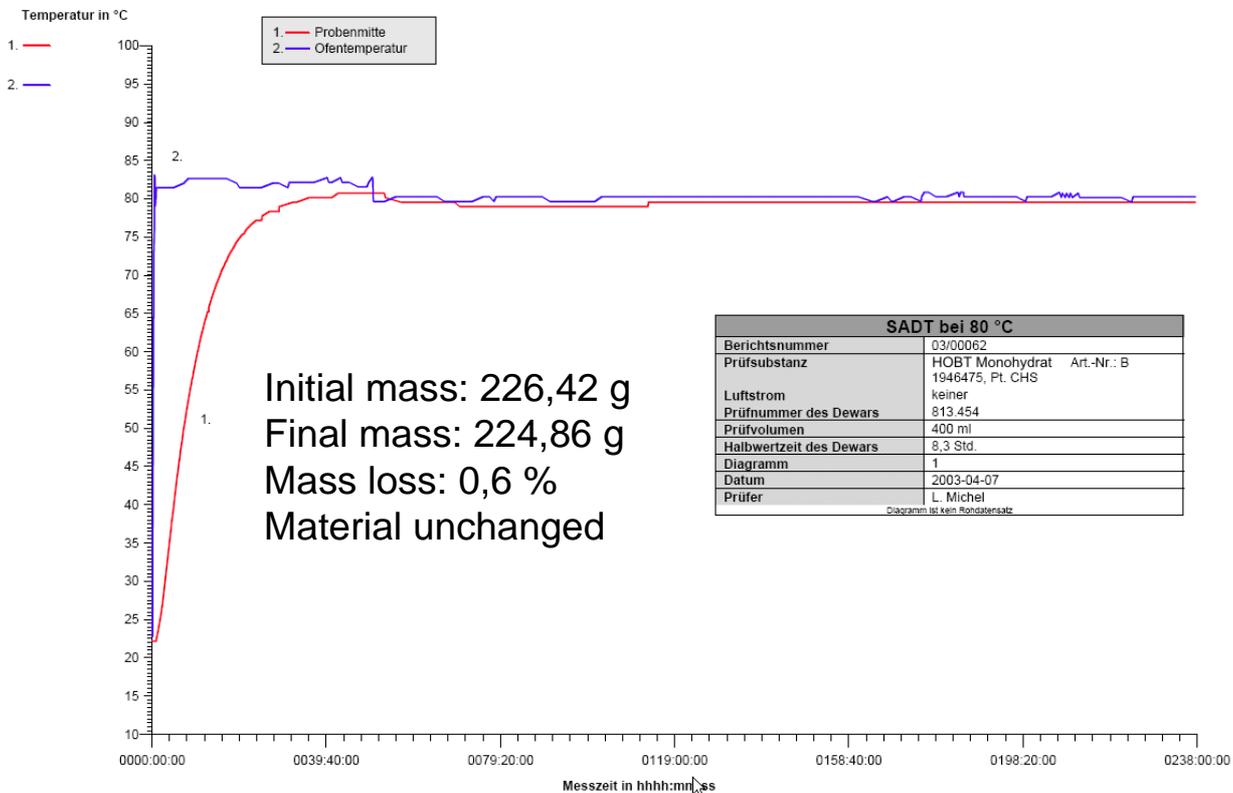


Figure 6: Heat accumulation storage test (UN H.4) at 80 °C