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Study on the early stage of runaway reaction using Dewar vessels

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Abstract

In this paper, compared with a UN cylindrical 500 mL Dewar (H.4 in the UN tests), a spherical 1 L Dewar vessel was used to study the early stages of runaway reactions of several liquid and solid samples, including three organic peroxides and a reactive material. The samples were filled in the vessels and the temperature profiles versus times at different positions of the samples were measured. As a result, the minimum temperatures, defined as the SADT, were averagely 10 K lower than those measured in the cylindrical Dewar vessels. At the same time, the temperature profiles of solids in the spherical Dewars tended to be homogeneous. The heat transfer coefficient of a spherical Dewar is only 0.18 W/K/m, one-eighth of a conventional cylindrical Dewar vessel. Meanwhile it has a low phi factor. These factors are essential to simulate low heat loss bulk conditions in the equilibrium process and at the early stage of a runaway reaction. To characterize the ability of the adiabaticity of a storage vessel, it can be seen that a spherical Dewar could simulate the plant process having critical storage size of a reactive-material, r_0, approximately 0.6 m. It is recommended that such a technique is used to investigate the SADT of an unstable material in larger scale packaging or a material with very weak heat release in industry.

Keywords: Early stage runaway reaction; Heat accumulation; Cylindrical Dewar; Spherical Dewar; Adiabatic conditions; SADT

1. Introduction

Methodology of small-scale replicas is required to predict accurately any hazard that could occur in the chemical industrial scale-up process. Many techniques are available for investigating reaction hazards. In particular, in the UN manual (UN, 2003), series H recommends several testing methods for the determination of one important safety parameter, the self-accelerating decomposition temperature (SADT) for transport of dangerous goods in order to avoid incidents. The SADT is defined as the lowest ambient temperature at which self-accelerative decomposition of an unstable substance is observed when the substance as packaged in its commercial container is subjected to that minimum temperature during one week in the testing facility, and it is a measure of the overall effect of the ambient temperature, decomposition kinetics, package size, and the heat transfer properties of the substance and its packaging. The heat accumulation storage test (HAST, UN H.4) (UN, 2003), BAM-Dewar-Test, is one of them which is used very often (Grewer, 1981; Grewer, Klusacek, Löffler, Rogers, & Steinbach, 1989; Kotoyori, 1988; Rogers, 1989). In the measurement, a 500 cm^3 cylindrical Dewar is filled with 400 cm^3 of an organic peroxide or a reactive material to be tested. The Dewar is closed with an appropriate closure system and heated to the desired storage temperature in a test chamber. The temperature of the substance as well as the test chamber temperature is measured. The SADT is reported as the lowest constant air environment temperature at which the sample undergoes exceeding the test chamber temperature by 6 K or more within one week. The pivotal point is that the heat loss of the Dewar should be at conditions representative of the packaging when filled with the substances. The SADT measured in the H.4 or other UN test can only match those in at most 50 kg packagings, including IBCs and small tanks. However, to obtain the SADTs of substances in larger containers and of substances with a very long induction time (longer than one week), some conclusions concerning the small scale applicability often lead to significant excursion due to the failures in many cases of cognizing the weak heat release at the early stage of a reaction which results in the process becoming uncontrolled and developing into a runaway reaction (Fierz, 2003a,b; Malow, Krause, & Wehrstedt, 2003; Steensma, Schuurman, Malow, Krause, & Wehrstedt, 2005).

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Therefore, to assess realistically the self heating behavior of unstable materials in bulk and simulate the worst conditions encountered during storage and/or transport, an accurate measurement with the adiabatic or nearly adiabatic mode of operation in the laboratory scale is of paramount importance (Barton & Rogers, 1997; Wright & Rogers, 1986). To this end, spherical Dewar flasks were utilized herewith to simulate the conditions of heat accumulation of liquid and solid organic peroxides and reactive materials that would otherwise only be encountered with large amounts of substances. Its adiabatic characteristic was compared with that of the H.4, cylindrical Dewar vessel.

2. Experimental

The similar test procedure, except for the vessel, was referred in UN H.4 (UN, 2003). An 1 L spherical glass Dewar flask was filled with four-fifth volume of sample to be tested and was equipped with an isowool lid which was fixed by three springs to the body. Three K type temperature probes with 0.3 mm in diameter, having reading excursions within 0.1 K, were installed into glass sheathes and inserted into the vessel at the bottom (T1), in the middle (T2), at the top (T3) along the central axis, as well as two others at the lateral areas of the vessel (up for T4 and down for T5). The Dewar setup was mounted in a test chamber which was set at the selected test temperature. T6 staying in the chamber monitored the ambient temperature. The construction of measuring system, including the dimension of the thermocouples, is schematically drawn in Fig. 1.

Samples were t-Butyl peroxy acetate (TBPA), Cumen hydroperoxide (CHP), 2,2′-Azobis(isobutyronitrile) (AIBN) and Bis-(4-t-butyl cyclohexyl) peroxy dicarbonate, (TCP), as listed in Table 1. Three of them are organic peroxides and AIBN is azo compound.

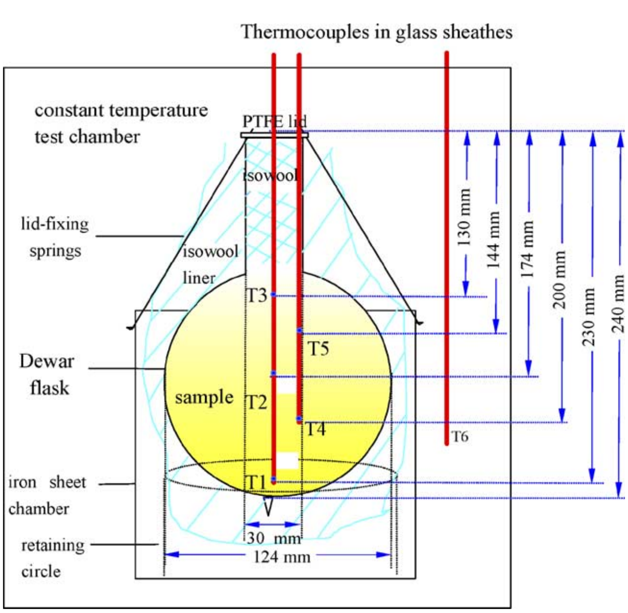

Fig. 1. The scheming construction of measuring system.

Table 1
Samples in the tests

	(t-Butyl peroxy acetate, TBPA	Cumen hydroperoxide, CHP	2,2′-Azobis (isobutyronitrile) dicarbonate, AIBN	Bis-(4-t-butyl cyclohexyl) peroxy, TCP
State	Liquid	Liquid	Solid	Solid
Mass/g	770	820	492	300
Test temperature /°C	55, 60, 65, 70, 75	65, 70	40, 45	40, 45

3. Results and discussion

Figs. 2 to 5 are the spatial temperature profile versus time respectively for the two liquids, TBPA and CHP, and the two solids, AIBN and TCP, in a spherical Dewar flask at oven-temperatures which are very close to the critical temperature between occurrence of runaway and non-runaway. The lowest constant air environment temperature at which the sample undergoes exceeding the test chamber temperature by 6 K or more was the SADT under a certain induction time. The records of the induction time began at the stage when the temperature throughout the sample reached a temperature of 2 K below the test chamber and was counted until a temperature increase of the sample at least 6 K measured (UN, 2003). Table 2 shows the results of the SADT values and their corresponding induction times in cylindrical and spherical Dewar flasks.

It is seen that there is a considerable discrepancy of the induction time and SADT for various substances. In the conventional H4 cylindrical Dewar, the SADT of TBPA is 83 °C; its corresponding induction time was 9.8 h and soon after this period a runaway reaction occurred. At 76 °C, nothing occurred within seven days. Whereas in the spherical Dewar in Fig. 2, at similar 75 °C, a runaway reaction occurred after 14 h; Below this temperature, a runaway reaction still occurred after 42.8 h at 70 °C, after 74 h at 65 °C, and after 253.7 h even at 60 °C. It is apparent that the 7 day criterion in the UN recommendation (UN, 2003) is not applied here, because that at 60 °C, a runaway reaction of TBPA occurred after a much longer induction time than this standard period. However, this may happen in some large container and the case of longer induction time than one week. So the SADT determination according to UN H.4 test is not applicable to these cases. On the other hand, the spherical Dewar, instead, provides an important extension to simulate the SADT in these extreme cases.

As in Table 2, similarly, the SADTs of CHP, AIBN and TCP in the cylindrical Dewar were 83, 50, and 50 °C, respectively (Nippon Oil and Fats Co., LTD, 1996). Their corresponding induction times were 114.5, 123 and 68.6 h.