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Azodicarboxylates: Explosive Properties and Thermal Hazards

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Abstract

The specific aim of our study was based on the versatile applications of Azodicarboxylates in universities and in the chemical industry for chemical synthesis. Diethylazodicarboxylate (DEAD) for instance is a very important reagent used in many chemical reactions [1, 2]. On the other hand DEAD represents an explosive hazard. It is very shock-sensitive and thermally unstable - it is sensitive if heated under defined confinement [3]. The result in the Koenen test (UN test E.1) carried out at BAM, shows for DEAD a limiting diameter of 20 mm (!), $t_1 = 32$ s, $t_2 = 3$ s, "violent". The sensitivity to drop-weight impact (BAM Fallhammer) had a value of 4 J. In comparison Trinitrotoluene (TNT) has a limiting diameter of 5 mm and a sensitivity to drop-weight impact of 15 J [4]. Therefore DEAD is only available in solution (e.g. 35% in toluene). But even in solution the Dutch pressure vessel test (UN test E.2), carried out at BAM, showed a "violent" result (limiting diameter \geq 24,0 mm (!!) t_1 = 29 s, t_2 = 73 s). Toluene seems to be not suitable to suppress the explosive properties of DEAD. Because of the hazard risks the use of DEAD decreases and exchanges partly against the more stable Diisopropylazocarboxylate (DIAD) [5].

As BAM is the competent authority in Germany for testing, classification and assignment of substances showing explosive properties, tests on selected Azodicarboxylates have been performed on the basis of the criteria given in the UN Recommendations on the Transport of Dangerous Goods [6]. Differential scanning calorimetry (DSC) was used to describe the thermal hazards of the pure and diluted Azodicarboxylates. Dibenzylazocarboxylate (DBAD) is not sensitive in the Koenen test at an orifice of 2,0 mm and 6,0 mm. DBAD is also not sensitive to drop-weight, impact and friction stimuli. The DSC measurement of DBAD shows a decomposition energy of -632 J/g which is much smaller than that of DEAD (-1466 J/g). DSC measurements can only provide first indications for the explosive behaviour. Therefore BAM recommends additional tests on the basis of the UN Manual in order to assure the safe handling of such high energetic substances.

References

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