consilab
Gesellschaft für Anlagensicherheit
Höchst zuverlässig.

consiLetter No. 19
October 2020

When does decomposition actually begin?

If a decomposition temperature is specified for a substance, does this mean that it is always safe to use the substance below the specified temperature? No. Unfortunately, it is not always safe! This is because it is often unclear how this temperature was determined and what exactly happens at this temperature. In addition, the term "decomposition temperature" is not defined at all in the regulations.

TRAS 410 deals with the recognition and control of exothermic chemical reactions and defines important parameters that can be obtained from thermal analysis. One of the most important parameters here is the limit temperature for safe handling, i.e. the T_{exo}. It is derived from the measured values of laboratory tests with an added safety margin, taking into account the measurement procedure.

How is this limit temperature set for safe handling and use?

In differential scanning calorimetry (DSC, see consiletter No. 5), the onset temperature is defined as the significant increase of the measurement signal from the baseline. However, this onset temperature does not correspond to the actual start of decomposition because the sensitivity is dependent on the heating rate, among other things. The faster the heating rate and lower the sensitivity, the later the start of decomposition is detected. In screening methods such as DSC, with high heating rates, a large safety margin of 100 K must therefore be used to derive the T_{exo} (*Figure 1*).

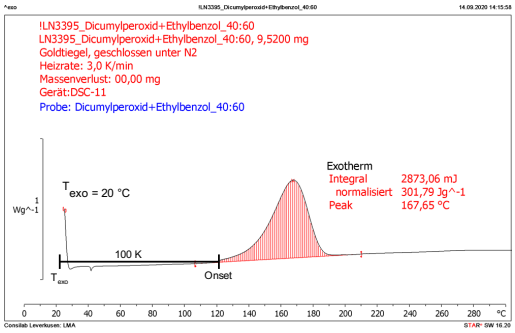

Figure 1 T_{exo} on the basis of a DSC

Depending on the measuring method, decomposition can occur unnoticed well before the onset temperature. For this reason, an onset temperature must not be equated with the safe limit temperature T_{exo}. The decomposition reaction could already be fully underway at the DSC onset and would then no longer be controllable in the large-scale process, despite cooling. Measurement methods such as long-term differential thermal analysis (DTA), (*Figure 2*) or pressure-heat storage (*Druck-Wärme-Lagerung* or DWL, *Figure 3*, see consiletter no. 6) are more sensitive and the T_{exo} can be determined with a smaller safety margin. Different measuring methods can therefore result in varying limit temperatures.

The following rules have been defined in *Technical Rules for Plant Safety 410* (TRAS 410), depending on the measurement method: The T_{exo} is the

- temperature, reduced by 100 K, of the (visible) beginning of an exothermic reaction in the DSC
- temperature, reduced by 10 K, at which the system reaches a reaction power of 0.1 W/kg
- temperature, reduced by 10 K, for an adiabatic induction time of 24 h (AZT24)

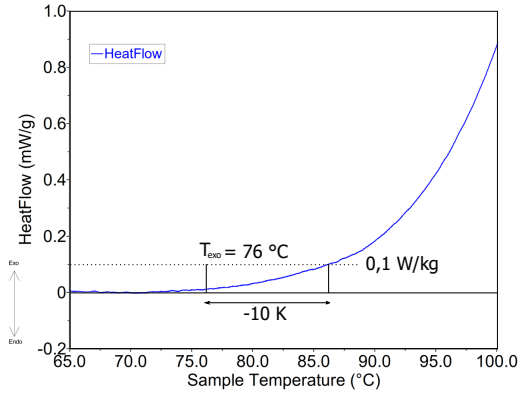

Figure 2 Determination of T_{exo} using the 0.1 W/kg criterion

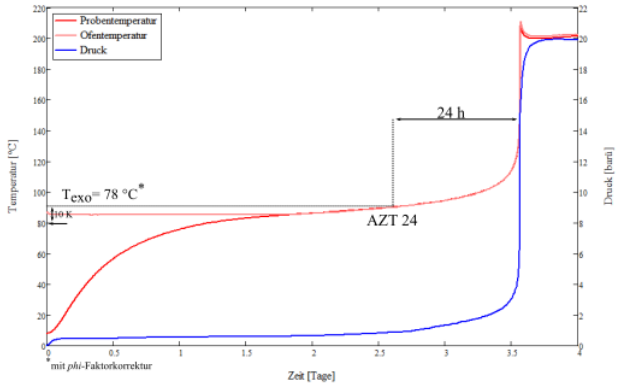

Figure 3 Determination of T_{exo} using the AZT24

For any given decomposition temperature, the question should always be asked: How was it measured? Is a safety margin already included?

A prescribed T_{exo} may only be exceeded if countermeasures and safety devices have been prescribed in a safety assessment. If you have any questions on this topic, please contact us.

Our experts will be happy to help you.

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