LIFETIME EXPECTANCY OF (SLOW) AUTOCATALYTIC DECOMPOSING MATERIALS

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A large number of materials and substances show decomposition reactions during handling, production and transport. The amount of heat and pressure generated during this decomposition will determine if a substance can be considered thermally stable in a specific packaging size and temperature. Often the so called Self Accelerating Decomposition Temperature (SADT) is calculated for materials showing decomposition. This temperature is defined as the temperature at which the amount of heat produced by the decomposition reaction is equal to the heat loss of its packaging. For materials decomposing according to a pseudo zero order reaction (Arrhenius like reactions) this method can be considered correct. For materials showing autocatalytic decompositions the amount of heat generated is dependent on product lifetime and the conditions it was exposed to, which we will call history. This is in sharp contrast to the constant heat production that is shown in case of a pseudo zero order reaction.

In order to calculate a conservative value for the SADT of autocatalytic decomposing materials the heat generated at the maximum speed of the reaction should be used. The speed of decomposition varies a lot among different autocatalytic decomposing materials the under storage conditions. The time it takes to reach critical levels of heat production can vary between hours to years depending on the type of material. For these type of materials it is not relevant to determine the temperature at which self-heating occurs, but the time it takes to reach a critical level of heat production at a certain temperature and package size.

This paper will first discuss the flaws of the different methods to determine the SADT in case of autocatalytic decomposing materials. Secondly a method is proposed to determine the life time expectancy of autocatalytic decomposing materials, taken into account for the history of the material.

INTRODUCTION IN THERMAL STABILITY

Many materials are able to show self-heating during storage, handling, production and transport. The self heating is usually caused by a slow oxidation or decomposition reaction of which the produced heat is transferred to the surroundings. Therefore the most important factors that influence the (rate of) self-heating of a material are the reactive properties of the material and heat transfer properties through the material and from the material to the surroundings. These factors are partly determined by the material properties, but also by the way the material is stored or handled. In many processes where external heating is applied, the heat transfer from the bulk material to the surroundings is limited, and therefore the self-heating properties of the material can even become (almost) adiabatic, which means that all the produced heat is used for heating of the material. In most cases the heat production rises exponentially with the temperature, while the heat loss to the surroundings rises linearly with the temperature difference. Also the heat loss to the surroundings decreases with the size. This means that a material that is thermally stable at a certain temperature in a small package can be unstable in a large package. Figure 1 gives a simulated representation of the behaviour with temperature of the different parameters involved in self-heating.

Classical methods for determining the thermal stability are usually based on standardized methods [1] and most of result in the calculations of the so called Self Accelerating Decomposition Temperature (SADT). The SADT is defined as the lowest surrounding temperature at which a material in a certain configuration will show thermal instability. This surrounding temperature can directly be derived from the critical internal temperature the condition described by the heat balance [2] as given in Equation 1 is met, with Equation 3

$$m \cdot c_p \cdot \left\{ \frac{dT}{dt} \right\}_{T_S} = q_{produced} - q_{loss} \qquad \text{(Equation 1)}$$

In which:

m	=	total mass of the material [kg]
c_p	=	heat capacity of the material [$kJ \cdot kg^{-1} \cdot K^{-1}$]
$\left\{ \frac{dT}{dt} \right\}_{T_S}$	=	Heating rate of the material surrounding temperature [$K \cdot s^{-1}$]
$q_{produced}$	=	Heat produced by the material [$J \cdot s^{-1}$]
q_{loss}	=	Heat loss to the surroundings [$J \cdot s^{-1}$]

The SADT can be calculated for different dimensions for a material based on the kinetics of the decomposition reaction or on the results of screening methods as described in the UN Recommendations on the transport of dangerous Goods, Manual of tests and criteria, fourth revised edition (UN manual) [1]. Both types of approaches are quite accurate for materials that show decomposition according to a Pseudo first order reaction and their reactions kinetics are according to the Arrhenius-equation [3] (Equation 2). The SADT can than be calculated based on the heat production characteristics (Equation 2) and the critical internal

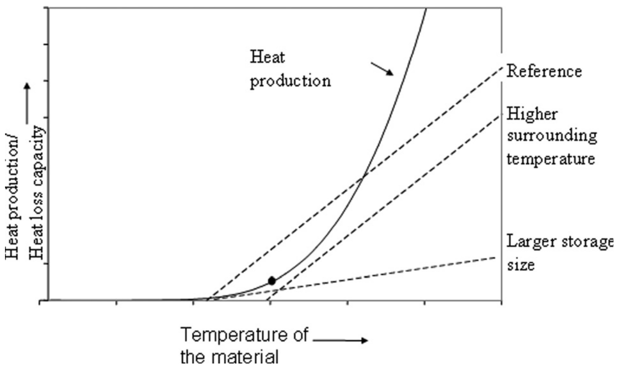

Figure 1. Simulated representation of heat production and loss of a material. The dashed lines represent heat loss capacities and the straight line represents the heat production of the material. The heat loss capacity of the material is given for three situations with the dashed line. At the heat production at the position of the dot the material is stable in the reference situation, but not at a higher surrounding temperature and storage size.

temperature (Equation 1) by means of Equation 3 [4].

$$q_{produced} = f(x) \cdot Q_0 \cdot z \cdot \exp^{(-E_a/RT)} \qquad \text{(Equation 2)}$$

In which:

$q_{produced}$	=	Heat production [W·kg^{-1}]
$f(x)\cdot Q_0\cdot z$	=	Pre exponential factor or heat production factor (HPF) [W·kg^{-1}]
E_a	=	(Apparent) Activation energy [kJ·mol^{-1}]
R	=	Molar constant [kJ·mol^{-1}·K^{-1}]
T	=	Temperature [K]

$$T_{SADT} = T_{ic} - \frac{HPF \cdot m}{U \cdot S} \cdot \exp^{\frac{E_A}{R \cdot T_{ic}}} \qquad \text{(Equation 3)}$$

In which:

T_{SADT}	=	Self Accelerating Decomposition Temperature [K]
T_{iC}	=	Critical internal temperature [K]
HPF	=	Heat production factor [W·kg^{-1}]
U	=	Heat transfer coefficient [W·m^{-2}·K^{-1}]
S	=	Heat transfer area [m^2]
m	=	total mass of the material [kg]
E_A	=	(Apparent) Activation energy [kJ·mol^{-1}]
R	=	Molar constant [kJ · mol^{-1}·K^{-1}]
T	=	Temperature [K]

When using screening tests described in the UN manual [1] (UN H.1 and UN H.4) to determine the SADT for (slow) autocatalytic decomposing materials the results can be considered unconservative when materials are stored for longer times eg. 6 to 12 months. This is due to the fact that shortly after production the heat production is much lower than the heat loss during in these tests. When using the UN H.2 or UN H.3 can in a large number of cases be seen as over conservative. This is due to the fact that in most cases the materials are not stored in the calculated configurations for such a long time. Therefore the safety of these kinds of materials should not be assessed by means of SADT but by means of a safe lifetime expectancy for certain configurations

SADT CALCULATION BASED ON THERMAL ANALYSIS

For a certain autocatalytic decomposing material the heat production was measured with the isothermal storage test [1] at three different temperatures. The results of these measurements are shown in Figure 2.

It was found that this reaction at the maximum rate of decomposition shows an activation energy of 80.9 kJ·K^{-1} and a heat production factor of 4.12.10^{12} W·kg^{-1}. This material is normally transported in a tank container with a heat loss 2.3 mW·kg^{-1}·K^{-1}. These parameters result, by using equations 1 to 3, in a calculated SADT of 13.5 °C for this material, resulting is a SADT of 15 °C. This corresponds to a heat production of at the SADT temperature is 0.0087 W·kg^{-1} as can be derived from Figure 3. When the material would have been tested with the UN H.1 or UN H.4 test the tested material needs to produce at least this amount of heat in order to show self heating, within 7 days.

As can be seen Figure 2 it takes approximately 25 hours at 55 °C, 44 hours at 50 °C and 144 hours at an oven temperature of 40 °C. This will result is an oven temperature of at least 40 °C to see an onset in self heating within 7 days when using the UN H.1 or UN H.4 tests. So it can be concluded that the results of such test are not conservative and these screening test can not be used for the determination of slowly autocatalytic decomposing materials.

Also from Figure 2 it can be derived that it will take a very long storage time to reach the maximum heat production levels. When using the time to maximum rate of heat productions as measured during the testing it will

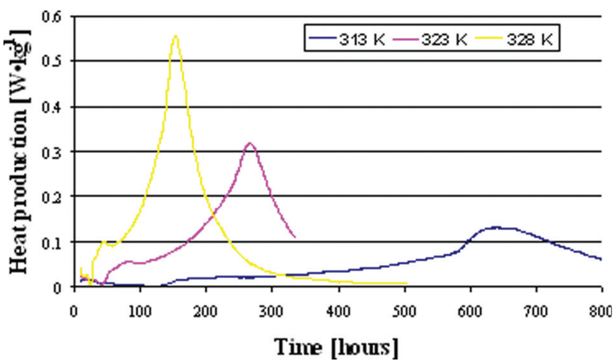

Figure 2. Heat production measurements on an autocatalytic decomposing material.

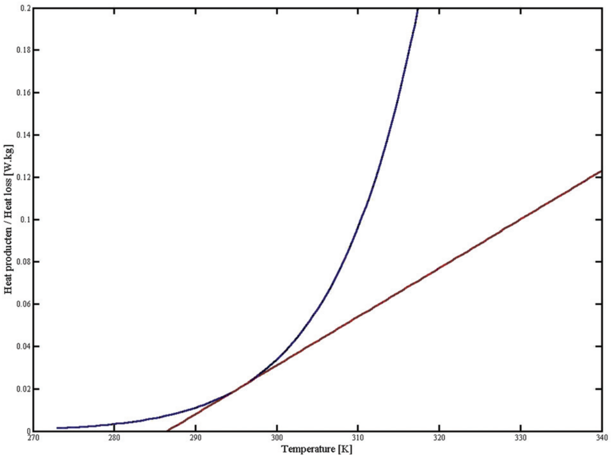

Figure 3. Maximum heat production for the tested material (blue) and heat loss of the tank container (red).

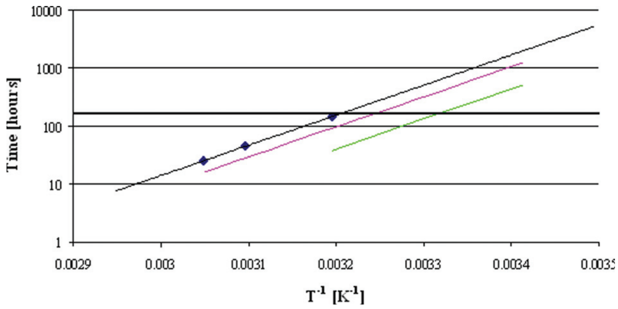

Figure 4. Arrhenius plot of the time it takes at different temperatures to reach level of heat production that causes self heating of the tested material in a tank container with 2.3 mW·kg-1·K-1 of heat loss for the measure ed samples is given in blue. Additionally the same is done for when the material is being stored for 30 days (pink) and 60 days (green). Below the black line the material will start to show self heating within 7 days in a tank container with 2.3 mW·kg^{-1}·K^{-1} of heat loss.

take 229 days storage at 20 °C to reach the maximum amount of heat production. This makes the use of kinetics based tests UN H.2 and UN H.4 will result in extreme conservative SADT, since most products will not be stored for such long times. So it can be concluded that the results of such test are too conservative and these kinetics based methods can not be used for the determination of slowly autocatalytic decomposing materials. So a new approach should be developed to asses the storage, handling, production and transport safety of slowly autocatalytic decomposing materials.

SAFE LIFETIME EXPECTANCY

In the previous section we concluded that the tests given in the UN manual [1] (UN H.1 to H.4) are not suited to asses the thermal stability of slow autocatalytic decomposing materials. So we would like to propose a method which will give a more realistic assessment of the safety of these types of materials. To do so you need to investigate the reaction kinetics of the material very thoroughly and determine the heat loss characteristics of your storage, handling, production and transport situations. Based on these values you can determine the critical amount of heat production for this material. From the investigation of reaction kinetics you determine the time it takes to reach this level of heat production and determine the Arrhenius curve. In Figure 4 an example is given for the case of the material given in the previous section (blue line). So is the material selected material is produced and stored at 20 °C it takes 81 days to reach a level of heat production that is high enough to cause self heating. When the material is stored at 20 °C for thirty days the safe life time has gone down as can be seen in Figure 4 (pink line) and will start self heating within 7 days at 35 °C.

CONCLUSIONS

This paper has shown that using screening thermal stability assessments for slow autocatalytic decomposing materials can give SADT results that can be considered not conservative and lead to fire or explosions during storage, handling, production and transport of the material. Also it shows that using kinetics based methods to assess the SADT of a slow autocatalytic decomposing material will lead to much to conservative results. This can be considered safe at any time, but will lead to unpractical and expensive consequences.

To prevent these types of situations this paper presents a method to assess the safe lifetime of slow autocatalytic decomposing materials. When the material reaches the end of it safe lifetime it can be repacked to a new situation with a higher heat loss capacity than the original situation to create a safe situation again.

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