Self-Accelerating Decomposition Temperature (SADT) Determination of Styrene System Using Accelerating Rate Calorimeter (ARC®)

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Abstract

The United States Department of Transportation (US DOT) and United Nations (UN) have developed a transport systemization based on a classification of certain types of dangerous goods and descriptions of tests and procedures. Dangerous goods are chemical substances, or articles containing chemical substances, which pose a threat to public safety or the environment during transportation if not properly identified or packaged. If they are accidently released, outcomes such as fires or explosions can occur. The purpose of the various tests is to provide adequate protection against the risk to life and property inherent in the transportation of hazardous materials in commerce.

A self-accelerating decomposition temperature (SADT or also commonly T_{SADT}) is the lowest ambient air temperature at which a self-reactive substance of specified stability undergoes an exothermic reaction in a specified commercial package in a period of seven days or less. The same substance and package must be able to survive for seven days at a temperature within 6°C of the temperature at which the reaction occurred.

Introduction

Why We Need to Determine SADT:

1. If the substance is being tested to determine if it meets the SADT criteria for a *self-reactive substance*, sufficient tests are performed to determine if the SADT for a 50 kg package is 75°C or less.
2. If the substance is being tested to determine if *temperature control is necessary*, sufficient tests are performed to determine if SADT is higher than 60°C.
3. If the substance is being tested to determine the temperature control condition, sufficient tests are performed to determine SADT to the nearest 5°C.

SADT values are determined on the assumption that the substance will only be subjected to a maximum ambient temperature of 55°C for a brief period on any day during transport. All substances that exhibit a self-accelerating reaction when tested at 55°C or less should be subjected to temperature control while transported.

Self-reactive substances are thermally unstable solids or liquids able to undergo a strong exothermic reaction / decomposition without participation of oxygen (air). Substances capable of producing an exothermic reaction and offered for transport should be subjected to the classification procedures.

The SADT is a measure of the combined effect of the ambient temperature, decomposition kinetics, package size and the heat transfer properties of the substance and its packaging. The series of H Tests described in the manual of tests and criteria by UN's Recommendations on the Transport of Dangerous Goods[i] reports following four official tests for the determination of SADT (see Table 1).

Table 1: List of UN Recommended Test for SADT Determination 1

Test Name	Sample Size
H1: United States SADT test	Actual shipping package
H2: Adiabatic storage test (AST)	1 liter
H3: Isothermal storage test (IST)	20g/test and multiple tests
H4: Heat accumulation storage test	400 cm^3

United States SADT Test

The United States SADT Test is used to estimate safe storage and transportation temperatures for a self-reactive substance in a specific package. Commercial packages are tested in an isothermal oven to determine the temperature at which the package survives and at which the sample undergoes an auto accelerative reaction, damaging the package. The difference between survival and damage must be less than 6°C over a period of 7 days (168 hrs). SADT is reported as the temperature at which reaction occurs. This method can be used to indicate explosion hazards from the decomposition reaction and may be used to test of up to 220 liters in volume.

Adiabatic Storage Test

The Adiabatic Storage Test determines the rate of heat generation produced by a reacting substance as a function of temperature. A temperature rise caused by the self-heating of one liter of material in a 1.5 liter Dewar vessel is monitored as a function of time. The heat generation parameters obtained are used in conjunction with the package's heat loss data to determine the SADT of a substance in its package. The method is appropriate for every type of package, including IBCs and tanks.

Isothermal Storage Test

The Isothermal Storage Test determines the rate of heat generation produced by reacting or decomposing substances as a function of time at constant temperature. The heat generation parameters obtained are used in conjunction with the package's heat loss data to determine the SADT of a substance in its packaging. The apparatus consists of an air insulated heat sink (an aluminum block) and two sample holes into which identical sample holders (70cm^3) are placed. Heat flow meters compare the heat flow at constant temperature from the sample and an inert substance. 20g of the sample are required for the test, and an equilibrium time of 12hrs is needed for each temperature step. The test is continued for a minimum of 24hrs in case of self-heating or stopped if the heat generation rate is falling from the maximum. The method is appropriate for every type of packaging including IBCs and tanks. Some substances may show an increase in the rate of heat generation with increasing decomposition and is taken into account by this test method.

Heat Accumulation Storage Test

The Heat Accumulation Storage Test determines the minimum constant air environment temperature at which thermally unstable substances undergo exothermic decomposition at conditions representative of the substance when packaged as for transport. The effectiveness of the method depends on selecting a Dewar vessel with heat loss per unit mass characteristics similar to the package offered for transport. Equipped with thermocouple to monitor the sample temperature, the Dewar vessel ($500cm^3$) is filled with $400cm^3$ of the substance and placed in a temperature controlled oven. . The temperatures at which the sample undergoes an auto-accelerative reaction and survive for a period of seven days are determined. This temperature difference should be less than 5°C for a reaction up to 50°C and less than 10°C if above 50°C. The SADT is the minimum self-reactive temperature. The method can be used for the determination of SADT of a substance in its packaging, including IBCs and small tanks (up to $2m^3$).

If a substance is being tested to determine whether it is a self-reactive substance of Division 4.1, SADT should be determined using either one of the above test methods or a suitable alternate test. If its SADT is less than or equal to 75°C when transported in a 50 Kg package, the sample is considered to be a Division 4.1 substance. Table 2 shows the control and emergency temperatures for transport based on the SADT values.

Table 2: Derivation of Control and Emergency Temperatures

Type of Receptacle	SADT for as packaged for transport	Control Temperature	Emergency Temperature
Single packaging and IBCs	≤20°C or less	20°C below SADT	10°C below SADT
	Over 20°C to 35°C	15°C below SADT	10°C below SADT
	Over 35°C	10°C below SADT	5°C below SADT
Portable tanks	<50°C	10°C below SADT	5°C below SADT

The official tests, described above, are very time consuming and, because of the large sample size, potentially dangerous. Because some pharmaceutical and specialty chemicals are expensive, substantial quantities are not available for testing. Alternate methods have been published by Fisher and Goetz[ii] which involve the use of an Accelerating Rate Calorimeter (ARC®), using a small sample (<10g) to determine the necessary kinetic information. This information together with a cooling curve (model suggested by UN[i]) not only provides an accurate SADT of the substance but also can estimate the SADT for different shapes, sizes and materials of packages without further testing. This method is safe and cost effective, generating a negligible amount of hazardous waste.

Proposed Method and Results

Fisher and Goetz[ii] present two methods that define SADT. Both methods use a single ARC® test for simple reactions and are defined by T_{NR} (temperature of no return) and activation energy (*E*). Wilberforce method uses the time to maximum rate (t_{MR}) curve to generate the T_{NR} value while analytical method uses time to maximum rate (t_{MR}) expression. In the case of the material having autocatalytic behavior or inhibitor depletion, where catalyst generation or inhibitor depletion is temperature dependent, time to maximum rate curve is developed by running the iso-aging test at a minimum of three temperatures. Styrene monomer is one example where the system undergoes polymerization with the release of heat when exposed to heat. It contains an inhibitor to avoid the polymerization. Although the inhibitor decomposes at certain temperatures, depletion of the inhibitor starts as a result thermal polymerization. The objective is to determine whether the Styrene in its package requires a controlled temperature for transport or storage.

Wilberforce method was used to estimate the SADT of Styrene monomer. ARC® was used to collect the thermally initiated polymerization reaction of styrene monomer (10-15ppm TBC inhibitor). The onset temperature and heat of reaction of polymerization reaction was 95°C and -240Btu/lb respectively. Since inhibitor depletion rate is temperature dependent, three iso-aging tests, each at 80°C (Figure 2), 85°C (Figure 3) and 90°C (Figure 4) at thermal inertia between 1.4-1.5 (calculated without fitting) were carried out to develop time to maximum rate (t_{MR}) curve (Figure 5) and estimation of kinetic activation energy. Time to maximum rates (t_{MR}) were corrected for thermal inertia of ARC® test cell by the methods explained by Townsend and Tou[iii]. For calculation purposes, the package was defined as a 55 gal drum, 22.5" inside diameter, 35.25" high, 1.2 mm thick top and bottom, 0.9 mm thick body, 43 W/m.K thermal conductivity and universal heat transfer coefficient (*U*) of 2.0 Btu hr^{-1} ft^{-2} C^{-1}. The time to maximum rate (t_{MR}) curve as used in the Wilberforce method is demonstrated in Figure 3. The time constant (*t*) is obtained from cooling curve for a package when full of inert substance of equivalent material.

$$\tau = \frac{m.Cp}{U(1.8)S}$$

Using time constant, T_{NR} is determined from Time to maximum rate curve (Phi = 1) (Figure 3) obtained from ARC® tests (Figure 2). The activation energy (*E*) can be determined by the following equation from the ARC® data:

$$E = \frac{R(T_2)T_1}{T_2 - T_1} \ln \frac{t_1(T_2)^2}{t_2(T_1)^2}$$

T_1 and *T_2* temperatures at time t1 and t2 respectively.

T_{SADT} could be calculated by the following equation:

$$SADT = T_{NR} - \frac{R(T_{NR} + 273.15)^2}{E}$$

Figure 1: Heat Generation Curve (A), Cooling Curve (B), and Thermal Equilibrium and Temperature of No Return (T_{NR})

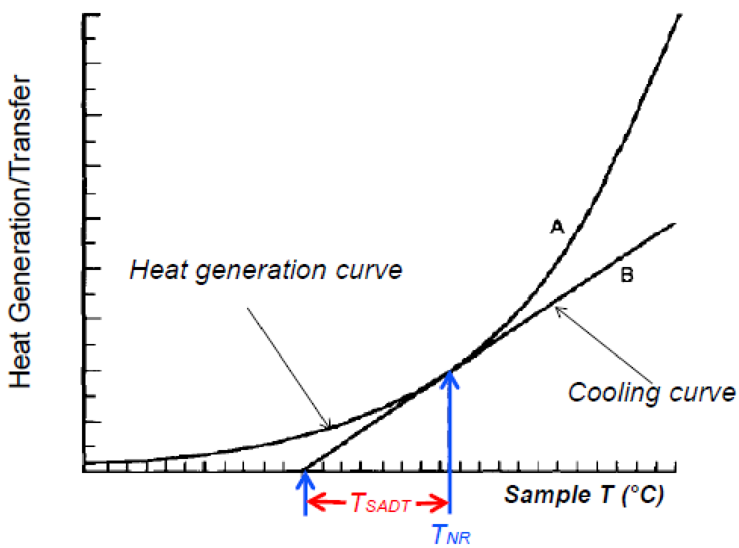


Figure 2: Iso-Aging Test at 80°C

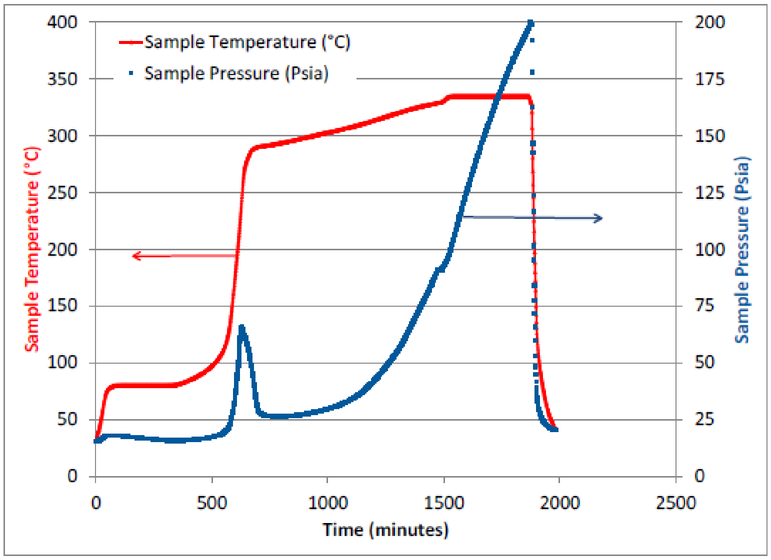


Figure 3: Iso-Aging Test at 85°C

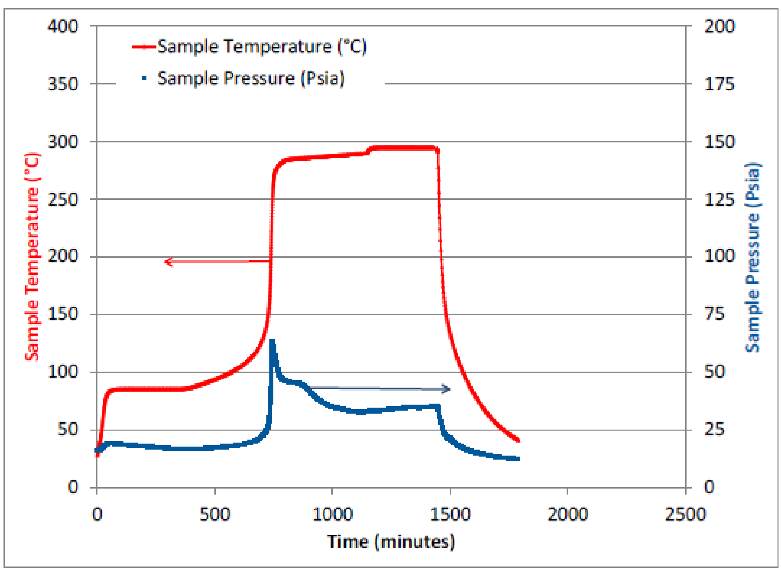


Figure 4: Iso-Aging Test at 90°C

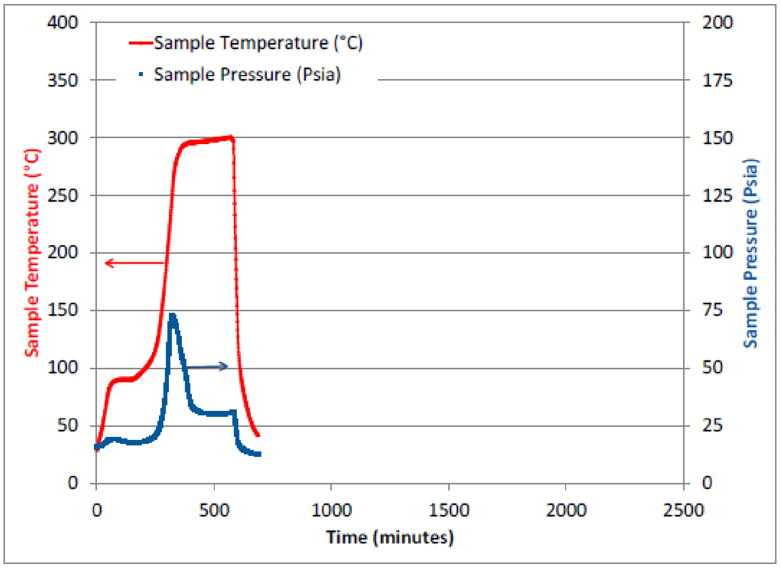
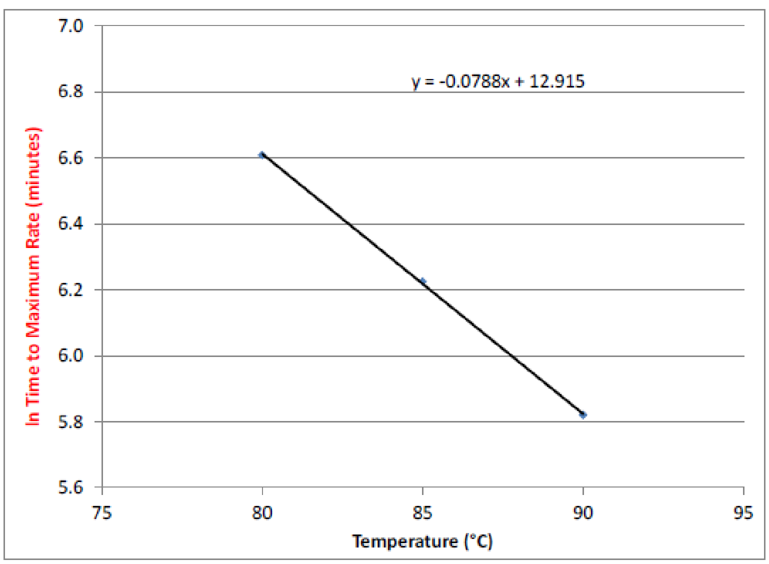


Figure 5: Time to Maximum Rate Curve



Time constant (τ) for system is calculated by equation:

$$\tau = m \frac{cp}{U(1.8)S} = 5.00 \text{ hr}$$

where,

m = 412.5 lb,

C_p = 0.755 Btu/lb/°

U = 2.0 Btu/lb/°C

S = 17.31 sq ft

Using time constant, T_{NR} (temperature of no return) is calculated from t_{MR} (time to maximum rate) plot.

T_{NR} at time constant of 5.00hr = 91.6 °C

Activation energy (*E*) was calculated from the slope of time to maximum rate curve as following:

$$E = \frac{R(T_2)T_1}{T_2 - T_1} \ln \frac{t_1(T_2)^2}{t_2(T_1)^2} = 73.6\, Btu/lb$$

Using T_{NR} and activation energy, T_{SADT} is calculated:

$$SADT = TN_R - R(T_{NR} + 273.15)2)/E \quad = 77°C$$

Conclusion

Styrene monomer inhibited with 15ppm TCB was found to have a self-accelerated decomposition temperature of 77°C when stored in a 55 gallon drum. Material is not subjected to a control temperature in its package for shipping or storage since SADT is >55°C.

Use of accelerating rate calorimeter for the determination of TSADT of reactive substances uses a very small sample quantity. Once data is generated, SADT can be calculated for different shapes, sizes and materials of the container. This method has been proven safe and generates negligible amount of hazardous waste while being cost effective.

References

[i] *Recommendations on the Transport of Dangerous Goods*, 5th Revised Edition, United Nations, New York, 2009.

[ii] Fisher, H.G. and Goetz, D.D. (1991). *Determination of Self-Accelerating Decomposition Temperatures Using the Accelerating Rate Calorimeter*. Journal of Loss Prevention in the Process Industries, Volume 4, Issue 5, 305-315.

[iii] Townsend, D.I. and Tou, J.C. (1980). *Thermal Hazard Evaluation by an Accelerating Rate Calorimeter*. Thermochim Acta, Volume 37, Issue 1, 1 – 30.

Additional Resources

1. Surendra K. Singh, Ph.D., 2014