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IDENTIFICATION OF POTENTIAL THERMAL RUNAWAYS USING SMALL SCALE THERMAL ANALYTICAL TECHNIQUES

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Abstract

With industry's focus on the early identification of potential thermal runaways in chemical processes, it is important that these potential thermal hazards be identified early in a process' development. Thermal runaways can be initiated in several ways: through an uncontrolled heat of reaction, the initiation of an exothermic decomposition/oxidation, or a combination of these two. It is therefore critical that information on exothermic decomposition/oxidation and heat of reaction be easily obtainable using small scale laboratory reactions.

A small scale thermal hazards identification program, using process samples from a 200 ml reaction and small scale thermal analytical techniques, identifies potential thermal runaways rapidly. The small scale thermal hazards identification program utilizes three small scale thermal analytical techniques developed at the Merck Research Laboratories. These include the use of specially designed DSC reusable metal crucibles to identify closed system exothermic activity in process samples, the Small Scale Isothermal Age Technique to accurately determine exothermic onset temperatures and Syringe Injection calorimetry to determine heat of reactions which occur at room temperature.

Keywords: decomposition, isothermal, process hazards, safety, small scale

Introduction

A critical aspect in the development of any chemical process is the early identification of potential thermal hazards associated with the process. Once the thermal hazards have been identified, the potential risk for thermal runaway can be assessed. Thermal runaways can be initiated in several ways: through an uncontrollable heat of reaction, the initiation of an exothermic decomposition/oxidation or a combination of these two. It is therefore critical that information on exothermic decomposition be easily obtainable using small scale laboratory reactions.

Merck has developed a two tier hazards assessment program to identify potential thermal hazards. The Tier I evaluation consists of thermal analytical screening methods which identify exothermic activity in the process and calorimetric methods to determine heats of reaction. The Tier II evaluation identifies potential thermal hazards, which could arise from the identified exotherms/heat of reactions, using methods which seek to identify exothermic onset temperatures and the rates of temperature and pressure increases associated with the decomposition. This two tier

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thermal hazards identification program utilizes small scale thermal analytical techniques developed at the Merck Research Laboratories. The Tier I program utilizes specially designed reusable metal crucibles, the Merck Closed Bomb [1], to identify exothermic activity in a closed reaction system and Syringe Injection Calorimetry (SIC) [2] to determine the heats of reaction. The Tier II program utilizes the Small Scale Isothermal Age (SSIA) [3] to identify exothermic onset temperatures. Using these small scale thermal analytical techniques and samples from a 200 ml reaction, safety screening for a process can be performed in ~2 to 3 days.

Identification of closed system exotherms using the Merck closed bomb

Differential scanning calorimetry is a technique frequently used to determine quantitatively if an exotherm is present in a closed reaction system. Typically, high pressure DSC or crimped aluminum pans are used. The problems of low pressure containment and chemical reactivity associated with the use of a crimped aluminum pan and noisy baseline and reproducibly with high pressure DSC are overcome with a specially designed reusable sample crucible, the Merck 'closed bomb' (CB).

Experimental

The design of the reusable CB is shown in Fig. 1 and consists of a screw-on cap, with a replaceable 20 μm Teflon rupture disk which can withstand a pressure of ~400 spi, and a threaded bottom. The CB is made of either Hastelloy B or 316L stainless steel, to provide overall corrosion resistance,and has a capacity of ~60 μl and an operating temperature rate from ~ −20 to 300°C. A removable glass liner is available for use with highly corrosive samples. A specially designed set of

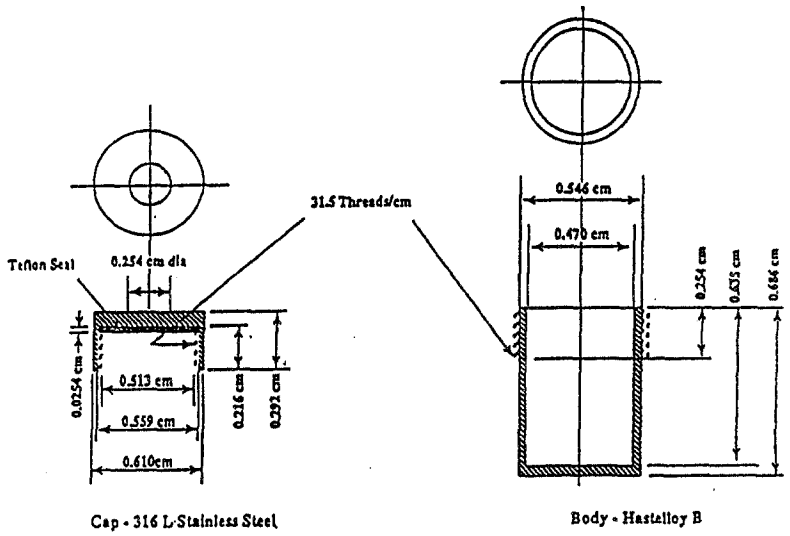

Fig. 1 Reusable closed bomb

wrenches is used in holding the bottom of the CB assembly and in tightening the cap. The closed bomb's thermal characteristics (with and without a liner) are compared with those of a crimped aluminum pan.

Heat transfer ability

The heat transferability was determined using an indium melt to determine the thermal resistance factor of the three sample containers. A constant weight of indium was used with a 5°C min^{-1} heat rate.

Repeatability of results

Repeatability of results, for the three sample containers, was evaluated by carrying out a series of indium melt runs using a consistent weight of indium and a heating rate of 5°C min^{-1}.

Quantitative measurement of data

The calibration coefficient E for the three types of sample holders was determined by utilizing a constant weight of indium (9.2 mg) and varying the heating rates (1,2,5,10 and 20°C min^{-1}).

Pressure rating and containment

The closed bomb pressure rating was determined by heating samples of acetone, methanol and water at 5°C min^{-1} until the Teflon seal ruptured. Each run was repeated five times. The vapor pressure containment was measured by heating each of the samples at 5°C min^{-1} to ~10°C above its boiling temperature and holding at the temperature for ~16 h and comparing the weight of each sample before and after the aging.

Results

Heat transfer ability

The thermal resistance, presented in Table 1, of the CB is ~1/3 that of the glass-lined bomb and twice that of the crimped aluminum pan.

Table 1 Heat transfer ability

Containers	Thermal resistance factor/ °C mW^{-1}	Heat of fusion[a]/ J g^{-1}	Calibration factor[b]
Aluminum pan	0.2203	26.929	1.0557
Closed bomb (without glass liner)	0.4386	25.590	1.1110
Closed bomb (with glass liner)	1.2346	25.349	1.1202

[a]For heat of fusion data, *E* was set to 1.00.; [b]*E*(cal)= heat of fusion (theoretical/heat of fusion) (experimental)

Repeatability of results

The repeatability of results is demonstrated by overlaying five runs of the melt of indium for all three samples holders with the results presented in Fig. 2. The repeatability for both the aluminum pan and closed bomb is good. The relatively poor results obtained form the glass liner are a result of the loose fit of the liner and its movement, which resulted in changes in the position of the indium in respect to the bottom of the closed bomb (CB).

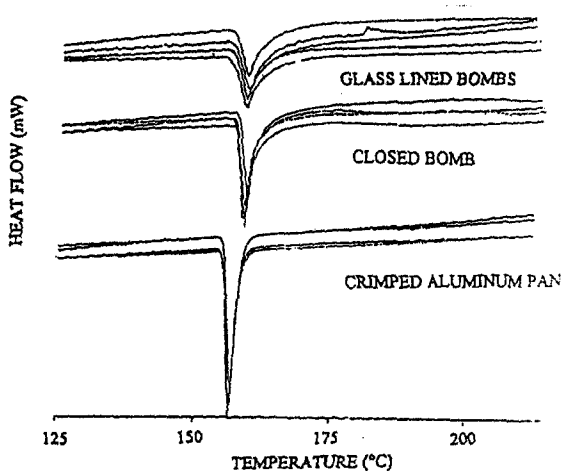

Fig. 2 Comparison of DSC indium melt for the three sample containers

Quantitative measurement of data

The results, presented in Table 2, indicate that the coefficient E increases linearly with increase in heating rate and are consistent with those reported by Van Humbreck and Bijvoet [4].

Pressure rating and containment

The CB has a pressure rating of ~400 psia as determined using the Teflon seal rupture temperature compared to the psia values reported in Lange's Handbook of Chemistry. The results are presented in Table 3.

Determination of heats of reaction

The standard methods used to determine heats of reactions include calculations, dewar calorimetry, reaction calorimetry, etc. The most common calculation method uses simple bond energies, heat of formation and heat of combustion data. However, only a limited data base exists, making it difficult to perform the calculation in many cases. The experimental procedures require large amounts of reactants and take considerable experimental effort. Syringe Injection Calorimetry (SIC) is a

Table 2 Instrument calibration using indium with constant weight of indium (9.2 mg)

Cell type	Heating rate/°C min^{-1}	Heat of fusion[a]/J g^{-1}	E_{exp}[b]	E_{corr}[c]
Al pan[d]	1	27.661	1.0278	1.0414
Al pan	2	27.169	1.0464	1.0449
Al pan	5	26.929	1.0557	1.0552
Al pan	10	26.422	1.0760	1.0724
Al pan	20	25.370	1.1206	1.1069
Al pan	50	23.609	1.2042	1.2102
CB[e]	1	26.570	1.0700	1.1035
CB	2	26.397	1.0770	1.1097
CB	5	25.590	1.1110	1.1283
CB	10	24.519	1.1595	1.1592
CB	20	23.791	1.1950	1.2211
CB	50	20.235	1.4050	1.4068
GL[f]	1	26.940	1.0553	1.0807
GL	2	26.341	1.0793	1.0945
GL	5	25.349	1.1202	1.1142
GL	10	24.349	1.1676	1.1470
GL	20	23.480	1.2108	1.2128
GL	50	20.210	1.4067	1.4099

Theoretical heat of fusion for indium =28.43 J g^{-1}.

[a]For heat of fusion data E was set to 1.000; [b]E_{exp} =theoretial heat of fusion/experimental heat of fusion; [c]$E_{corrected}$ is the result of the straight line fit of data points where $y=mx+b$;

[d]Al pan=crimped aluminum pan; [e]CB=Merck closed bomb; [f] GL=Merck closed bomb with glass liner

novel DSC calorimetric technique which has been developed for use with TA Instruments, Inc. [5] thermal analytical system to overcome the drawbacks of the calculation and experimental techniques and provides reasonably accurate data for liquid-liquid and liquid-solid reactions. A typical heat of reaction can be studied in less than two hours, using ~1 ml of each reactant and within 3% of theoretical values. The reactions studied must meet the following criteria: reaction occurs rapidly at room temperature, reactants mix easily, solution is homogeneous after the reaction and there is negligible gas generation.

Experimental procedure

A weighed amount of reactant A is injected into the Hastelloy B CB crucible using a microsyringe and allowed to come to thermal equilibrium before an excess amount of the second reactant B is injected into the system. Heat flow is recorded *vs.* time and is integrated using a sigmoidal baseline with E equal to 1. The results are then adjusted using a calibration factor, E_{sic}.

Table 3 Closed bomb's vapor pressure containment

Part 1: Vapor pressure rupture[a]

Sample	Rupture pressure/psia		
	lowest	highest	mean
Acetone	~433	~518	~462
Methanol	~445	~530	~498
Water	~414	~451	~433

[a]The sample was heated until the Teflon seal ruptured. Each run was repeated five times. The psia values reported are taken from Lange's Handbook of Chemistry

Part 2: Vapor containment[b]

Acetone	Mass of sample/mg		Mass loss/%
	before aging	after aging	
Acetone	67.4	67.3	0.15
Methanol	61.1	61.1	0.00
Water	58.5	58.5	0.00

[b]Each sample was heated to ~10°C above its boiling point and held at that temperature for ~16 h

Determination of calibration factor E_{SIC}

The calibration to determine the E_{sic}, which will compensate for the amount of unmeasured heat which is lost to the surroundings due to the system's configuration, was run using the neutralization of HCl with 0.5, 1.0, 2.0, 3.0 and 4.0 *M* NaOH solutions. The solutions were assayed to determine the exact weight percent of NaOH present in each solution used in the calibration. Using the experimental procedure above, the heat of reaction (ΔH_{mix}) in kcal mol^{-1} of NaOH for the neutralization of HCl was determined and calculated.

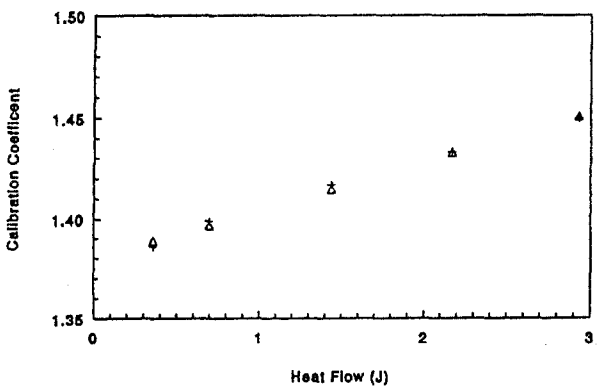

Fig. 3 SIC calibration; $HCl+NaOH \rightarrow NaCl+H_2O$; +: E_{EXP}, Δ: E_{SIC}

Results

The plot of Q *vs.* E_{EXP} for the HCl+NaOH reaction is linear over the range of 0.4 to 3.0 J of total heat measured and has a positive slope which is consistent with the data published by Van Humbeeck and Bijvoet. The data is presented in Fig. 3.

Several classical heats of reactions, heats of solutions and heats of dilution have been studied using the SIC technique and indicate that SIC is capable of determining heats of reaction within ±3% of the theoretical values. The results are presented in Table 4.

Table 4 SIC determined heats of reactions, solutions and dilutions

Test reactions	C/M	$\%\Delta_{th}$ measured
HCl+NaOH	0.5	100.2
HCl+NaOH	1.0	99.8
HCl+NaOH	2.0	99.9
HCl+NaOH	3.0	100.0
HCl+NaOH	4.0	100.1
HNO_3+NaOH	1.0	101.3
HNO_3+NaOH	2.0	98.1
HNO_3+NaOH	3.0	99.0
HNO_3+NaOH	4.0	98.2
KCl+H_2O	NA	99.0
$CaSO_4$+H_2O	NA	97.6
H_2SO_4+H_2O	NA	102.5

Determination of exothermic onset temperatures

The Small Scale Isothermal Age (SSIA) was developed to provide reliable information as to exothermic onset temperatures during the early stages of process development before large quantities of material are available. The SSIA technique is a novel isothermal DSC calorimetry technique which has been developed for use with TA Instruments Inc. DSC calorimeter instrument to provide accurate exothermic onset temperatures utilizing small samples (50 to 75 mg) and the Merck reusable closed bomb crucible (CB).

Experimental technique

Step 1

A temperature scan from ambient to ~300°C at 2°C min^{-1} is run on a sample using the CB with a 5–10 mg solid or 10 µl liquid sample. It is important that as small a sample as possible is used in the Merck reusable metal crucible so that the cruci-

ble is able to contain the pressure generated during the sample's decomposition. Therefore, if the crucible seal ruptures, the data obtained is not useable. The resulting exotherm (ΔH) of this run is evaluated and the lowest exothermic onset temperature is used for the first isothermal age.

Step 2

A DSC isothermal age, utilizing the CB, is run for ~12 h at the decomposition onset temperature determined in step 1. A 50 to 75 mg mass is used for solids and ~65 µl for liquids. A solid sample is packed tightly, with the crucible being filled almost to the top, to minimize heat loss from the sample.

Step 3

A DSC CB scan of the aged sample from step 2 is run at 2°C min^{-1} and the size of the exotherm (ΔH) is compared to that of the original exotherm in the unaged sample. The cell base, Merck metal crucible, sample weight and heat up rate are identical to that used in determining the size of the exotherm (ΔH) and the exothermic onset temperature of the unaged sample. A decrease in the size of the exotherm (ΔH) indicates heat evolution during the age, and therefore, the initiation of the exotherm during the age. When using liquids for the age period, the sample must be carefully weighed both before and after the age and any weight loss must be compensated for when calculating the size of the exotherm after the age period.

To provide for accurate results, from 3 to 5 scanning DSC runs must be performed on the unaged and aged samples. The start and end points for the exotherms, both before and after the age, must be carefully evaluated and selected using a sigmoidal curve in the analysis of the exotherm.

Step 4

Steps 2 and 3 are repeated at lower temperatures in ~5°C increments until no change in the size of the exotherm is observed for the aged sample.

Table 5 SSIA determination of exotherm onset temperatures for dicumyl peroxide solid and 40% mass in ethyl benzene

Instrument	Type of cell	$Time_{age}$/ h	T_{age}/ °C	% Change in size of exotherm in	
				solid/cal g^{-1}	EtBz solution/cal g^{-1}
DSC	Hast B Crucible[2]	12	90	0	0
DSC	Hast B Crucible	12	92.5	–1.5	–1.9
DSC	Hast B Crucible	12	95	–9.8	–10.3
DSC	Hast B Crucible[2]	12	100	–13.4	–14.5

Calibration

The SSIA technique was calibrated, using the above experimental technique, with solid dicumyl peroxide and a 40 wt% solution of dicumyl peroxide in ethyl benzene. The results are presented in Table 5. A Round Robin testing program, sponsored by the DIERS Users Group, identified the onset temperature for the decomposition for a 40 wt% solution of dicumyl peroxide in ethyl benzene using standard DSC, ARC [6], RSST [7] and VSP [7] test cells and procedures [8]. The ARC predicted a decomposition temperature of 103.4±3.2°C.

Results

Calibration

The SSIA technique determined a decomposition onset temperature of greater than 92.5°C for both the solid and solution samples of dicumyl peroxide which is equivalent to the ARC Round Robin test results.

Sensitivity

The SSIA technique, using dicumyl peroxide has a sensitivity of 0.01 to 0.013°C min^{-1}, which is lower than that selected for the DIERS Round Robin ARC studies (0.02°C min^{-1}).

Conclusions

The SSIA test method developed by Merck & Company is capable of predicting decomposition onset temperatures comparable to that of an ARC or Small Scale Adiabatic Dewar Technique [9] and better than those obtainable with standard dewar techniques.

This methodology is useful for determining decomposition onset temperatures only. The consequences of the initiation of the decomposition must be further evaluated via RSST, VSP or other suitable techniques in order to determine the consequence of initiation on chemical processing.

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