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Small scale isothermal age technique to determine exothermic onset temperatures[1]

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Abstract

With the increased focus on safety in the chemical industry, there is a greater demand for reliable information as to exothermic onset temperatures before the scale-up of any process. The Small Scale Isothermal Age (SSIA) test is an isothermal DSC technique in which reusable metal crucibles are used to accurately determine exothermic onset temperatures. A typical solid sample, 50–75 mg, is held isothermally at a preset temperature for an extended period of time, usually 12–16 h. The aged sample is then run at a standard heat-up ramp to determine any decrease in the size of the original exotherm relative to the unaged sample. The same DSC cell, metal crucible, heat-up rate and sample weight are used to determine the exotherm size in both the unaged and aged sample.

The SSIA technique is applicable to both solids and liquids and has the advantages of: i) small sample size, (ii) handling of compounds in which exothermic activity is accompanied by large pressure increases without damaging experimental equipment, (iii) accurate determination of exothermic onset temperature, (iv) ease of experimental set-up, (v) ease of data interpretation, and (vi) rapid experimental turn-around time.

The determination of the exothermic onset temperature using the small scale isothermal age technique will be presented and results compared to data obtained using standard and small dewar techniques.

Keywords: SSIA; DSC; Exothermic onset temperatures

1. Introduction

The Small Scale Isothermal Age technique (SSIA) was developed to provide reliable information as to exothermic onset temperatures during the early stages of process

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development before large quantities of materials are available. Typically, adiabatic dewar ages or Accelerating Rate Calorimetry (ARC) studies are used in determining exothermic onset temperatures. These test methods require relatively large samples and are time-consuming to run. The SSIA technique is a novel DSC calorimetry technique which has been developed for use with TA's DSC calorimetry instrument to provide reasonably accurate exothermic onset temperatures utilizing small samples (50–75 mg for solids). The SSIA technique uses a standard isothermal DSC technique and a sealable, reusable metal crucible [1]. The sample is held isothermally at a preset temperature for an extended period of time, usually overnight, with the aged sample being reevaluated for any change in the size of the original exotherm. A decrease in the size of the original exotherm indicates that heat was evolved during the age, and thus the exotherm initiated during the age. The consequences of the initiation of the exotherm must be further evaluated via Reactive System Screening Tool (RSST), Vent Size Packaging (VSP) or other suitable methodology in order to determine the consequence of initiation on chemical processing.

The determination of decomposition onset temperatures for dicumyl peroxide and two properietry compounds using the small scale isothermal age technique are presented in comparison to those determined using the Fauske [2] RSST (glass and Merck-designed dewar cell [3]), ASI [4] Radex (glass and Merck-designed dewar cell [3]) and a standard adiabatic dewar. In addition, the data for dicumyl peroxide in a Design Institute for Emergency Relief Systems (DIERS) Users Group Phase VII Round-Robin Test [5] are compared to the data obtained for dicumyl on this study.

2. Experimental

Four different test systems/methods utilizing four different test cells: (i) Fauske RSST with standard glass and Merck-designed dewar cell, (ii) ASI Radex with standard glass and Merck-designed dewar cell; (iii) TA 2200 [6] DSC with the Merck reusable metal crucible, and (iv) adiabatic calorimetry with standard dewar cell and a specially designed temperature-controlled oven, were used to determine the exothermic onset temperatures for three different compounds. Two different heat profile programs were used: a temperature scan utilizing a constant heat-up rate and an isothermal age technique using a set temperature.

2.1. Experimental Technique

2.1.1 Step #1

A temperature scan from ambient to ~ 300°C at 2°C min^{-1} was run on each sample using the four experimental test systems/methods. In the Merck reusable metal crucible, a 5–10 mg solid or 10 μl liquid sample are used. It is important that as small a sample as possible is used in the Merck reusable metal crucible so that the crucible seal is able to contain the pressure generated during the sample's decomposition. The size of the exotherm from this metal crucible run was compared to that of the aged sample. Therefore, if the crucible seal ruptures, the data obtained are not usable. The RSST, Radex and Merck-designed dewar cells are approximately half-filled with sample. The typical quantity used in the RSST is ~ 2 g of a solid and 3–4 ml of a liquid. Radex cells use ~ 0.5 g for solids and ~ 2 ml for liquids. The weights will vary somewhat depending on the type of sample being tested. Please note that the sample was not compacted for the temperature scan runs. The results of these tests were evaluated and the lowest exothermic onset temperature was used for the first isothermal age test.

2.1.2. Step #2

A DSC isothermal age, at the exothermic onset temperature determined in step #1, is run for ~ 12 h in each of the test cells used in step #1. In the Merck reusable metal crucible, the sample was packed tightly, with the crucible being filled almost to the top to minimize heat loss from the sample. This is necessary due to the small sample size utilized. A typical sample quantity used in the metal crucible is ~ 50–75 mg for a solid and ~ 65 μl for a liquid sample. In the RSST, Radex and Merck-designed dewar cells, the sample was compacted by lightly tapping the cell. The typical quantity used in the RSST was ~ 5 g for a solid and ~ 8 ml for a liquid sample. Radex cells use ~ 1 g for solids and ~ 5 ml for a liquid. The weights used vary somewhat depending upon the type of sample being tested.

2.1.3. Step # 3

A Dsc scan, utilizing the Merck metal crucible, was run on the aged sample from step # 2 utilizing a TA 2200 system. The size of the resulting exotherm was compared to the original exotherm in the unaged sample. The cell base, Merck metal crucible , sample weight and heat-up rate were identical to those used to determine the exotherm size in the unaged sample (step # 1). A decrease in the size of the exotherm indicated that heat was evolved during the age, and thus the exotherm initiated during the age. With liquids, the sample must be carefully weighed both before and after the ago so that any weight loss can be compensated for in calculating the size of the exotherm after the age. 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 ages, must be carefully evaluated and selected using a sigmoidal curve in the analysis of the size of the exotherm.

2.1.4. Step # 4

Step # 2 and 3 were repeated at lower temperatures in ~ 5°C increments until no change in the size of the exotherm was observed for the aged sample.

2.2. Calibration of the small scale adiabatic dewar system

The SSIA technique was calibrated using solid dicumyl peroxide and a 40% weight solution in ethyl benzene. A Round-Robin testing program, sponsored by the DIERS Users Group, identified the onset temperature for the decomposition for a 40% weight solution of dicumyl peroxide in ethyl benzene using standard DSC, ARC, RSST and VSP test cells and procedures [5].

In the first step of the calibration of the SSIA technique, the decomposition onset temperatures for both the solid and ethyl benzene solution of dicumyl peroxide were determined using the DSC (sealed Merck metal Hast B crucible), RSST (standard glass and Merck-designed dewar cell), RADEX (standard glass and Merck-designed dewar cell) and the adiabatic oven with a standard corked dewar, as per step # 1 of the experimental. These results were compared to those of the DIERS Round-Robin test and are presented in Table 1.

In the second step of the calibration of the SSIA technique, both the solid and liquid samples were isothermally aged in a TA DSC cell using a Hast B metal crucible, a RSST unit using a Merck-designed dewar cell and a RADEX unit using a Merck-designed dewar cell at three predetermined temperatures (90, 95 and 100°C) as per step # 2 of the experimental. The aged samples were then rerun, as per step # 3 of the experimental, in a Hast B metal crucible and compared to that of the unaged sample to determine if decomposition had occurred. The results are presented in Table 2. The results of a subsequent SSIA evaluation of the liquid sample at 92.5°C, using only the DSC isothermal ages, are also included to demonstrate the sensitivity (°C min^{-1} detection of heat release) of the SSIA technique. A decrease in the size of the original exotherm in the dicumyl peroxide indicates indicates that heat was evolved and thus decomposition initiated during the age; see Figs. 1 and 2 for a comparison of the DSC reruns of the isothermally aged solid and ehtyl benzene solution of dicumyl peroxide.

Table 1
Comparison of exotherm onset temperatures for dicumyl peroxide, solid and 40 wt% ethyl benzene

Results from	Type of instrument	Type of cell	Onset temp. solid/°C	Onset temp EtBz solution/°C
DIERS Round-Robin[a]	DSC	Stainless steel test cell	Test not run	109.4 to 159.2 (avg. 150 ± 6.1)
SSIA calibration	DSC	Hast B crucible[b]	125	124
DIERS Round-Robin[a]	RADEX	Glass cell	Not available	Not AVAILABLE
SSIA calibration	RADEX	Glass cell	112	117
DIERS Round-Robin[a]	RSST	Glass cell	Not available	110 To 125 (avg. 115.2 ± 4.1)
SSIA calibration	RSST	Glass cell	112.5	118
DIERS Round-Robin[a]	ARC	Regular test cell	Not available	97 to 107 (avg. 103.4 ± 3.2)
SSIA calibration	RADEX	Special RADEX dewar cell[c]	103	105
SSIA calibration	RSST	Special RSST dewar cell[c]	104	103
SSIA calibration	Adiabatic dewar oven	Regular dewar	104	Test not run[d]

[a] Ref. [5]. [b] Ref. [1]. [c] Ref. [3]. [d] System can not be sealed to prevent solvent loss.

Table 2
SSIA determination of exotherm onset temperature for dicumyl peroxide, solid and 40 wt% in ethyl benzene

Instrument used to age sample	Type of cell	Hours aged	Age temp./ (°C)	% Change in size exotherm in solid/ (cal g^{-1} dicumyl peroxide)	% Change in size of exotherm in EtBz solution/ (cal g^{-1} dicumyl peroxide)
DSC	Hast B crucible[a]	12	90	0	0
RADEX	Dewar Cell[b]	12	90	0	0
RSST	Dewar cell[b]	12	90	0	0
DSC	Hast B crucible[a]	12	92.5[c]	1.5	−1.9
DSC	Hast B crucible[a]	12	95	−9.8	−10.2
RADEX	Dewar cell[b]	12	95	−10.2	−9.4
RSST	Dewar cell[b]	12	95	−9.6	−10.3
DSC	Hast B crucible[a]	12	100	−13.4	−14.5
RADEX	Dewar cell[b]	12	100	−13.3	−14.6
RSST	Dewar cell[b]	12	100	−14.9	−13.4

[a] Ref. [1]. [b] Ref [3]. [c] The data for the 92.5°C run are provided to allow for the determination of the sensitivity level of the SSIA technique.

3. Case studies

The evaluation of two Merck propertietary compounds using the SSIA technique are compared those determined using standard adiabatic dewar, RSST and RADEX dewar studies.

As per step # 1 of the experimental, the decomposition onset temperature for both proprietary compounds were determined using the DSC (sealed Merck metal Hast B crucible), RSST (standard glass and Merck-designed dewar cell), RADEX (standard glass and Merck-designed dewar cell) and the adiabatic oven with a standard corked dewar. These results are presented in Tables 3 and 4.

Both proprietary compounds were isothermally aged in the Merck Hast B metal crucible, RSST and RADEX Merck-designed dewar cells at three predetermined temperatures, as per step # 2 of the experimental. The aged samples were then rerun, as per step # 3 of the experimental, in a Merck Hast B metal crucible and compared to that of the unaged sample to determine if decomposition had occurred. The results are presented in Tables 5 and 6.

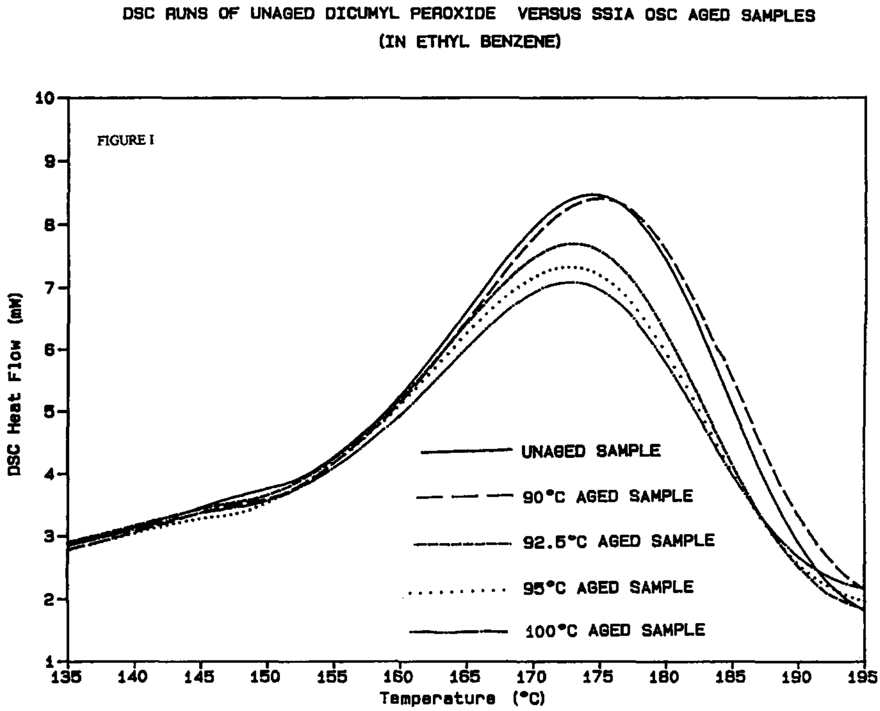

Fig. 1. DSC runs of unaged dicumyl peroxide versus SSIA DSC aged samples (in ethyl benzene).

4. Results

4.1. Calibration

The small scale isothermal age (SSIA) technique determined a decomposition onset temperature greater than 90°C for both the solid and 40 wt% ethyl benzene solution of dicumyl peroxide. The lowest ARC-predicted decomposition onset temperature was 97°C.

Both the SSIA and small scale adiabatic dewar age techniques determined a decomposition onset temperature ~ 9°C lower that predicted with standard dewar temperature scan runs.

4.2. Case Studies

The small scale isothermal age (SSIA) technique determined decomposition onset temperatures are comparable to those determined using adiabatic dewar age techniques. RSST dewar ages, RADEX dewar ages and SSIA ages all predict a decomposition onset temperature of greater than 35°C for both proprietary compounds.

The SSIA and the small scale adiabatic dewar age techniques both determined

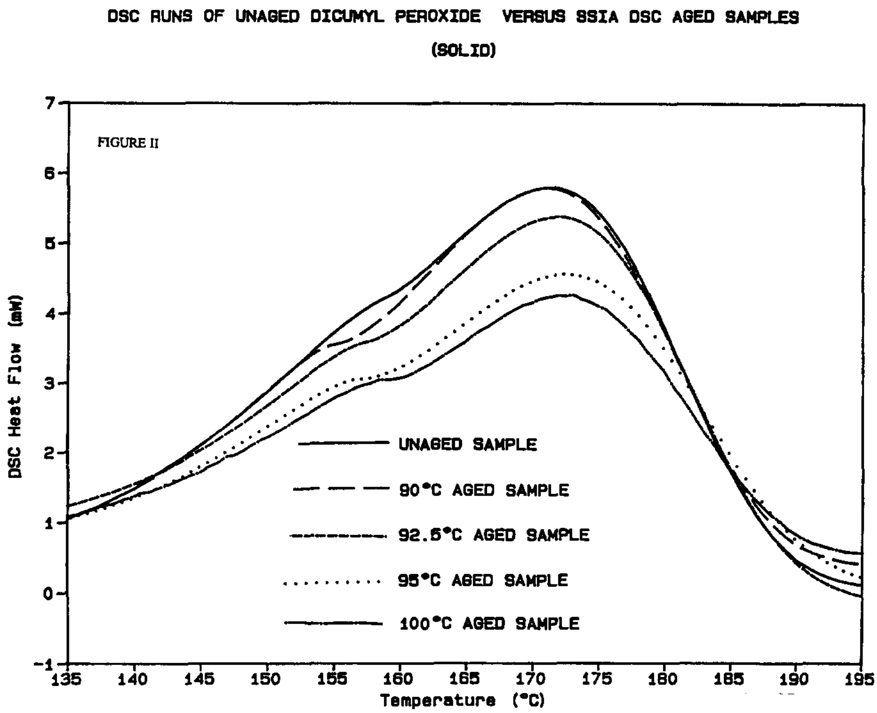

Fig. 2. DSC runs of unaged dicumyl peroxide versus SSIA DSC aged samples (Solid).

Table 3
Comparison of exotherm onset temperatures for proprietary compound # 1

Type of instrument	Type of cell	Onset temp./°C exotherm # 1 (premelt exotherm)	Onset temp./°C exotherm # 2	Onset temp./°C exotherm # 3
DSC	Hast B crucible[a]	None	108.3	175.3
RADEX	Glass cell	None	109.2	179.9
RADEX	Dewar cell[b]	58.7	108.6	173.4
RSST	Glass cell	NONE	108.3	178.1
RSST	Dewar cell[b]	58.3	108.6	173.4
Adiabatic dewar oven	Regular dewar	51.4	108.3	175.0

[a] Ref. [1]. [b] Ref. [3].

Table 4
Comparison of exotherm onset temperatures for proprietary compound # 2

Type of instrument	Type of cell	Onset temp./°C exotherm # 1 (premelt exotherm)	Onset temp./°C exotherm # 2
DSC	Hast B crucible[a]	70.0	122.0
RADEX	Glass cell	72.5	125.5
RADEX	Dewar cell[b]	57.6	124.5
RSST	Glass cell	66.8	125.0
RSST	Dewar cell[b]	51.5	120.5
Adiabatic dewar oven	Regular dewar	48.3	125.0

[a] Ref. [1]. [b] Ref. [3].

Table 5
SSIA determination of exotherm onset temperature for proprietary compound # 1

Instrument used to age sample	Type of cell	Hours aged	Age temp./°C	% change in the size of the exotherm
DSC	Hast B Crucible[a]	12	30	0
DSC	Hast B crucible[a]	12	35	0
RADEX	Dewar cell[b]	12	35	0
RSST	Dewar cell[b]	12	35	0
DSC	Hast B crucible[a]	12	40	−5.85
RADEX	Dewar cell[b]	12	40	−6.63
RSST	Dewar cell[b]	12	40	−5.23
DSC	Hast B crucible[a]	12	50	−21.30
RADEX	Dewar cell[b]	12	50	−16.34
RSST	Dewar cell[b]	12	50	−16.60

[a] Ref. [1]. [b] Ref. [3].

a lower decomposition onset temperature than that predicted with standard dewar temperature scan runs, ~ 6°C less for proprietary compound # 1 and ~ 8°C less for proprietary compound #2.

4.3. Sensitivity

Calibration of the SSIA technique, using dicumyl peroxide, has indicated that the system has a sensitivity level lower (0.01–0.013°C min^{-1}) than that selected for the ARC studies (0.02°C min^{-1}) in the DIERS Round-Robin Test [5].

Table 6
SSIA determination of exotherm onset temperature for proprietary compound # 2

Instrument used to age sample	Type of cell	Hours aged	Age temp./ °C	% change in the size of the exotherm
DSC	Hast B crucible[a]	12	30	0
DSC	Hast B crucible[a]	12	35	0
RADEX	Dewar cell[b]	12	35	0
RSST	Dewar cell[b]	12	35	0
DSC	Hast B crucible[a]	12	45	−1.21
RADEX	Dewar cell[b]	12	45	−1.74
RSST	Dewar cell[b]	12	45	Not available[c]
DSC	Hast B	12	55	−3.50
	crucible[a]	12	55	−3.50
RADEX	Dewar cell[b]	12	55	−3.06
RSST	Dewar cell[b]	12	55	−2.82
DSC	Hast B crucible[a]	12	65	−4.59
RADEX	Dewar cell[b]	12	65	−3.89
RSST	Dewar cell[b]	12	65	−4.98

[a] Ref. [1]. [b] Ref. [3]. [c] The percent change in the size of the exotherm at 45°C could not be measured due to sample decomposition upon storage.

Table 7
Comparison of sensitivity (°C min^{-1}) of test methods

Test method	Sample tested	Sensitivity/ (°C min^{-1})
ARC[a]	Dicumyl peroxide liquid	0.02[b]
SSIA	Dicumyl peroxide liquid	0.013[c]
SSIA	Dicumyl peroxide solid	0.01[c]
SSIA	Proprietary compound # 1	0.025[c]
SSIA	Proprietary compound # 2	0.011[c]

[a] Ref. [5]
[b] Sensitivity level used in DIERS Round Robin test.
[c] The sensitivity was calculated by dividing the heat release in cal^{-1} g by the time min. This results was divided by the heat capacity (0.5 cal^{-1} g °C^{-1} assumed).

The results of the case studies presented indicate that the SSIA system has a sensitivity of 0.011°C min^{-1}.

A comparison of the sensitivity for the detection of the exothermic onset temperature for dicumyl peroxide and the Merck proprietary compounds versus that of the ARC (present at 0.02°C min^{-1} for the DIERS Round-Robin test) are presented in Table 7. The results of a later SSIA evaluation of the solid and liquid sample at 92.5°C, using only the DSC isothermal ages, are also included for use in demonstrating the sensitivity (°C min^{-1} detection of heat release) of the SSIA technique.

5. Conclusions

Calibration of the SSIA technique, using dicumyl peroxide, indicates that the test method is capable of predicting decomposition onset temperatures comparable to that of an ARC or the small scale adiabatic aging dewar technique [3], and better than those obtainable with standard dewar temperature scan runs.

The results of the case studies presented indicate that the SSIA technique is capable of determining lower decomposition onset temperatures than any of the standard dewar temperature scan methods tested and are comparable to those obtained using the small scale adiabatic aging dewar technique [3].

The small scale adiabatic dewar systems [3] developed by Merck for use with the RADEX and RSST units, run in a temperature scanning mode, are capable of determining decomposition onset temperatures comparable to those obtained using standard large scale adiabatic dewar test methods and the ARC test method.

A sensitivity level of from 0.01 to 0.013°C min^{-1} was demonstrated for the SSIA technique.

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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