The self-accelerating decomposition temperature (SADT) of solids of the quasi-autocatalytic decomposition type [1]

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Abstract

Self-heating or thermally explosible chemicals are divided into two large groups, the thermal decomposition or TD type and the autocatalytic decomposition or AC type. The TD type is further divided into liquids, for each of which the critical temperature for thermal explosion or T_c is calculated by applying the Semenov equation, and, solids, for each of which the T_c is calculated by applying the Frank–Kamenetskii or F–K equation. On the other hand, the AC type is further divided into solids of the quasi-AC type, in each of which the exothermic decomposition reaction occurs almost simultaneously with the endothermic melting, and, liquid or solid high explosives of the true AC type, in each of which the self-accelerating exothermic decomposition reaction begins after an autocatalyst has appeared and accumulated. Neither of the two critical conditions for thermal explosion, i.e., the Semenov equation or the F–K equation, is applicable to the self-heating behaviour of each individual chemical of the AC type for the calculation of the T_c. Instead, the respective self-heating behaviour of them is in accord with the concept of the self-accelerating decomposition temperature (SADT) in principle. The SADT of each individual solid of the quasi-AC type discussed in this paper as well as the critical temperature for self-heating or T_{cs} of each individual high explosive of the true AC type is determined by the isothermal storage test. In this study, the respective SADTs of five solids of the quasi-AC type were determined using a simple and safe isothermal storage testing device. The SADT thus determined ranged from 28.4°C for 95% 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) to 86.5°C for 98% 1,1′-azobis(cyclohexanecarbonitrile). These temperature values are in fair agree-

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ment with a few corresponding values of the SADT measured by other researchers for them of large quantities. © 1999 Elsevier Science B.V. All rights reserved.

1. Relative position that solids of the quasi-AC type occupy amongst the whole family of self-heating chemicals

The self-heating or thermally explosible behaviour of each individual self-heating chemical is related closely to the appearance of the thermogravimetry–differential thermal analysis (TG–DTA) curve which it yields. Thus, one glance at the TG–DTA curve of each individual solid is enough for us to infer the self-heating behaviour to be either the TD type or the quasi-AC type and hence to infer the critical condition for thermal explosion applied to calculate the T_c to be either the Semenov equation or the Frank–Kamenetskii (F–K) equation, or neither equation.

In this section, the above is first elucidated with some figures and tables to clarify the relative position that solids of the quasi-AC type occupy amongst the whole family of self-heating chemicals.

1.1. Relationship between the TG–DTA curve of each individual self-heating solid and either of the two types of the self-heating behaviour, i.e. the TD type or the quasi-AC type

The TG–DTA curves, which were recorded with a glass open cell at a heating rate of 2.5 K/min in air at atmospheric pressure, of four solids of the TD type listed in Table 1, are presented in Fig. 1. It is clear that the characteristic feature of the DTA curve of each individual solid of this type is the absence of the melting point. Solids of this type decompose in advance of their melting. Solids like AIBN, which decompose explosively in advance of any remarkable exothermic decomposition reaction, also belong to the TD type. AIBN, when confined in a glass closed cell and exposed to the surroundings maintained at a temperature in the range of 65–74°C in an adiabatic self-heating test, shows such a self-heating behaviour which is typical of chemicals of the TD type as will be presented in Fig. 5. On the other hand, TG–DTA curves, which were also recorded with a glass open cell at a heating rate of 2.5 K/min in air at atmospheric pressure, of four in the five solids of the quasi-AC type listed in Table 3 in Section 4, are presented in Fig. 2. It is clear in this figure that one characteristic feature of the DTA curve of

Table 1
The four solids of the TD type

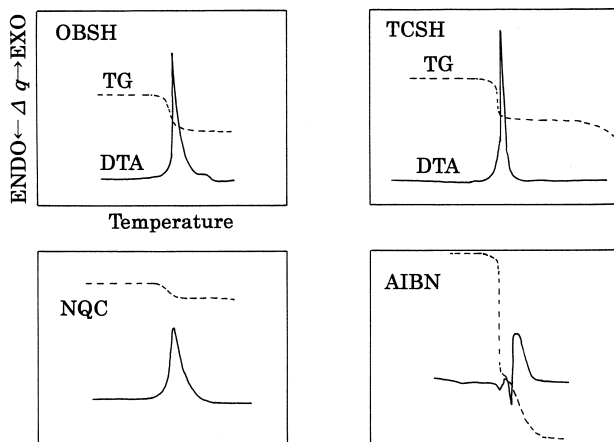|	
OBSH	95% 4,4′-Oxybis(benzenesulphonyl hydrazide)
TCSH	98% 2,4,5-Trichlorobenzenesulphonyl hydrazide
NQC	98% 1,2-Naphthoquinone-2-diazido-5-sulphonyl chloride
AIBN	98% α, α′-Azobis(isobutyronitrile)

Fig. 1. The TG–DTA curves of the four solids of the TD type.

each individual solid of this type is the presence of the melting point [1]. Another characteristic feature of the DTA curve of each individual solid of this type is that the curve shifts successively from the endothermic peak due to melting to the exothermic peak due to decomposition reaction. TG curves of solids of the quasi-AC type show that they decompose slowly in most cases.

The property of the respective solid of the quasi-AC type varies in a continuous fashion with the interval between both peaks of the DTA curve. Both peaks are especially close together in the case of ABCN or AMVN, as seen in Fig. 2. The respective shape of DTA curves of some solids of the quasi-AC type, especially that of ABCN or AMVN, is thought to reflect a fact that, when heated, a chemical reaction,
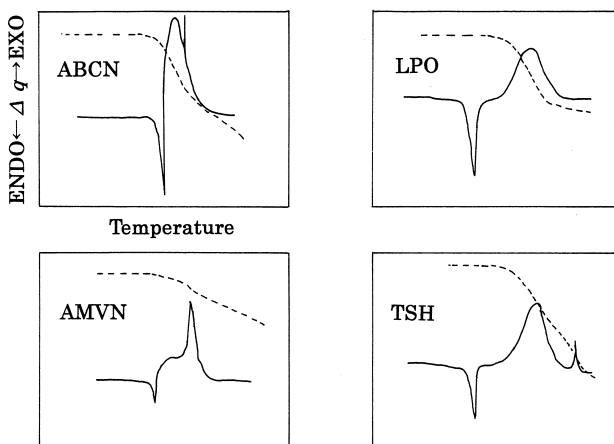

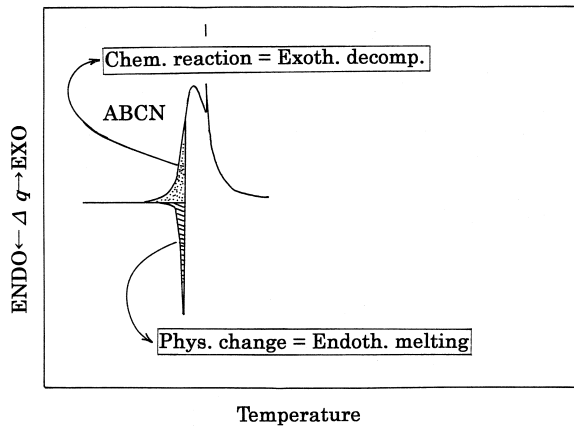Fig. 2. The TG–DTA curves of the four solids of the quasi-AC type.

Fig. 3. Simultaneous occurrence of a chemical reaction, the exothermic decomposition reaction, and a physical change, the endothermic melting, in ABCN as an example of solids of the quasi-AC type.

exothermic decomposition, takes place parallel with a physical change, endothermic melting, as shown diagrammatically in Fig. 3.

Under isothermal storage conditions, the exothermic decomposition reaction of each individual solid of this kind begins in the liquid phase while the liquid and the solid phase coexist, and the heat flux from the exothermically decomposing liquid is utilized for the endothermic melting of the solid, so that the system is maintained under quasi-isothermal conditions until the melting is completed. In this connection, when solids such as ABCN or AMVN are subjected to an isothermal storage test, they start to self-heat abruptly and rapidly while in a state similar in the appearance to the half-melted shaved ice.

It is inferred that the above phenomenon in which the exothermic decomposition reaction takes place parallel with the endothermic melting occurs in all solids of the quasi-AC type, although this fact is not necessarily explicitly revealed in their respective DTA curves.

1.2. Correlation amongst the DTA curve of each individual self-heating chemical, either of the two types of the self-heating behaviour and either of the two critical conditions for thermal explosion

We can infer systematically the type of self-heating behaviour of each individual chemical, with the exception of high explosives of the true AC type, and hence, can infer either of the two critical conditions for thermal explosion applied to calculate the T_c from the DTA curve in accordance with the diagram presented in Fig. 4.

The relative position of the exothermic onset temperature or EOT and the melting point of each individual chemical become the key for the correlation. For chemicals which are solid at room temperature but decompose exothermically as liquids at temperatures far higher than their melting points, their respective T_cs can be calculated by applying the Semenov equation. In addition to liquids of the TD type of this kind,
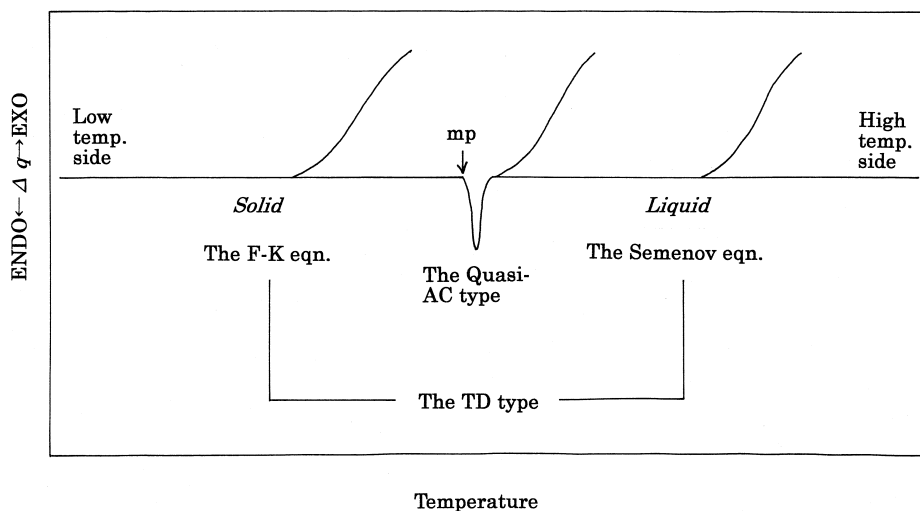
Fig. 4. Correlation amongst the DTA curve of each individual self-heating chemical, either of the two types of the self-heating behaviour and either of the two critical conditions for thermal explosion.

once either solids of the TD type or those of the quasi-AC type are dissolved in any solvents at room temperature, they also become liquids of the TD type to which the Semenov equation is applied to calculate their T_cs. In this connection, we may assume that chemicals which are liquid at room temperature naturally have their freezing points at temperatures sufficiently lower than room temperature. For chemicals which are solid at room temperature and decompose exothermically as solids at temperatures lower than their melting points, their respective T_cs can be calculated by applying the F–K equation. In other words, each individual molecule of liquids of the TD type decomposes as a free molecule in the liquid phase, and that of solids of the TD type decomposes while remaining fixed within the 'cage' composed of the surrounding crystal lattice in the solid phase.

Both are, however, the same at a point that their respective decompositions are not accompanied with any phase transition. Therefore, each of them continues to self-heat over the starting temperature or T_s in an adiabatic self-heating test, with a rate depending upon the temperature of the system in accordance with the Arrhenius equation, after each has been warmed up to the T_s. Consequently, the application of either of the two critical conditions for thermal explosion becomes possible, because each of the two critical conditions is derived on the premise that the rate of the exothermic decomposition reaction depends upon the temperature of the system in accordance with the Arrhenius equation. In this connection, we may assume that the T_s corresponds to the testing temperature in an isothermal storage test.

Besides the self-heating chemicals of the TD type, however, there is yet another large group of self-heating chemicals classified as the AC type, the self-heating behaviour of which is different from that of the TD type. Each solid of the quasi-AC type, when exposed to the surroundings maintained at a T_s in an isothermal storage test, warms
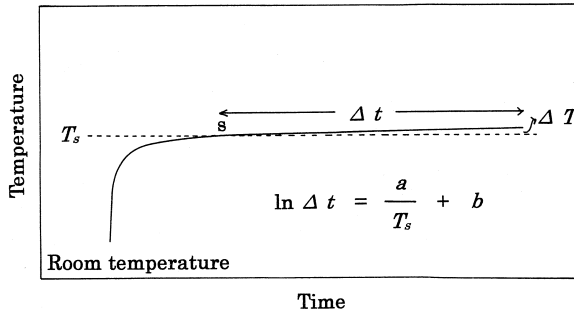
Fig. 5. A diagram of the typical self-heating behaviour of chemicals of the TD type placed under adiabatic conditions.

slowly up to the T_s; thereafter, the temperature of the solid remains near the T_s over a long period of time, because the phase transition, melting, of the solid occurs almost simultaneously with the exothermic decomposition reaction. But, once the melting is completed in the course of time, an abrupt self-heating of the resultant liquid starts. Probably, each individual molecule of solids of this type starts to decompose exothermically, once it is released from the 'cage' composed of the surrounding crystal lattice by melting. The reason why they are termed the quasi-AC type is that, although they do not decompose due to autocatalysis, their typical self-heating behaviour (Fig. 6) resembles apparently that of high explosives of the true AC type (Fig. 7). Solids of the quasi-AC type exist in considerable numbers. On the other hand, each liquid or solid high explosive of the true AC type, when exposed to the surroundings maintained at a T_s in an isothermal storage test, does not continue to self-heat over the T_s, but remains near the T_s over a long period of time; in the meantime, an autocatalyst like NO_2 radical appears and accumulates little by little in the high explosive. But, once the concentration of the autocatalyst attains a threshold value in the course of time, a very slow self-heating of the high explosive begins; thereafter, it accelerates gradually. It is well-known that such a self-heating behaviour as described above is observed in the
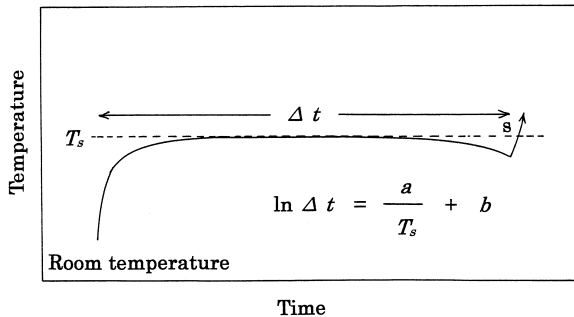

Fig. 6. A diagram of the typical self-heating behaviour of solids of the quasi-AC type placed under isothermal storage conditions.
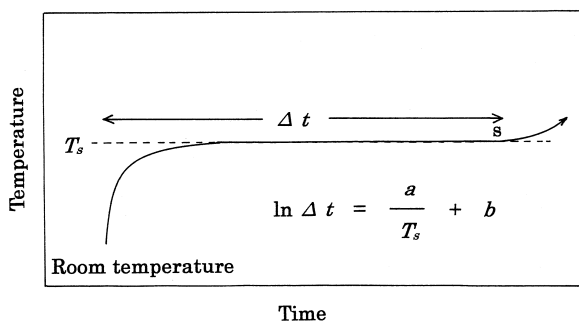
Fig. 7. A diagram of the typical self-heating behaviour of high explosives of the true AC type placed under isothermal storage conditions.

spontaneous ignition process of nitrate esters and polynitro compounds. High explosives of the true AC type thus form a group intrinsically different, in the decomposition reaction mechanism, from the other self-heating chemicals. However, they are comparatively small in number. For the empirical formula presented in Figs. 6 and 7, refer to Eq. (2).

In the last analysis, self-heating chemicals are divided into two large groups, the TD and the AC type, in accordance with the difference in the self-heating behaviour or in accordance with the difference in the characteristic temperature (the T_c, the SADT or the T_{cs}) to represent their respective thermal instabilities, as presented in Table 2.

Chemicals, with the exception of high explosives of the true AC type, chemicals which are solid at room temperature are classified into the following three groups in accordance with the difference in the respective self-heating behaviour of them.

Group I. Solids to which the Semenov equation is applied to calculate their respective T_cs. Each solid of this group, when exposed to the surroundings maintained at a T_s in an adiabatic self-heating test if the T_s is above the melting point of the solid, melts at once. The resultant liquid warms up to the T_s within tens of minutes; thereafter, it continues to self-heat over the T_s with a rate depending upon the temperature of the system in accordance with the Arrhenius equation (Fig. 5) [2].

Group II. Solids to which the F–K equation is applied to calculate their respective T_cs. Each solid of this group, when exposed to the surroundings maintained at a T_s in an adiabatic self-heating test, warms up to the T_s within tens of minutes; thereafter, it continues to self-heat over the T_s as a solid with a rate depending upon the temperature of the system in accordance with the Arrhenius equation (Fig. 5) [3].

Group III. Solids to which neither of the two critical conditions for thermal explosion is applicable to calculate their respective T_cs. Each solid of this group, when exposed to the surroundings maintained at a T_s in an isothermal storage test, warms slowly up to the T_s; thereafter, the temperature remains near the T_s all through the melting of the solid. But, once the melting is completed in the course of time, an abrupt self-heating of the resultant liquid starts.

As explained already, with the exception of high explosives of the true AC type, chemicals which are liquid themselves or dissolved in any solvents at room temperature,

Table 2
A classification of self-heating chemicals.

		Chemicals which are solid at room temperature		The characteristic temp. to represent the thermal instability of chemicals (T_c, SADT or T_{cs})
Self-heating chemicals	TD type	self-heat as liquids, after melting.	Chemicals which are liquid or dissolved at room temperature	T_c is calculated, applying the Semenov equation.
		self-heat as solids.		T_c is calculated, applying the F-K equation.
	AC type	Solids of the quasi-AC type		SADT is measured by the isothermal storage test.
		Liquid or solid high explosives of the true AC type		T_{cs} is measured by the isothermal storage test.

and solids of Groups I and II are referred to as the TD type, and solids of Group III are referred to as the quasi-AC type.

A diagram of the typical self-heating behaviour of chemicals of the TD type placed under adiabatic conditions is presented in Fig. 5. Each liquid or solid of this type, when exposed to the surroundings maintained at a T_s in an adiabatic self-heating test, continues to self-heat over the T_s, after having been warmed up to the T_s. Under these circumstances (as presented in Fig. 5), an empirical formula [Eq. (1)] holds between the T_s [K] and the time, Δt [min], required for the sample temperature to rise by a definite temperature increment, ΔT [K], from the T_s under adiabatic conditions.

$$\ln \Delta t = a/T_s + b, \tag{1}$$

where a and b are constants.

Both coefficients a and b are used to calculate the respective T_cs of liquids or solids of the TD type of practical sizes placed under isothermal storage conditions [2,3]. Adiabatic conditions are necessary to make Eq. (1) valid. An adiabatic self-heating process recorder, instead of an isothermal storage testing device, is thus indispensable to

calculate the respective T_c of chemicals of the TD type of practical sizes placed under isothermal storage conditions. The adiabatic control and recording of the process of adiabatic temperature-rise for each sample of chemicals of the TD type are started at the time point 's' in Fig. 5.

A diagram of the typical self-heating behaviour of solids of the quasi-AC type and that of high explosives of the true AC type, each of which is placed under isothermal storage conditions, is shown in Figs. 6 and 7, respectively. It is observed in general that the rate of temperature lowering due to the melting of each solid of the quasi-AC type increases as the melting proceeds. Such a melting behaviour of solids of the quasi-AC type, as described above, suggests evidently that their melting proceeds in accordance with the kinetics of the heterogeneous reaction. That is, the melting proceeds at the surface of separation between the liquid phase and the solid phase, and the rate of melting increases in proportion to the surface area, which in turn increases as the melting proceeds. In any event, a temperature curve such as that presented in Fig. 6 is recorded for the typical self-heating behaviour of solids of the quasi-AC type at a T_s on the high temperature side. However, the respective time interval up to the start of self-heating of solids of the quasi-AC type becomes far longer, and the temperature lowering due to the melting is of only 0.1–0.2 K at a T_s on the low temperature side. Despite this, the respective start of self-heating of solids of the quasi-AC type can be observed clearly even at a T_s on the low temperature side.

1.3. The SADT and the T_{cs}

It is impossible to apply either of the two critical conditions for thermal explosion to the characteristic self-heating behaviour of solids of the quasi-AC type and that of high explosives of the true AC type to calculate their respective T_cs, because each of them does not continue to self-heat over the respective T_s with a rate depending upon the temperature of the system in accordance with the Arrhenius equation, after having been warmed up to the T_s, regardless of whether it is subjected to an adiabatic self-heating test or to an isothermal storage test. Instead, taking advantage of an experimental fact that Eq. (2) holds for all chemicals of the AC type, including high explosives of the true AC type, between the T_s [K] and the time Δt [min] from the start of exposure of a sample to the surroundings maintained at a T_s until the start of self-heating of the sample in an isothermal storage test, the respective SADTs of all chemicals of this type can be determined by experimental measurements in principle. The SADT is defined as the minimum temperature of ambient air for a self-heating chemical at which the self-accelerating decomposition reaction starts after just 1 week when the chemical is packaged in its largest commercial container and placed in the testing facility.

$$\ln \Delta t = a/T_s + b, \tag{2}$$

where a and b are constants. It is obvious that both Eqs. (1) and (2) assume the identical configuration of the Arrhenius type.

The respective SADTs of chemicals of the AC type are calculated as T_s corresponding to a Δt value of 10 080 min or 7 days in Eq. (2).

However, in the respective cases of almost all high explosives tested in this series of studies, with the exception of picric acid, the self-heating phenomenon leading to the thermal explosion can occur even at a low T_s corresponding to a time Δt, longer than 7 days. Therefore, the concept of the SADT, which denotes, as stated above, originally a temperature at which the self-heating phenomenon leading to the thermal explosion of a chemical of the AC type begins just 7 days after the start of exposure of the chemical to the surroundings maintained at the temperature, but, which may in fact be regarded as the critical temperature below which the thermal explosion of a chemical of the AC type can hardly occur, does not hold for these high explosives.

On the other hand, in the respective cases of high explosives such as picric acid, the self-heating phenomenon leading to the thermal explosion cannot occur even at a high T_s corresponding to a time, Δt, shorter than 7 days. Therefore, the concept proper of the SADT does not hold for them as well.

That is to say, in the respective cases of solids of the quasi-AC type, the SADT is situated at the sufficiently low temperature region at which the thermal explosion can hardly occur. Consequently, the respective SADT has a practical meaning as the upper limit temperature in temperature control for the prevention of the thermal explosion of each individual solid of the quasi-AC type and therefore, it is worthwhile to measure the respective SADT for each of them. On the other hand, as exemplified above, the characteristic self-heating behaviour of high explosives of the true AC type is not necessarily in accord with the concept of the SADT. It thus follows that the concept of the SADT is not appropriate to represent the critical temperature below which the thermal explosion of each individual high explosive of the true AC type can hardly occur.

High explosives of the true AC type may be regarded as the most dangerous chemicals amongst the whole family of the self-heating chemicals. Thus, the T_{cs}, below which the respective self-heating leading to the thermal explosion of high explosives of the true AC type cannot occur absolutely, should be determined regardless of whether the time required for each of them to begin to self-heat is longer than 7 days or not, to utilize the T_{cs} thus determined as the upper limit temperature in temperature control for the prevention of the thermal explosion.

1.4. The difference amongst the T_c, the SADT and the T_{cs}

The three concepts of the T_c, the SADT and the T_{cs} are not necessarily distinguished from one another at the present time.

The concept of the T_c fits only the normal self-heating behaviour of chemicals of the TD type of practical sizes, each of which has a definite geometrical shape and an arbitrary dimension, and is placed under isothermal storage conditions. The T_c, in each of the two critical conditions for thermal explosion, denotes such a temperature that, if a chemical having a definite geometrical shape and an arbitrary dimension is exposed to the surroundings maintained at the T_c under isothermal storage conditions, the chemical continues to self-heat over the T_c, and, at the time when the chemical, as a whole, has self-heated up to a temperature at the critical state for the thermal explosion, which exists during the early stages of the self-heating process, the rate of heat evolution in the chemical becomes equal to the rate of heat transfer from the chemical to the surround-

ings. If the chemical is exposed to the surroundings maintained at a temperature higher than the T_c, the rate of heat evolution exceeds the rate of heat transfer at all stages of the self-heating process, so that the temperature of the chemical continues to rise acceleratedly to cause the ultimate thermal explosion. The T_c depends upon the geometrical shape and the dimension of the chemical, because the heat-accumulation conditions or the rate of heat transfer depends upon the ratio of surface area to volume of each individual self-heating body. But the T_c is not a function of time. The critical temperature, at which 400 ml of a liquid organic peroxide contained in a 500-ml Dewar flask used in the BAM heat-accumulation storage test will explode thermally, can be calculated as a T_c of the peroxide by applying the Semenov equation [2]. However, no information regarding the time, required for the peroxide to explode thermally, accompanies the T_c.

On the other hand, the concept of the SADT or the T_{cs} consists only with the characteristic self-heating behaviour of chemicals of the AC type. The time, Δt, including that corresponding to the SADT or the T_{cs}, from the start of exposure of a sample to the surroundings maintained at a T_s until the start of self-heating of the sample in an isothermal storage test, can be determined only for each individual chemical of the AC type as a function of the T_s in accordance with Eq. (2). In this connection, the T_s including the SADT or the T_{cs} is a function of time, Δt, alone, according to Eq. (2). It thus follows that the T_s, including the SADT or the T_{cs}, is independent of the quantity of each individual chemical of the AC type, in principle. It may arise from the fact that the respective SADT of solids of the quasi-AC type depends upon the physical change, melting, which is independent of the quantity of the respective solid; and the respective T_{cs} of high explosives of the true AC type depends upon autocatalysis, which is also independent of the quantity of the respective high explosive. In any event, we have no choice but to determine by experimental measurements the characteristic temperature to represent the respective thermal instability of two groups of chemicals of the AC type in terms of the SADT or the T_{cs}, by performing an isothermal storage test such as the U.S. SADT test or the method proposed herein, until a new method of calculation is established in the future.

The similarity between the T_c and the SADT is, however, as follows. According to the experience of a company where the respective T_cs of some dozens of liquid organic peroxides were actually measured by the BAM heat-accumulation storage test, the time required for most peroxides to explode thermally at the respective T_c was 1–2 days, or within 3 days at the longest, and, even if the respective peroxide was maintained at any temperature above or below the respective T_c, none of them exploded after just 7 days [2]. On the other hand, it has been ascertained also in the isothermal storage test carried out for solids of the quasi-AC type in this study that each of them starts to self-heat so rapidly and forcefully as to explode thermally with certainty at a T_s, on the high temperature side, corresponding to a Δt value of 1–2 days, in the meantime, each of them starts to self-heat so slowly and faintly as to explode hardly at a T_s, on the low temperature side, corresponding to a Δt value of 5–7 days.

In this regard, the respective T_{cs} of high explosives of the true AC type in general corresponds to a T_s, on the low temperature side, corresponding to a Δt value longer than 7 days.

2. An isothermal storage testing device

2.1. Structure and performance

A cross-section of the device is presented in Fig. 8. The base of the device is a heater and a thermoregulator constituting an aluminium block bath (the trade name: Dry thermounit DTU-1B and -1C) manufactured by Taitec, Koshigaya, Japan. An aluminium block, 107 mm × 107 mm × 79.6 mm^H, an aluminium lid and a glass closed cell having an inside volume of about 2 ml were newly prepared. The latter cell has fundamentally the same structure as that used for an adiabatic self-heating process recorder [2]. The confinement of samples in any closed cells is indispensable for experiments of this kind, because in the case of each individual solid of the quasi-AC type, the exothermic decomposition reaction accompanied with the gas evolution frequently starts once the solid completes the melting, and in the case of each individual high explosive of the true AC type, the presence of an autocatalyst like NO_2 radical is a prerequisite for the promotion of exothermic decomposition reaction of the high explosive.

The accuracy of the temperature control of the block is ±0.05 K. The analogue output of the reference or sample temperature is continuously recorded, in the meantime, the digital output is recorded every 30 min, with an analogue/digital temperature recorder. The digital output is read to 0.1 K.

2.2. Sensitivity of this device

It is severe circumstances for a self-heating chemical that a small quantity of the chemical is confined in the glass closed cell inserted into the hot aluminium block
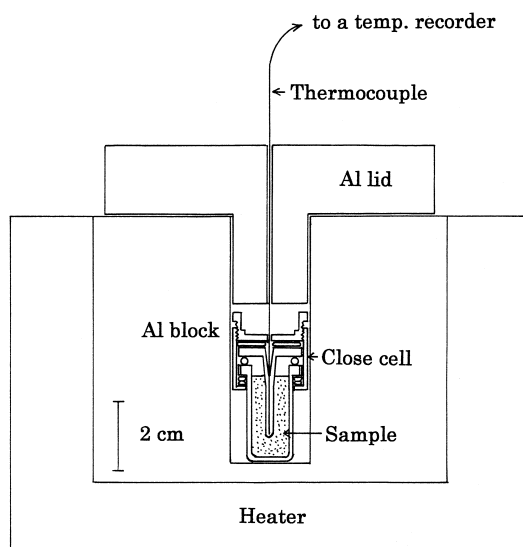

Fig. 8. Cross-section of an isothermal storage testing device.

having a large heat transfer coefficient. The large heat transfer coefficient of the aluminium block means that the heat flow into the sample is higher than that in normal storage conditions. Because the melting process of samples is accelerated under such circumstances, it follows that the SADT on the low temperature (or on the safety) side is brought about for each individual solid of the quasi-AC type.

Adiabatic conditions are unnecessary for an isothermal storage testing device used to determine the respective SADT of solids of the quasi-AC type, at least, because, as can be seen from Fig. 6, no heat loss occurs from the liquefied solid to the surroundings at the time point 's' because the condition:

$$T_s \text{ (the temperature of aluminium block)} > \text{the temperature of the liquefied solid,}$$

holds at 's,' when the melting of the solid has been completed. Under such circumstances, the thermocouple is capable of detecting sensitively the start of self-heating of the liquefied solid.

3. Experimental

(1) First, let us take Lauroyl peroxide (LPO) as an example to illustrate how to select the T_s in the isothermal storage test for a specific solid of the quasi-AC type. A DTA curve of LPO is given in Fig. 9. The melting point of LPO is 48°C, and the EOT appears to be 59°C. The latter temperature is, however, too high and dangerous at which to perform the isothermal storage test for LPO. Consequently, in practice, tests have to be performed at temperatures below the endothermic peak temperature, as illustrated for LPO in Fig. 10. As stated in Section 1.1, this necessity is caused by the fact that the exothermic decomposition reaction and the endothermic melting occur almost simultaneously in each solid of the quasi-AC type. Notes, like '1 day at 51.6°C', mean that, when
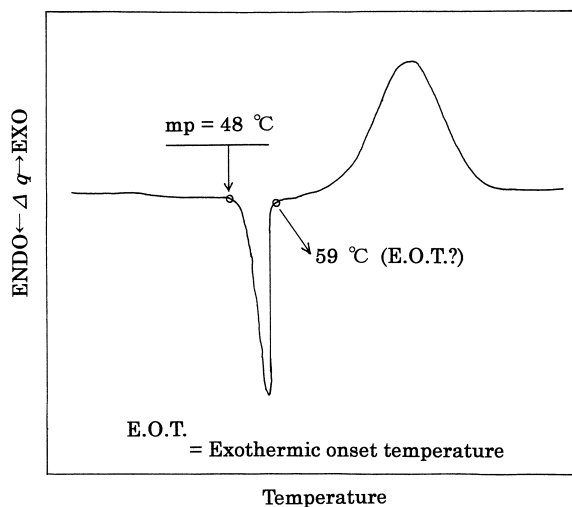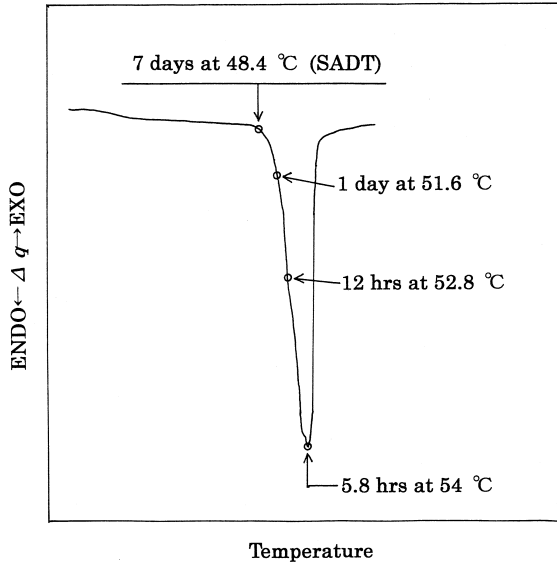

Fig. 9. A DTA curve of LPO.

Fig. 10. The actual isothermal storage testing temperatures for LPO.

maintained at the specified temperature, the sample completes the melting and starts to self-heat after just the time corresponding to the specified temperature.

(2) A glass closed cell, the reference cell in which 2 ml of silica powder as a thermally inert substance is contained, is placed in the bottom of a hole, 23 mm$^\phi$ × 75 mm deep, bored vertically in the center of the aluminium block, the temperature of which is maintained at a T_s [K]. The T_s of the run is then determined as the arithmetic mean of digital outputs of the T_s recorded for 2 days prior to the insertion of the sample cell into the aluminium block. Fluctuations of the value of T_s recorded as digital outputs during this period of time are within ±0.05 K.

(3) After the reference cell has been removed, another glass closed cell, the sample cell, in which about 2 ml of a sample of a solid of the quasi-AC type is confined, is placed in the bottom of the hole; in the meantime, the temperature of the aluminium block is maintained at the identical T_s. Tests in this study were performed for solids of the quasi-AC type of the industrial grade without further purification. The time, Δt [min], from the insertion of the cell until the start of self-heating of the sample is then measured. However, the time axis on the other side in Fig. 11 is graduated in days so as to meet the sense of long time. The block-heating is automatically interrupted, once the sample temperature has risen by 0.3 K from the T_s, to prevent the cell from exploding.

(4) A plot of ln Δt vs. $1/T_s$ is made, using a series of combinations of Δt with T_s which is obtained by a series of isothermal storage tests carried out at several values of T_s with mutual intervals of 1–2 K for each individual solid. Results confirmed for LPO are presented in Fig. 11. It is clear that the empirical formula, ln $\Delta t = a/T_s + b$, i.e. Eq. (2), presented in Fig. 6 holds in Fig. 11. The standard deviation of the linear plot is 0.03379 in this case.
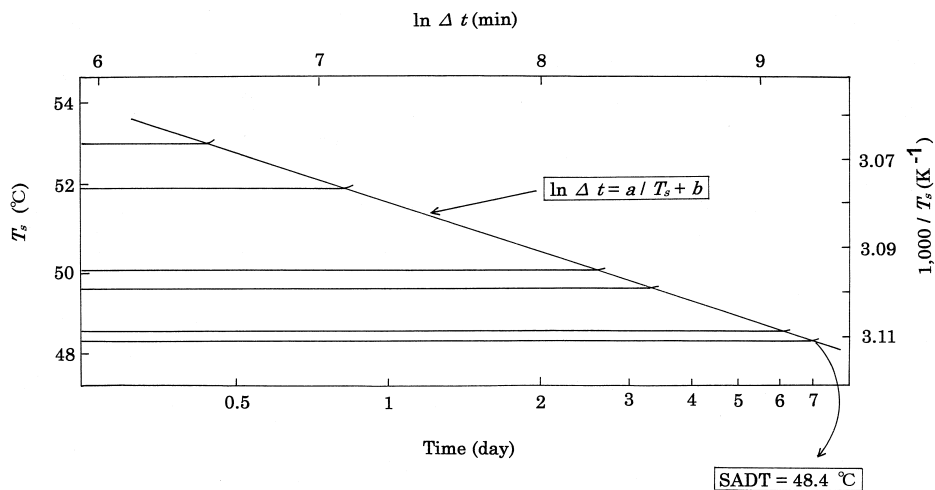
Fig. 11. Results of a series of isothermal storage tests carried out for LPO.

(5) The SADT of LPO is calculated at a T_s value, 48.4°C, which corresponds to a Δt value of 10,080 min or 7 days in Eq. (2), i.e., $\ln \Delta t = 63{,}097.79 / T_s - 187.03050$, established in (4).

(6) Finally, an isothermal storage test is carried out at the SADT calculated in (5) to ascertain whether or not the sample will melt completely and begin to self-heat very slowly just 7 days after the start of exposure.

(7) Once Eq. (2) has been established for a solid of the quasi-AC type, it is possible to calculate an arbitrary value of T_s, as well as the SADT, at which the solid will melt completely and start to self-heat after an arbitrary exposure time such as 1 day, 30 days or 60 days.

4. Results

A list of the five solids of the quasi-AC type tested is given in Table 3. The respective SADT values of them, each of which was determined in the same manner as done for LPO, are summarized in Table 4 together with a few corresponding values of

Table 3
The five solids of the quasi-AC type

AMVN	95% 2,2′-Azobis(4-methoxy-2,4-dimethylvaleronitrile)
LPO	99% Lauroyl peroxide
BSH	98% Benzenesulphonyl hydrazide
TSH	97% *p*-Toluenesulphonyl hydrazide
ABCN	98% 1,1′-Azobis(cyclohexanecarbonitrile)

Table 4

Comparison of the values of SADT determined for the five solids of the quasi-AC type with a few corresponding values of SADT measured by other researchers as well as the other reference temperatures

Solids of the quasi-AC-type	Coefficients of Eq. (2)		SADT		The other reference temperature	
	a	b	Determined [°C]	Reported [°C]	Catalogue[a] [°C]	EOT by DSC [7] [°C]
AMVN	19,100.19	− 54.12301	28.4		50 (dec.)	63
LPO	63,097.79	− 187.03050	48.4	49 [4]	54 (mp)	67
BSH	24,427.45	− 59.70561	81.3		102 (mp)	113
TSH	23,852.04	− 57.96617	81.9	86 [5]	108 (dec.)	124
ABCN	26,799.98	− 65.30295	86.5	80 [6]	115 (mp)	118

[a] For example, Catalog Handbook of Fine Chemicals, Aldrich Chemical, Milwaukee (1992–1993).

SADT measured by other researchers for these solids of large quantities, as well as the other reference temperatures, for comparison.

The respective value of SADT determined in this study in general is in fair agreement with the corresponding value of SADT measured. It has been stated in Section 1.4 that the T_s including the SADT is a function of time alone in Eq. (2) and therefore the SADT is independent of the quantity of chemicals of the AC type, in principle. This fact is substantiated by a few comparisons (in Table 4) of the respective values of SADT determined in this study for each 2 ml of samples with the corresponding value of SADT measured by other researchers for large quantities of samples.

In any event, it will be reasonable for us to consider a temperature about 20 K lower than the respective value of SADT determined in this study to be the actual upper limit temperature in temperature control for the prevention of thermal explosion of each individual solid of the quasi-AC type. For example, 10°C will be the actual upper limit temperature in temperature control for the prevention of thermal explosion of AMVN, 30°C for LPO, 60°C for BSH or TSH, and so on.

On the other hand, the respective values of SADT determined in this study are 20–30 K lower than any of the corresponding reference temperatures, such as the decomposition temperature and the melting point listed in some catalogue handbooks of fine chemicals, or, the EOT determined by the thermal analysis. This fact indicates that none of these reference temperatures is appropriate to be the upper limit temperature in temperature control for the prevention of thermal explosion of solids of the quasi-AC type.

5. Discussions

5.1. The value of T_s of the respective solid of the quasi-AC type converges to its lowest, limiting or true melting point on the low temperature side

As mentioned in (7) of Section 3, once the empirical formula (Eq. (2)) has been established for the respective solid of the quasi-AC type, it is possible to calculate an
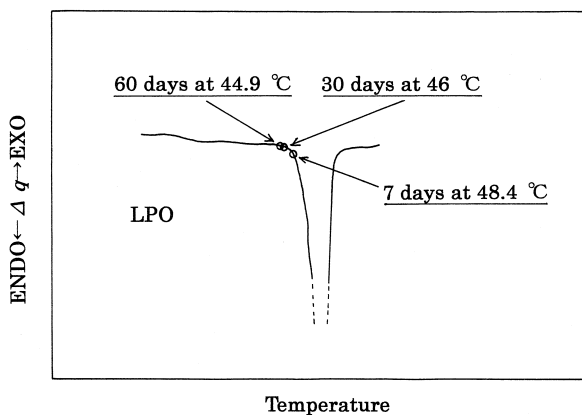
Fig. 12. Two values of T_s for LPO corresponding to the two values of Δt of 30 days and 60 days.

arbitrary value of T_s, as well as the SADT, at which the solid will melt completely and start to self-heat after an arbitrary exposure time. In Fig. 12 are given two values of T_s, 46°C and 44.9°C, on the endothermic peak of LPO. Each of them denotes the temperature at which LPO will melt completely and begin to self-heat 30 days or 60 days after the start of exposure, respectively.

This result suggests that the value of T_s of the respective solid of the quasi-AC type does not shift boundlessly to the low temperature side with an arbitrary large value of Δt, but converges to its lowest, limiting or true melting point on the low temperature side.

5.2. Solids of the quasi-AC type exist in considerable numbers

As presented in Fig. 13, the specific behaviour of a self-heating solid organic compound that first melts, thereafter successively decomposes exothermically is frequently seen in the thermal analysis. It has repeatedly been stated herein that such a DTA curve as presented in Fig. 13 is nothing less than that of each solid of the quasi-AC type. It thus follows that solids of the quasi-AC type exist in considerable numbers. On the other hand, according to the author's experience, the number of liquids or solids of the TD type, to each of which the Semenov or F–K equation is applied to calculate the T_c, is comparatively limited.

However, there is a subtle difference between a liquid of the TD type and a solid of the quasi-AC type in terms of the interval between the endothermic peak and the exothermic peak of the DTA curve (see Fig. 14). A chemical which is solid at room temperature, and, shows a large interval between the two peaks of the DTA curve is a liquid of the TD type, in principle. In a solid of this type, the melting is isolated, as a perfectly separate physical change, from the exothermic decomposition reaction of the resultant liquid. In other words, the resultant liquid of this type decomposes exothermically, independent of the melting, so that the Semenov equation can be applied to calculate the T_c.
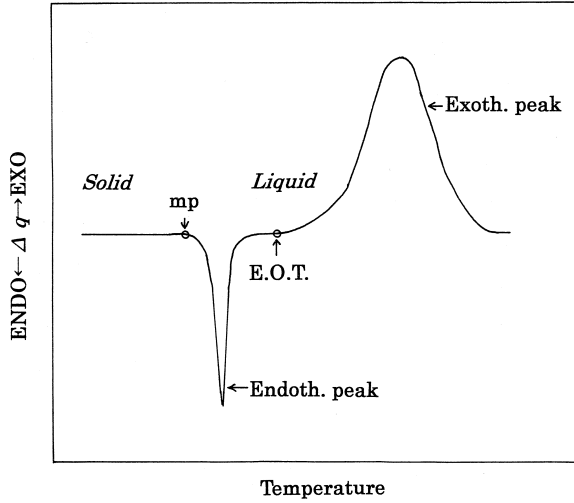
Fig. 13. The typical DTA curve of a self-heating solid organic compound.

On the other hand, a chemical which is solid at room temperature, but shows a small interval between the two peaks of the DTA curve is a solid of the quasi-AC type, for which the isothermal storage test should be performed to determine the SADT. But there is also a solid having such an interval that the magnitude is so subtle that it is difficult for us to judge the solid to be a liquid of the TD type or a solid of the quasi-AC type. For such a solid, both the adiabatic self-heating test to calculate the T_c by applying the Semenov equation and the isothermal storage test to determine the SADT by experimen-
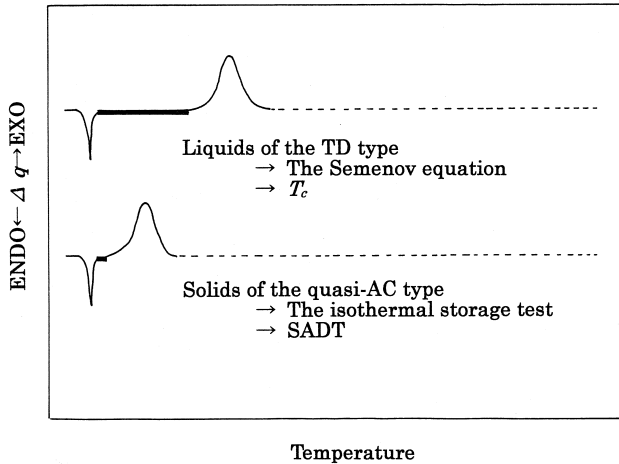

Fig. 14. The subtle difference between the DTA curve of a liquid of the TD type and that of a solid of the quasi-AC type.

tal measurements should be performed separately. A lower temperature value thus obtained is to be adopted as the characteristic temperature to represent the thermal instability of the solid.

6. Some comments on the isothermal storage testing device

It has been derived above that the proportion which solids of the quasi-AC type occupy amongst the whole family of self-heating chemicals is considerably large.

We have no choice in the present situation but to determine the respective SADT of solids of the quasi-AC type or the respective T_{cs} of high explosives of the true AC type by experimental measurements, i.e., by performing an isothermal storage test such as the U.S. SADT test, until a new method of calculation is established in the future. The latter test requires, however, much effort, time, space and material and therefore is expensive and dangerous.

In this regard, it may be noted that it has been ascertained in this study that it is possible to perform the isothermal storage test for all chemicals of the AC type easily, safely and inexpensively with a simple device such as that introduced herein.

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