

Thermal hazard research of smokeless fireworks

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Abstract The problem of dealing with expired military propellant is paid wide attention throughout the world. Currently, destruction is adopted as the main disposal route; however, the process is cumbersome, dangerous, costly, and even more non-environment-friendly. As a result, it is absolutely necessary to find out an appropriate recycling method. Nowadays a feasible method, by which the expired military powders are used to make smokeless fireworks, has already been proposed. However, the security of expired military propellant is still making all those concerned anxious on account of the stabilizer's volatilization during long-term storage. In this article, waste single base propellant (named powder 128, one of expired military propellants) and waste single base propellant/potassium perchlorate mixed powder are analyzed by differential scanning calorimeter (DSC) and accelerating rate calorimeter (ARC). The mixtures of these two are considered as the ideal raw materials of smokeless fireworks. DSC results show onset temperature, peak temperature, and normalized heat release of thermal decomposition under the condition of linear heating. Based on DSC data, activation energy and pre-exponential factor of the test samples are calculated according to Kissinger method, Ozawa method, and Friedman method. Furthermore, T_{D24} is derived by means of AKTS-Thermokinetics software using DSC data. ARC results reveal onset temperature, adiabatic temperature rise, self-heat rate, time to maximum rate and pressure–temperature profile. T_{D24} , which can be applied for the evaluation of thermal and

pressure hazards, can be obtained in two ways from the data measured by ARC. One is calculated directly from the experiment, and the other indirectly from the fit-calculations. Based on these results, the thermal hazards of these two mixtures were analyzed preliminarily.

Keywords DSC · ARC · SADT · Thermal hazard research · AKTS

List of symbols

TMR/min	Time to maximum rate
$T_{D24}/^{\circ}\text{C}$	Environment temperature when TMR = 24 h
$E_a/\text{kJ mol}^{-1}$	Apparent activation energy
A	Pre-exponential factor
α	The extent of conversion
$c_p/\text{J g}^{-1} \text{K}^{-1}$	Specific heat capacity
M/g	Mass of sample
$T_{o,s}/^{\circ}\text{C}$	Onset temperature of decomposition
$m_{o,s}/^{\circ}\text{C min}^{-1}$	Initial exothermic rate
$T_{f,s}/^{\circ}\text{C}$	Final temperature of decomposition
$\Delta T_{ad,s}/^{\circ}\text{C}$	Time to maximum rate under adiabatic condition
$m_{m,s}/^{\circ}\text{C min}^{-1}$	Maximum exothermic rate
$T_{m,s}/^{\circ}\text{C}$	Maximum temperature
$\theta_{m,s}/\text{min}$	Time to maximum rate
$p_{m,s}/\text{bar}$	Maximum pressure
φ	Thermal inertia
$T_o/^{\circ}\text{C}$	Phi-corrected $T_{o,s}$
$m_o/^{\circ}\text{C min}^{-1}$	Phi-corrected $m_{o,s}$
$T_f/^{\circ}\text{C}$	Phi-corrected $T_{f,s}$
$\Delta T_{ad}/^{\circ}\text{C}$	Phi-corrected $\Delta T_{ad,s}$
θ_m/min	Phi-corrected $\theta_{m,s}$
k^*	Reaction rate constant

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Introduction

Expired military propellant [1], as the name suggests, is the gunpowder which is withdrawn from the leading post because of the material having exceeded the storage duration limit (expiry date) or eliminated weapons or removed ammunition. The problem of dealing with them has become the world's major concern. Nowadays, destruction is adopted as the main disposal route, but in the meantime, the process is cumbersome, dangerous, costly, and even more non-environment-friendly. As a result, it is absolutely necessary to seek out an appropriate recycling method to allow reusing these reactive substances keeping in mind the safety and environment factors. So far, many scholars have spent a lot of energy in search of such a method for the recycling utilization.

Waste single base propellant, commonly called powder 128, which is the ideal raw material for smokeless fireworks, is fragmented directly from the expired military single base propellant. The products of the decomposition of smokeless fireworks made by waste single base propellant are wholly gaseous and these products are pollution free, tasteless, and safe [2]. However, many problems, like the stabilizer's volatilization during long-term storage, the probability of self-heating leading to thermal runaway, etc., still persist. Yuhai and Shilin [2] investigated the preparation technology and the safety analysis of the production process of smokeless fireworks made by the expired single base propellant. However, the literature focusing on thermal decomposition of expired military propellant is extremely rare in China until now. Therefore, the thermal decomposition of the two mixtures involving waste single base propellant is researched in this article. The experiments are conducted in linear temperature program and

under adiabatic condition by means of differential scanning calorimeter (DSC) and accelerating rate calorimeter (ARC) to evaluate the thermal hazards and pave the way for helping other scholars interested in further research.

Experiments

DSC experiments

DSC is an effective tool for the analysis on the thermal stability [3–5], heat generation owing to phase transition and chemical reaction, kinetic parameters, and decomposition of reactive substances, etc. In this article, the DSC apparatus used is manufactured by Mettler Toledo (type: DSC1). A small amount of sample (about 1 mg) was added into a steel-sealed crucible and heated at a constant rate (1–20 °C/min) in the temperature ranging from 50 to 500 °C.

Two samples were tested here, one is the powder 128 (nitrogen content = 13 %, oxygen balance <0), and the other is the mixed powder containing powder 128 and KClO_4 oxygen balance value of which is zero. The mass proportion of the components is listed in Table 1.

Figure 1 shows the relationship between heat flows and temperatures of markers 1# and 2# (atmosphere: N_2). The numbers following the markers reveal the respective heating rates.

After constructing the baseline of DSC curves, some data like onset temperature and heat release around exothermic peak were obtained. To examine the influence of the decomposition of the powder 128 after adding KClO_4 intuitively, the comparison results are shown in Fig. 2.

From Fig. 2, it is clear that since some KClO_4 powders are added into 1#, T_{onset} and T_{P} of 2# are almost the same as those of 1#, while normalized heat decreases obviously. It is speculated that KClO_4 does not catalyze the decomposition of waste single base propellant at low temperature. On the contrary, KClO_4 absorbs instead the heat released by decomposition of waste single base propellant to promote its own decomposition. The endothermic peak at

Table 1 Sample markers and contents

Sample contents	Markers
Waste single base propellant = 100 %	1#
Waste single base propellant: KClO_4 = 62:38 %	2#

Fig. 1 DSC curves of 1# and 2#

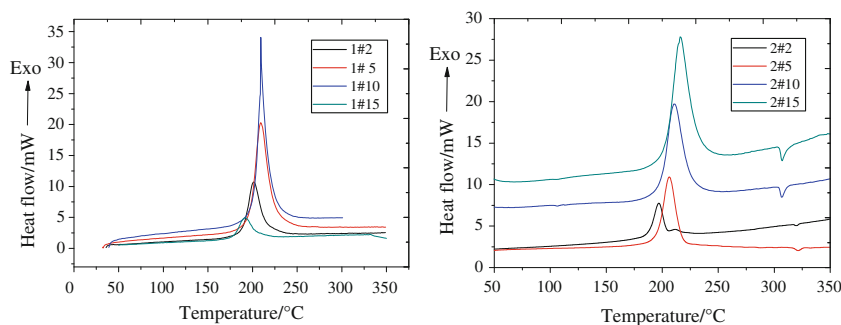
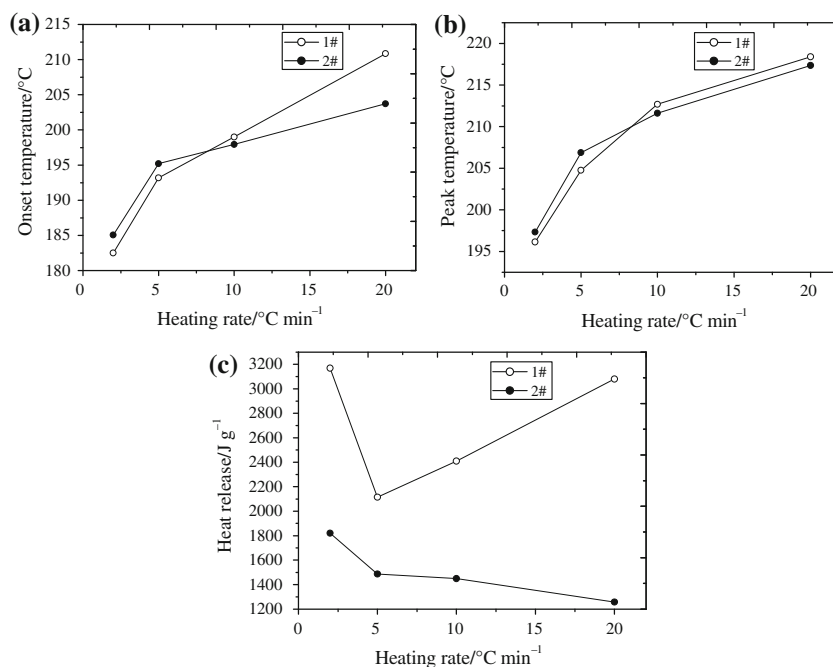


Fig. 2 Comparison results of decomposition data of 1# and 2#: **a** Onset temperature; **b** Peak temperature; and **c** Normalized heat release



around 310 °C provides evidence for this inference because KClO_3 , the decomposition product of KClO_4 , melts at 310 °C according to the literature.

Several typical kinetic methods [6] are chosen to calculate the kinetic parameters. In addition, AKTS-Thermokinetics software is used to investigate these two solid-state reactions. The results are shown in Table 2.

It is clear that E_a calculated by Kissinger method is in agreement with that by Ozawa method and ASTM E698. There is a negligible difference between kinetic parameters of 1# and 2#. Besides, as we know, the apparent activation energy calculated by Friedman method is not a constant. It varies with the extent of conversion. After the determination of kinetic parameters, the predictions of these two investigated reactions under adiabatic conditions similar to

Table 2 The kinetic parameters of thermal decomposition reaction calculated by Kissinger method and AKTS software

Sample	Methods	$E_a/\text{kJ mol}^{-1}$	$\lg A/\text{s}^{-1}$
1#	Kissinger	186.4	20.06
	Friedman	Low α 179 \pm 16	
		High α 200 \pm 10	
	Ozawa–Flynn–Wall	184.9	
ASTM E698	182.7		
2#	Kissinger	189.9	20.39
	Friedman	Low α 178 \pm 33	
		High α 160 \pm 40	
	Ozawa–Flynn–Wall	188.2	
ASTM E698	184.4		

ARC experiment are made [7]. The results are shown in Fig. 3.

From Fig. 3, it is concluded that when initial temperature of 1# is 132 °C, the runaway time under adiabatic condition is 1 day. In other words, T_{D24} of 1# equals to 132 °C. Similarly, T_{D24} of 2# is 141 °C.

ARC experiments

ARC is an effective tool for hazards evaluation of reactive substance [8, 9], because self-heating is a major hazard in the chemical industry, and the assessment of reactive chemical hazards comes under the field of adiabatic calorimetry. ARC allows arriving at a safe simulation of hazard using laboratory scale testing. A stainless steel bomb is used in the experiment. The instrument used is manufactured by Thermal Hazard Technology (model: esARC).

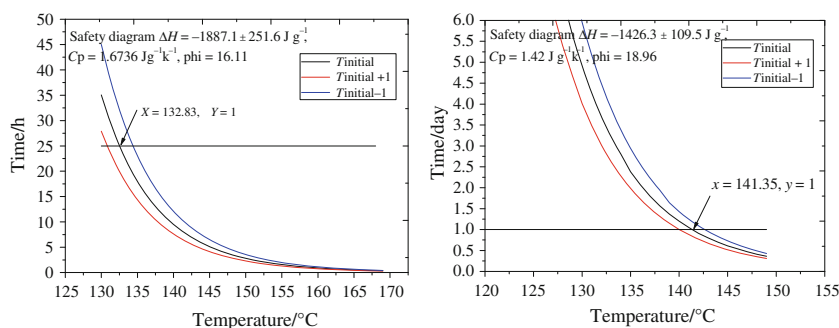
The experimental conditions and their results are listed in Table 3.

Once the self-heating rate exceeds 100 °C/min, the apparatus used in this article cannot maintain adiabatic conditions any longer, so the data recorded in the later part of the experiment are just for reference only. The data marked with ‘*’ in Table 3 indicate that they are not available because they exceed the ARC’s test range. The initial parts of data are selected to perform the kinetic analysis to obtain reliable results.

From Table 3, the following messages about 1# are obtained: the onset temperature of decomposition ($T_{o,s}$) is 150.369 °C, and the corresponding initial exothermic rate ($m_{o,s}$) is 0.026 °C min⁻¹. After ARC detects the

Fig. 3 Safety diagram of two samples in prediction.

Left: sample 1#,
 $c_p = 1.6736 \text{ J g}^{-1} \text{ K}^{-1}$;
 right: sample 2#,
 $c_p = 1.42 \text{ J g}^{-1} \text{ K}^{-1}$

**Table 3** (A): ARC test conditions and test results and (B): Phi-corrected experimental data

(A) Sample	M/g	$T_{o,s}/^\circ\text{C}$	$m_{o,s}/^\circ\text{C min}^{-1}$	$*T_{f,s}/^\circ\text{C}$	$*\Delta T_{ad,s}/^\circ\text{C}$	$*m_{m,s}/^\circ\text{C min}^{-1}$	$*T_{m,s}/^\circ\text{C}$	$\theta_{m,s}/\text{min}$	$*p_{m,s}/\text{bar}$
1#	0.249	150.369	0.026	166.99	23.405	275.957	171.302	737.776	14.119
2#	0.247	155.604	0.046	183.914	28.310	444.438	179.055	727.086	12.694
(B) Sample	ϕ	$T_o/^\circ\text{C}$	$m_o/^\circ\text{C min}^{-1}$	$*T_f/^\circ\text{C}$	$*\Delta T_{ad}/^\circ\text{C}$	θ_m/min			
1#	16.11	150.369	0.419	527.424	377.055	45.796			
2#	18.96	155.604	0.949	739.356	583.752	35.261			

exothermic signal, the temperature and the pressure of reaction system begin to rise slowly. When the temperature reaches at 167.849°C , the self-heating rate rises sharply to $65.785^\circ\text{C min}^{-1}$ and in a very short time, it reaches to the maximum value $275.957^\circ\text{C min}^{-1}$ ($m_{m,s}$). At the same time, the system temperature is 171.302°C . Afterward, the heating rate begins to decline, while the system temperature increases to a maximum of 173.774°C ($T_{m,s}$) and the pressure to a maximum of 14.119 bar ($p_{m,s}$).

On the other hand, at the beginning of this exothermic reaction, the onset temperature of decomposition of 2# is 155.604°C , and the corresponding initial exothermic rate is $0.046^\circ\text{C min}^{-1}$. When the temperature reaches 179.055°C , the self-heating rate rises sharply to the $444.348^\circ\text{C min}^{-1}$. Soon afterward, the system records the highest temperature of 183.914°C and the pressure of 12.694 bar .

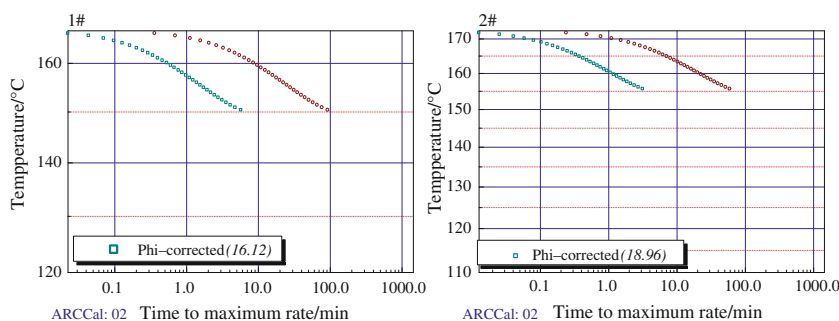
Actually, the temperature tested in the experiment is not the sample's real temperature, because the released heat not only contributed to the sample itself but also to the bombs of the sample. Assuming that the heat released from the reaction is used to heat the sample, the actual temperature rising and rising rate will be higher than obtained from the experiment obviously. Therefore, we need to modify the experimental data before applying them into practice. The data modified by thermal inertia factor are listed in Table 3, part 2. It is obvious that once the sample reaches its decomposition temperature, the reaction will proceed in a great rate and arrive at the maximum rate in less than 1 h which is considered as a very short period. Until now, the interpretation of pressure data derived from ARC cannot be done commendably. However, one point

worthy of our paying attention to is that the pressure and pressure release ultimately cause the damage which occurs in a runaway reaction. In the experiment, a small quantity of sample produces large pressure because the products of these two samples are almost gaseous. Though some of these data are not real, the certain inspiration that can be received from the data is that, as the reaction progresses, the self-heating rate continues to rise. Therefore, the decomposition of waste single base propellant is an auto-catalytic reaction, and the gaseous product of the reaction will cause huge damage.

An important parameter derived from ARC experiment is the time to maximum rate (TMR). It is the time period available before the occurrence of an incident at any specific temperature in the worst case of damage [10]. Based on this time, alarm temperatures will be set, and the time available for remedial measures or evacuation will be known. Figure 4 shows TMR of two samples under the worst case, fully adiabatic conditions. The symbol of cycle means the raw experiment data, and data of square means are phi corrected.

Because this TMR plot has been obtained directly in an adiabatic test that has simulated runaway reaction, it is possible to directly apply the data. At every point, it is possible to know the actual worst case, TMR or explosion. But it may be necessary to extrapolate to lower temperatures to get an estimation of TMR from a temperature of interest. Therefore, in contrast to T_{D24} obtained by DSC data, when TMR equals to $1,440 \text{ min}$, the corresponding temperature is T_{D24} . From Fig. 4, it is concluded that T_{D24} of 1# equals to 128°C . Similarly, T_{D24} of 2# is 130°C .

Fig. 4 Raw data time to maximum rate



The above result is directly obtained by experiment; in this article, another calculation-fit method is also used to get the same parameters using ARCCal and Origin. ARCCal is the data analysis software that has been developed specifically by THT for analysis of the data from the ARC. The self-heating rate plot of the raw data and the fitted model data are shown together such that a comparison can be made in Fig. 5. The reaction order calculated of 1# is 0.39, and the apparent activation energy is 445 kJ/mol. The corresponding values for 2# are 0.2, and 386 kJ/mol respectively.

In adiabatic system, the self-heating rate can be expressed as per the following equation:

$$\frac{dT}{dt} = A\Delta Tc_0^{n-1} \exp\left(-\frac{E}{RT_0}\right) \exp\left(-\frac{E}{RT}\right) \times \exp\left(-\frac{E}{RT}\right) \left(\frac{T_f - T}{\Delta T}\right)^n$$

Defining $k^* = \frac{dT}{dt} \left(\frac{\Delta T}{T_f - T}\right)^n \Delta T^{-1}$, then

Fig. 5 Temperature rate as a function of temperature

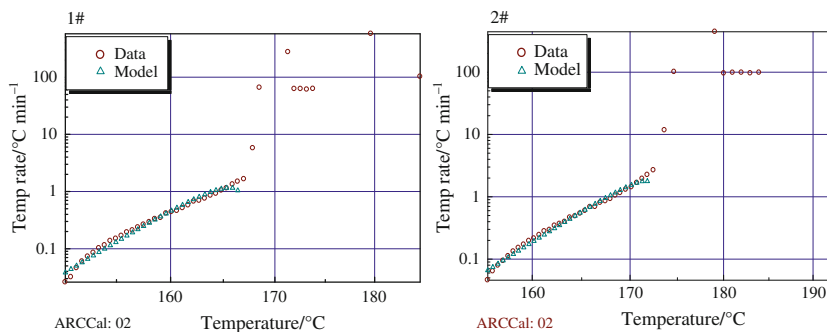
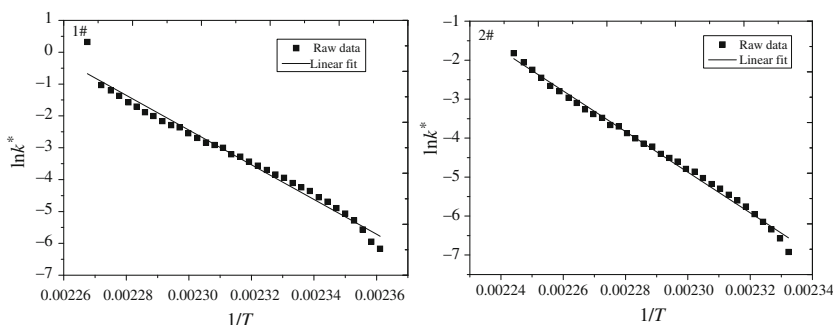


Fig. 6 $\ln k^* - \frac{1}{T}$



$$\ln k^* = \ln Ac_0^{n-1} - \frac{E}{RT}$$

The dependence of the logarithm of k^* on $\frac{1}{T}$ will show a straight line if the appropriate reaction order is put into the above equation. In order to check the veracity of n , E_a , and $\ln A$ fitted from ARCCal, Origin software is used to see the linearity of the raw data as shown in Fig. 6. The data plots shown in the figure correspond to the calculated data from experimental data and the fitted value. It can be seen that the linear correlations of the line and the plot are high: 0.98 and 0.99, respectively.

The apparent activation energy calculated by ARCCal is much higher than the real value. Considering that reaction rate of the thermal decomposition of NC, the main content of 1# does not only refer to temperature as well as reaction conversion rate, but also to the dynamics of the compensation effect of pre-exponential factor and the parameters of activation energy. Therefore, the parameter does not

Table 4 T_{D24} obtained by three approaches

	T_{D24} of 1#/ $^{\circ}\text{C}$	T_{D24} of 2#/ $^{\circ}\text{C}$
AKTS based on DSC data	132	141
Raw data from ARC data	128	130
Fit-calculation of ARC data	142	144

have the chemical and physical significance, but only contribute to calculation purpose of the other parameters.

The following formula is used to infer the relationship of the onset temperature and the TMR (θ):

$$\ln \theta = \frac{E}{R} \frac{1}{T} - \ln A.$$

We substitute the calculated parameters and the phi-corrected θ into the formula, and so we obtain as follows: for 1#, $T_{D24} = 142$ $^{\circ}\text{C}$; and for 2#, $T_{D24} = 144$ $^{\circ}\text{C}$ which is a little larger than the former results. However, caution should be exercised when applying such calculated results, in actual use. In the equation, errors in A will have a linear effect; errors in n are not likely; but errors in E are likely and will have a significant effect.

Comparative analysis of T_{D24} obtained by three approaches

The main results are listed in Table 4. In this article, three approaches are used to obtain T_{D24} . One is the prediction by AKTS-Thermokinetics based on DSC data. The second is raw data TMR. The third is calculated based on adiabatic rate equation from ARC data.

From Table 4, it can be observed that the temperature obtained by the second method is the lowest of the three because it is extrapolated to obtain the result under completely adiabatic condition of the worst case. The third is the highest due to the error in apparent activation energy and pre-exponential. In order to ensure the security of the process, the worst case should be considered.

Conclusions

(1) Judging from the DSC results, there are no notable differences in activation energy and pre-exponential factor between 1# and 2#. T_{D24} obtained from the prediction by AKTS-Thermokinetics is therefore credible.

(2) Though some of ARC raw data are not real, they can also reflect some problems. Which is more dangerous cannot be judged, but we know that both of them are worth being given our due care. Based on the initial part of ARC raw data, TMR against temperature plot is realized, and then T_{D24} is read from the figure directly. Meanwhile, the same part of ARC data is used to calculate T_{D24} using linear fitting of kinetic parameters. These two results have an error of 6 $^{\circ}\text{C}$.

(3) To sum up, though these two raw materials of smokeless fireworks perform very well during actual use and can solve the problem of expired military propellant, very great attention must be paid during manufacture, transportation, use, and storage because of T_{D24} and the potential for the huge destructive power if the decomposition happens.

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