



Study on the influence of moisture content on thermal stability of propellant

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ABSTRACT

This paper studies the influence of moisture content on the thermal stabilities of double-base propellant and multi-nitro ester propellant. The thermal behaviors and chemical kinetic parameters of the above two propellants and their mixtures with water were analyzed by using a CALVET heat flux calorimeter, C80. The thermal decomposition mechanisms of these two propellants with water were conjectured based on the tests. And then, the self-accelerating decomposition temperatures (SADT) of these two propellants and their mixtures with water were calculated and compared according to the kinetic parameters and Semenov model. The results show that the thermal decomposition mechanism of double-base propellant with water may be changing with the varying moisture content by transferring hydrogen proton (H^+). However, the thermal decomposition mechanism of multi-nitro ester propellant with water may be unchanging due to the excess of formaldehyde (HCHO). Water plays the external physical factor on the thermal decomposition of multi-nitro ester propellant, and it plays both the physical and the chemical factors on the thermal decomposition of double-base propellant. The SADTs of their mixtures with water are much lower than that of pure propellants, and keep decreasing with the increasing of moisture content.

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1. Introduction

Propellants are widely used for military applications as the main energy in launching weapons with pipes. Generally, they consist of organic compounds including nitro, azide and hydrazine groups in the molecules. Propellants belong to self-reactive chemical substances, and they are undergoing a sharp exothermic runaway reaction at elevated, even normal temperatures on account of the characteristic of high energy material [1,2]. It is great dangerous during its production, storage or transportation. Therefore, it is extraordinary necessary to develop correlative in-depth researches on the thermal stability of propellants. As a rule, the water content should be controlled in the process of propellants' production, as the residual water will cause hydrolyzation, which will result in the accelerated decomposition of propellants during the long-term storage (usually up to several years). The ambient temperature and humidity in storeroom must be also restricted severely. However, a lot of water is probably mixed as alleviant into propellants to decrease the friction and impact sensitivity during transportation (just several days). Therefore, the research on the effect of water as impurity on thermal stability of propellants should be taken into

adequate account. At present, some researches on the humidity effect on the failure mechanism and ageing kinetics of propellants during long-term storage were done [3–18]. The influences of ambient humidity or water content on the properties of the specified component or the whole mechanical property also were explored [7–18]. However, the influence of moisture on the thermal stability of double-base and multi-nitro ester propellant was not clear yet.

The relationships between heat release and temperature of pure propellants and their mixtures with different mass of water were measured by using a heat flux calorimeter C80. And the thermal kinetic and reaction dynamic parameters of pure propellants and their mixtures with water were calculated based on heat flow data. Furthermore, according to the Semenov thermal explosion model, the self-accelerating decomposition temperature (SADT) was used by comparison for assessing the thermal stabilization of propellants and their mixtures with water.

2. Experimental

2.1. Sample preparation

In this study, the samples were prepared by mixing different mass of water into two kinds of propellants. Double-base propellant consists of about 57 wt.% nitrocellulose (NC), 42 wt.% nitroglycerine (NG) and 1 wt.% Centralite (C2). Multi-nitro ester propellant

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Nomenclature

A	kinetic pre-exponential factor (s^{-1})
C_p	specific heat ($J g^{-1} K^{-1}$)
dH/dt	overall heat flow (W)
E_a	kinetic activation energy ($kJ mol^{-1}$)
ΔH	heat of reaction ($J g^{-1}$)
H_m	maximum heat flow (mW)
M	mass of reactant (g)
M_0	initial mass of reactant (g)
n	reaction order
R	correlation coefficient
S	contact area between package surface and ambient (m^2)
T_{onset}	onset temperature of reaction ($^{\circ}C$)
T_m	temperature at maximum heat flow ($^{\circ}C$)
t	time (s)
T	temperature of system (K)
T_{NR}	no return temperature (K)
T_0	ambient temperature (K)
U	overall heat transfer coefficient ($J m^{-2} K^{-1} s^{-1}$)

Greek letter

θ	duration between the beginning of thermal decomposition and the maximum heat flow (s)
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consists of about 59 wt.% nitrocellulose (NC), 29 wt.% nitroglycerine, 10 wt.% triethylene glycol dinitrate and (TEGDN) and 2 wt.% Cenralite (C2). Table 1 shows the weights of each element in the samples. The total mass of double-base propellant and multi-nitro ester propellant is 0.03 and 0.05 g, respectively.

2.2. Measuring apparatus

All the tests were performed by using a CALVET heat flux calorimeter C80 manufactured by SETARAM Scientific & Industrial Equipment Company in France. The calorimetry has the merits of high sensitivity (with several μW at least), many functions and a quite wide testing temperature range from room temperature to $300^{\circ}C$ by using different types of experiment vessel with sample mass up to about 10g and different functions. A great number of measurements can be made with C80, such as heat capacity determination of substances; heat generation by a change of state, mixing or a chemical reaction; determination of reactivity and kinetic parameters of reactive substance; hazards evaluation of reactive substance and so on [19,20]. For these experiments, the samples were sealed in an 8.5 ml high pressure vessel, pressure-proof at 100 bar with air condition, and then temperature was raised from ambient up to $300^{\circ}C$ at a $0.2 K/min$ heating rate.

Table 1

Experimental samples.

Sample	No.	Water content (wt.%)	Propellant (wt.)/g	Water (wt.)/g
Double-base propellant	1	0	0.03	0
	2	10	0.027	0.003
	3	20	0.024	0.006
	4	30	0.021	0.009
Multi-nitro Ester propellant	5	0	0.05	0
	6	5	0.0475	0.0025
	7	20	0.04	0.01
	8	30	0.035	0.015

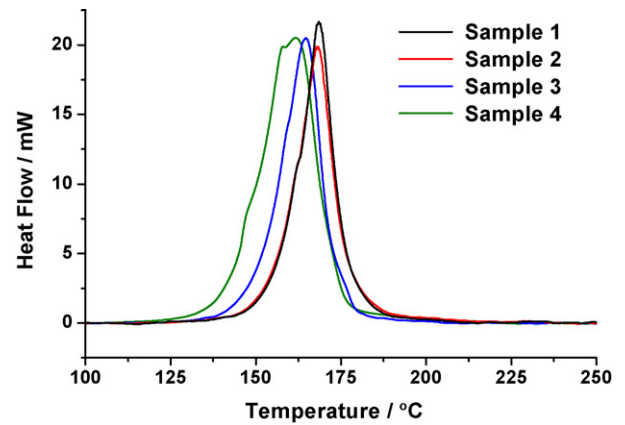


Fig. 1. Heat flow curves of double-base propellant and its mixture with different mass of water.

3. Results and discussions

3.1. Experiment results

Constant temperature rising-rate experiments were executed to research the thermal behavior of pure propellants and their mixtures with water.

Fig. 1 shows the heat flow curves of double-base propellant and its mixtures with different mass of water. Only one exothermic peak was detected on all the curves. In addition, the curves present the interruption during the rise before the peak. It is considered to be caused by endothermic evaporation of NG [21,22]. For double-base propellant without water (sample 1), it begins to decompose at $147.76^{\circ}C$, and then the heat flow increases very slowly before $155^{\circ}C$. After that, the maximum heat flow reaches to $21.66 mW$ at $168.47^{\circ}C$. It lasts about 1.76 h from the beginning of thermal decomposition to the maximum heat flow. For double-base propellant with 10% water (Sample 2), it starts to decompose at $147.15^{\circ}C$, and the close exothermic peak was detected comparing with that of sample 1. The maximum heat flow ($19.87 mW$) appears at $167.86^{\circ}C$, and it lasts about 1.76 h from the beginning of thermal decomposition to the maximum heat flow. It can be seen that a little water (below 10 wt.%) plays little influence on the thermal decomposition of double-base propellant based on the curves of sample 1 and sample 2. For double-base propellant with 20% water (sample 3), the thermal decomposition starts at $142.01^{\circ}C$, which is earlier than that of sample 1 and sample 2. The heat flow increases gradually with the temperature increasing in the range of 142.01 – $152^{\circ}C$, and increases sharply above $152^{\circ}C$. It reaches the peak temperature at $164.71^{\circ}C$ in sample 3, which is reduced from $168.47^{\circ}C$ in sample 1 and $167.86^{\circ}C$ in sample 2. The reaction time increases to 1.93 h in sample 3, which is longer than that of in sample 1 and sample 2. For double-base propellant with 30% water (sample 4), the onset and the peak temperatures decrease to 134.99 and $161.74^{\circ}C$, respectively. A gradual increasing heat flow in the range of 134.99 – $145^{\circ}C$ and a sharp increasing heat flow above $145^{\circ}C$ were found. It lasts about 2.27 h from the beginning of thermal decomposition to the maximum heat flow. The thermal decomposition parameters of double-base propellant and its mixtures with water is listed in Table 2. It can be seen that with the increase of water mass, the maximum heat flows are close, and the onset and the peak temperatures are lower. Furthermore, the lasting time from the beginning of thermal decomposition to the maximum heat flow shows an ascending tendency.

Fig. 2 shows the heat flow curves of multi-nitro ester propellant and its mixtures with different mass of water. All the

Table 2
Decomposition characteristic parameters of propellants and their mixtures with different mass.

Sample no.	Double-base propellant				Multi-nitro ester propellant			
	1	2	3	4	5	6	7	8
Water content (%)	0	10	20	30	0	5	20	30
H_m (mW)	21.66	19.87	20.49	20.51	36.65	37.60	35.64	36.60
T_{onset} (°C)	147.76	147.15	142.01	134.99	138.94	138.09	137.62	134.12
T_m (°C)	168.47	167.86	164.71	161.74	169.27	168.63	166.83	163.11
θ (h)	1.76	1.76	1.93	2.27	2.66	2.59	2.48	2.46

curves in Fig. 2 show that there is only one exothermic peak too. And the curves present the interruption during the rise before the peak. It may be caused by endothermic evaporation of NG and TEGDN [21,22]. For the heat flow curve of multi-nitro ester propellant (sample 5), the exothermic peak is the same as that of multi-nitro ester propellant with 5% water (sample 6). The decomposition processes in these two samples have the approximate onset temperature at 137.94 and 138.09 °C, and almost same peak temperature at 169.27 and 168.63 °C, respectively. They last 2.66 and 2.59 h from the beginning of thermal decomposition to the maximum heat flow. The above experiments show that a little water (below 5 wt.%) plays little influence on the thermal decomposition of multi-nitro ester propellant. However, the exothermic peak of sample 5 or sample 6 is different from that of multi-nitro ester propellant with 20% water (sample 7), and more different with 30% water (sample 8). Comparing with sample 5 or sample 6, the thermal decomposition parameters of sample 7 and sample 8 are altered obviously, such as the temperature corresponding to initiation point, the peak temperature, and the time between the beginning of thermal decomposition and the maximum heat flow. Table 2 also presents the thermal decomposition parameters of multi-nitro ester propellant and its mixtures with different mass of water, all of which except the maximum heat flow are decreased obviously with the increase of water mass.

By combining those curves in Figs. 1 and 2 with the data in Table 2, it can be confirmed that with the increase of water mass contained in two kinds of propellants, the thermal decomposition peaks move towards the lower temperature direction. The more moisture content in double-base propellant and multi-nitro ester propellant, the more influence on the thermal decomposition of these two propellants. Therefore, the moisture content affects the thermal stability of the two propellants.

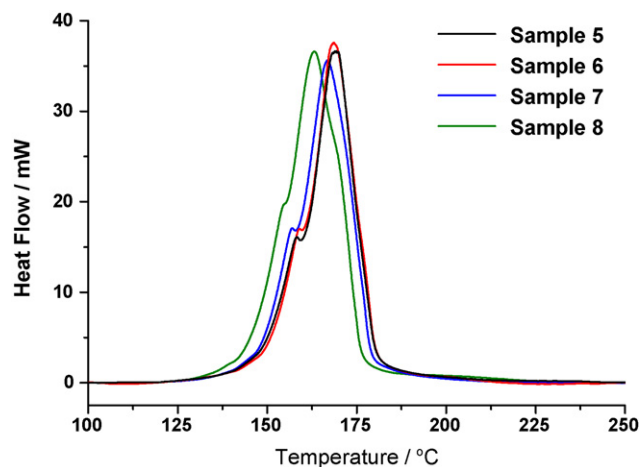


Fig. 2. Heat flow curves of multi-nitro ester propellant and its mixture with different mass of water.

3.2. Discussions

3.2.1. Chemical kinetic and thermal dynamic parameters

A reaction mechanism is assumed to be dependent on the Arrhenius law to calculate the chemical kinetic and thermal dynamic parameters of reaction materials by using C80 data, so the rate expression for the consumption of reaction can be defined as Eq. (1)

$$\frac{dx}{dt} = A \exp\left(\frac{-E_a}{RT}\right) (1-x)^n \quad (1)$$

where $x = (M_0 - M)/M_0$ is conversion rate, substituting x into Eq. (1), Eq. (2) can be easily obtained.

$$-\frac{dM}{M_0 dt} = A \exp\left(\frac{-E_a}{RT}\right) \left(\frac{M}{M_0}\right)^n \quad (2)$$

At the initial stage, the consumption of the reactant can be negligible. Therefore, M is approximately equal to M_0 . Multiplying Eq. (2) with the heat of reaction ΔH , expressed as $\Delta H = \frac{1}{M_0} \int_{t_0}^{t_{end}} (dH/dt) dt$, Eq. (3) is obtained as:

$$\frac{(dH/dt)}{\Delta H M_0} = A \exp\left(\frac{-E_a}{RT}\right) \quad (3)$$

Taking natural logarithm of Eq. (3),

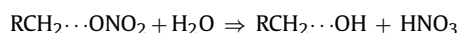
$$\ln\left(\frac{dH/dt}{\Delta H M_0}\right) = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln A \quad (4)$$

By plotting the curve of $\ln((dH/dt)/\Delta H M_0)$ versus inverse temperature (T^{-1}), the activation energy (E_a) and pre-exponential factor (A) could be easily acquired [23,24]. The calculated chemical kinetic and thermal dynamic parameters of two kinds of propellants and their mixtures with different mass of water are listed in Table 3.

According to Table 3, it can be seen that with the increase of water mass, the heat of reaction of these two propellants enlarges from 3171.43 kJ/kg in sample 1 and 4461.07 kJ/kg in sample 5 to 6559.44 kJ/kg in sample 4 and 5917.93 kJ/kg in sample 8, respectively. However, with the increase of water mass, double-base propellant is distinct in the tendency of kinetic parameters, such as activation energy and pre-exponential factor from multi-nitro ester propellant, i.e. the E_a and A of double-base propellant decrease and multi-nitro ester propellant keeps constant.

3.2.2. Thermal decomposition mechanism

Generally, water is always capable of bringing forth great impact on propellants in the form of hydrolyzation. The reaction between propellant and water could be held as follows.



Nitric acid (HNO_3) is produced in the propellant with water, and this reaction can occur in the air. Moreover, when it undergoes thermal decomposition, it can be accelerated by the increasing temperature, and the production of nitric acid (HNO_3) can also be enhanced. However, the most production of nitric acid (HNO_3) does not depend on this type of reaction in the thermal decomposition of

Table 3
Thermal kinetic parameters of propellants and their mixtures with different mass of water.

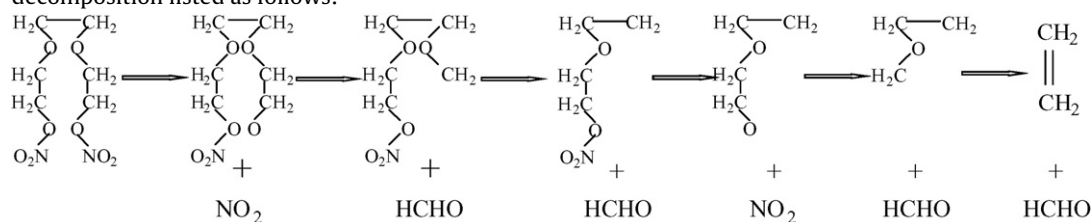
Sample no.	Double-base propellant				Multi-nitro ester propellant			
	1	2	3	4	5	6	7	8
Water content (%)	0	10	20	30	0	5	20	30
ΔH (kJ/kg)	3171.43	3489.78	4227.53	6559.44	4461.07	4781.47	5085.18	5917.93
E_a (kJ/mol)	260.24	249.96	231.89	228.34	211.00	212.38	212.80	209.91
$\ln A$ (s^{-1})	62.91	60.1	55.72	55.47	49.40	49.67	50.07	49.70
R^2	0.9998	0.9996	0.9992	0.9991	0.9938	0.9875	0.9885	0.9918
SADT ($^{\circ}C$)	117.17	115.05	107.78	100.83	106.98	106.58	105.01	100.36

propellant with water, but rather be determined by the hydration reaction, between water and nitrogen dioxide (NO_2) from the initial decomposition of propellant. Under this condition, nitric acid (HNO_3) exists mainly in the form of nitrate anion (NO_3^-) with hydrogen proton (H^+). It means that the thermal decomposition of propellant with water can be initiated by transferring hydrogen proton (H^+). The mechanism changes from the unimolecular reaction with C– NO_2 bond breaks to elimination reaction with quinary transition state. Because the activation energy of this elimination reaction is far lower than the dissociation energy of C– NO_2 bond, the thermal decomposition of propellant with water occurs much easily at the lower temperature [1,25,26].

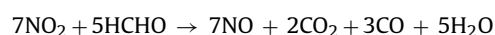
In Table 3, the change on thermal decomposition mechanism of double-base propellant with water is displayed by the reducing activation energy with the increase of water mass. In other words, with the increase of water mass, elimination reaction with quinary transition state accounts for a larger proportion, which leads to decreasing the apparent activation energy E_a of double-base propellant. So the thermal decomposition curve of double-base propellant removes moves towards the lower temperature direction.

The activation energy of multi-nitro ester propellant with water is shown in Table 3. The unchanged activation energy indicates that water plays little effect on the thermal decomposition of multi-nitro ester propellant. The possible cause is conjectured as the following steps.

At first, multi-nitro ester propellant contains about 10 wt.% triethylene glycol dinitrateand (TEGDN), which is not in double-base propellant. According to the research on thermal decomposition mechanism of triethylene glycol dinitrateand (TEGDN) [27–30], it can be speculated that nitrogen dioxide (NO_2) and formaldehyde (HCHO) can be produced, and the output of formaldehyde (HCHO) is several times more than nitrogen dioxide (NO_2) in the process of decomposition listed as follows:



Secondly, nitrogen dioxide (NO_2) reacts with formaldehyde (HCHO) under the elevated temperature. The reaction equation is shown as follows:



If the reaction rate is so fast, all the nitrogen dioxide (NO_2) produced by thermal decomposition of triethylene glycol dinitrateand (TEGDN) will be consumed in liquid phase. Subsequently, the excess of formaldehyde (HCHO) will react with the nitrogen dioxide (NO_2) produced by C– NO_2 bond breaking from other ingredients of multi-nitro ester propellant.

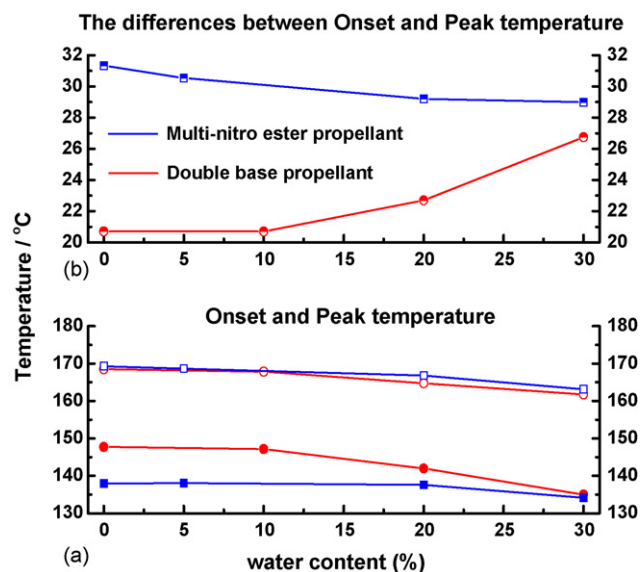


Fig. 3. Onset temperature, peak temperature, and the differences between them on two kinds of propellants mentioned here with different mass of water.

Finally, a very small quantity of nitrogen dioxide (NO_2) can be only escaped into gas phase. Simultaneously, water will have been gasified at ambient temperature over $100^{\circ}C$. So the reaction between nitrogen dioxide (NO_2) and water can only occur in gas phase, but it is so weak on account of few reactants that the apparent activation energy of multi-nitro ester propellant cannot be influenced.

3.2.3. Cause analysis

The thermal decomposition analysis of two kinds of propellants and their mixtures with different mass of water was studied in the before-mentioned sections. It can be confirmed that there are appreciable influences of water on these two kinds of propellants. The influences on decomposition characteristic parameters, such as onset temperature, peak temperature, and the differences between them were displayed in Fig. 3(a) and (b). Here, the temperature difference is defined as the temperature increment from the beginning of decomposition reaction to the maximum heat flow.

Table 4
Comparison on the SADTs of two kinds of propellants with other propellants/explosives.

Propellant	Double-base propellant	Multi-nitro ester propellant	Black power	TNT	RDX	PETN
SADT (°C)	117.17	106.98	105.3	137.5	188.7	101.4

Both the onset temperature and the peak temperature on these two kinds of propellants decrease with the increase of water mass. The conclusion from Section 3.2.2 revealed that water is unable to alter the decomposition mechanism of multi-nitro ester propellant. Therefore, the influence of water on thermal decomposition of multi-nitro ester propellant should be not caused by internal chemical action, but rather by external physical effect. Notably, pressure plays a clear impact on chemical reaction, and reaction rate increases with ambient pressure. In these experiments, the pressure in the sealed vessel had already increased with moisture content due to evaporation under ambient temperature over 100 °C before the thermal decomposition of multi-nitro ester propellant. When the initial mass of water reaches to 30% in sample 8, and it evaporates completely, the ambient pressure could ascend at least to about 0.43 MPa or higher. The subsequent thermal decomposition of multi-nitro ester propellant would be compelled by the unceasing elevated ambient pressure to be accelerated. The higher ambient pressure, the faster rate on thermal decomposition is taken. Therefore, with the increase of moisture content, the thermal decomposition character parameters of multi-nitro ester propellant, such as onset temperature and peak temperature can be detected earlier at the lower temperature. On the other side, the thermal decomposition of double-base propellant is affected by water evaporation, which means that the onset temperature and the peak temperature of double-base propellant is reduced to the same extent as multi-nitro ester propellant with the increase of water mass. However, as seen from Fig. 3(b), an opposite trend on the differences of these two propellants between onset temperature and peak temperature was detected. With the increase of water content, the difference of multi-nitro ester propellant between the onset and peak temperature decreases gradually, but that of double-base propellant increases progressively. This phenomenon is attributed to internal chemical action as elucidated in Section 3.2.2. The influence of water on thermal decomposition of multi-nitro ester propellant is caused by external physical effect, but the influence of water on thermal decomposition of double-base propellant is caused by concurrent physical and chemical action.

3.3. Evaluation on thermal stability of propellants

A self-accelerating decomposition temperature (SADT) was recommended by United Nations committee of Experts on the Transport of Dangerous Goods and on the Globally of Harmonized System of Classification and Labeling of Chemicals (UNCETDG & GHS) to estimate whether the substance should be subjected to temperature control during transport. It is defined in the United Nations' Recommendation as the lowest temperature at which self-accelerating decomposition may occur in an organic peroxide or self-reactive substance in the packaging for transportation purposes [31]. The calculation method has been put forward by previous researchers [23] as follows.

According to the Semenov model [32,33], the rate of the uniform temperature rise in a system is established by the difference between the rate of heat generation from the system and the rate of heat transfer to the environment as the following equation:

$$C_p M_0 \frac{dT}{dt} = \Delta H M_0^n A \exp\left(\frac{-E_a}{RT}\right) - US(T - T_0) \quad (5)$$

Further, at the temperature of no return (T_{NR}), both $dT/dt = 0$ and $d(dT/dt)/dT = 0$ must be held. Thus Eq. (5) is obtained as:

$$\frac{E_a}{R} = \frac{T_{NR}^2}{T_{NR} - T_0} \quad (6)$$

where T_0 is the surrounding temperature which is equal to the SADT, so

$$SADT = T_0 = T_{NR} - \left(\frac{RT_{NR}^2}{E_a}\right) \quad (7)$$

Using this equation and the thermal-kinetic parameters estimated from the C80 experiment results, the SADTs of two kinds of propellants and their mixtures with different mass of water were calculated using 25 kg standard package, the wetted area $S = 4812.4 \text{ cm}^2$, and an overall heat transfer coefficient $U = 2.8386 \times 10^{-4} \text{ J cm}^{-2} \text{ K}^{-1} \text{ s}^{-1}$ in Table 3. For comparison, the SADTs of other propellants including TNT, RDX, PETN, and Black power are cited from [34], and displayed in Table 4.

Seen from the last row of Table 3, the SADTs of two kinds of propellants with water under the same packaging conditions are much lower than that of pure propellants, and they decrease with the increase of moisture content. It indicates that water cause the two kinds of propellants unstable. Also, the relationship between SADT and water content is presented in Fig. 4. Although the SADT of pure double-base propellant is much higher than that of pure multi-nitro ester propellant, the SADTs of these two propellants with 30% water are almost equal to 100 °C. That is, with the increase of water content, the decrease on SADT for multi-nitro ester propellant is less marked than that for double-base propellant. It indicates that water plays less influence on thermal stability of multi-nitro ester propellant. However, the lower SADTs at 100.83 and 100.36 °C for samples 4 and 8 can be obtained by external heat resource, such as rapid elevated ambient temperature, radiation or close-by fire. Combining it with experimental condition, it can be summarized that auto-ignition and explosion may occur easily under the airtight condition with external heat resource for such materials. Therefore, during manufacture, storage, transportation and practice use, much care should be taken for propellants with water.

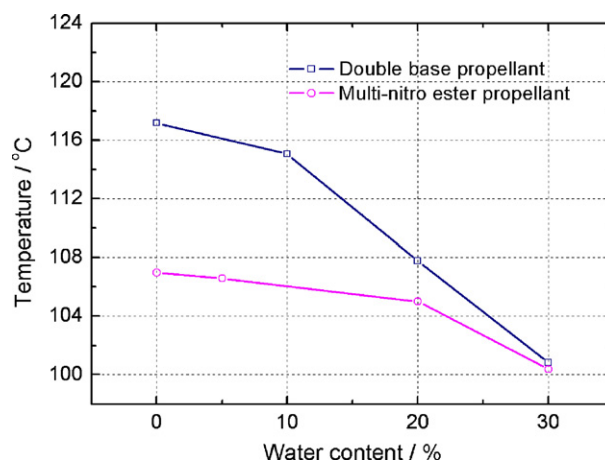


Fig. 4. Self-accelerated decomposition temperatures of two kinds of propellants mentioned here with different mass of water.

4. Conclusions

The decomposition reaction characteristics and the heat generation of two kinds of propellants, i.e. double-base propellant and multi-nitro ester propellant, and their mixtures with water were investigated by using a CALVET heat flux calorimeter C80. The thermal stability of these two propellants with water was estimated. Furthermore, the thermal decomposition mechanisms of these two propellants with water were conjectured. The following results were obtained:

- (1) The water shows remarkable influences on the thermal decomposition of double-base propellant and multi-nitro ester propellant. With the increase of water mass, the heat flow curves of these two propellants moves towards the lower temperature direction. The larger value of moisture content, the more evident the influence of moisture content on thermal decomposition of these two propellants is revealed. The activation energy E_a and pre-exponential factor A of double-base propellant decrease and it keeps constant for multi-nitro ester propellant.
- (2) The thermal decomposition mechanisms of these two propellants with water were conjectured. The obvious influence of water on thermal decomposition mechanism of double-base propellant is detected. With the increase of water mass, thermal decomposition mechanism of double-base propellant with water may be changed from the unimolecular reaction starting with C–NO₂ bond breaking to elimination reaction with quinary transition state by transferring hydrogen proton (H⁺). Water does not play any effects on the thermal decomposition mechanism of multi-nitro ester propellant. The excess of formaldehyde (HCHO) produced by triethylene glycol dinitrate and (TEGDN) may react in liquid phase with the nitrogen dioxide (NO₂) produced by C–NO₂ bond breaking from other ingredients of multi-nitro ester propellant. This reaction leads to few hydrogen protons (H⁺), which is not sufficient to influence the thermal decomposition mechanism of multi-nitro ester propellant.
- (3) The causes on the influence of water on thermal decomposition of these two propellants were analyzed. The influence of water on thermal decomposition of multi-nitro ester propellant is caused by external physical effect, and the influence of water on thermal decomposition of double-base propellant is caused by concurrent physical and chemical action.
- (4) The SADTs for 25 kg standard package were calculated and compared based on the Semenov model and the decomposition kinetic parameters of two kinds of propellant and their mixtures with water. With the increase of moisture content, the SADTs of two kinds of propellants keep decreasing, but the decrease on SADT for multi-nitro ester propellant is less marked than that for double-base propellant. Auto-ignition and explosion may occur easily under the airtight condition with external heat resource for double-base propellant and multi-nitro ester propellant. More care should be taken for propellants with water during manufacture, storage, transportation and practice use.

References

- [1] Z.Sh. Wang, Y.X. Ou, W.Zh. Renk, Science and Technology of Explosives & Propellants, Beijing Institute of Technology Press, Beijing, 2002.
- [2] B.X. Wang, Z.G. Feng, R.J. Yang, Propellant Combustion Theory, Beijing Institute of Technology Press, Beijing, 1997.
- [3] M.I. Muhammad, L. Wang, Modeling the moisture effects of solid ingredients on composite propellant properties, *Aerosp. Sci. Technol.* 10 (2006) 695–699.
- [4] L.G. Svensson, Using isothermal microcalorimetry for the prediction and testing of long-term properties of materials and products, *J. Therm. Anal.* 49 (1997) 1017–1023.
- [5] I. Tuukkanen, S.D. Brown, E.L. Charsley, et al., Studies on the ageing of a magnesium–strontium nitrate pyrotechnic composition using isothermal microcalorimetry and thermal analysis techniques, *Thermochim. Acta* 417 (2004) 223–229.
- [6] D.J. Michael, An investigation of composite propellant accelerated ageing mechanisms and kinetics, *Propellants Explos. Pyrotech.* 28 (3) (2003) 114–119.
- [7] Zh.B. Zhan, J.Y. Jiang, M.H. Chen, Effect of temperature and humidity on thermal self-ignition of propellant, *Chin. J. Explos. Propell.* 30 (5) (2007) 74–76.
- [8] Zh.B. Zhan, M.H. Chen, J.Y. Jiang, et al., Influence of environment temperature on thermal self-ignition of propellant, *Chin. J. Adv. Manuf. Manage.* 26 (6) (2007) 31–33.
- [9] Y.X. Yin, S.L. Xu, X.Zh. Zhang, Zh.L. Xiao, A study on hygroscopicity and thermal stability of caseless propellant, *Chin. J. Energ. Mater.* 8 (1) (2000) 34–36.
- [10] M.H. Chen, J.Y. Jiang, G.E. Lu, L.B. Liu, Influence of humidity on the thermal self-ignition propellant, *Chin. J. Explos. Propell.* 23 (3) (2000) 45–47.
- [11] Y.F. Zuo, X.M. Luo, J.H. Zhou, Compatibility of explosives with relative materials under the conditions of temperature and moisture circulation, *Chin. J. Energ. Mater.* 8 (4) (2000) 171–174.
- [12] D.Sh. Fu, Effect of humidity on HTPB propellant and its adhesion characteristics, *Chin. J. Chem. Propell. Polymeric Mater.* 4 (4) (2006) 43–45.
- [13] Y.P. Wang, B.H. Wang, Effect of environmental humidity on elongation of HTPB propellants at different stretching rate, *Chin. J. Energ. Mater.* 6 (2) (1998) 59–64.
- [14] Y.D. He, J.Q. Liu, The effects of environmental humidity on the mechanical properties of HTPB propellant, *Chin. J. Solid Rocket Technol.* 19 (3) (1996) 47–52.
- [15] W.G. Pan, X.M. Wang, M. Tao, W.B. Li, The failure mechanism analysis of long-stored ammunition, *Chin. J. Proj. Rockets Missiles Guidance* 27 (1) (2007) 122–125.
- [16] Q.Zh. Cui, M. Li, Function of water in black power, *Chin. J. Initiators Pyrotech.* 1 (2000) 35–37.
- [17] R.H. Zhang, G.E. Lu, K.L. Liu, et al., Influence of humidity on the heat decomposition speed of single-base propellant, *Chin. J. Ordnance Eng. Coll.* 19 (6) (2007) 46–52.
- [18] Y. Li, W.L. Song, Ch.Sh. Xie, et al., Influence of humidity on the thermal behavior of aluminum nanopowders, *Chin. J. Mater. Chem. Phys.* 97 (2006) 127–131.
- [19] J.H. Sun, X.R. Li, K. Hasegawa, et al., Thermal hazard evaluation of complex reactive substance using calorimeters and Dewar vessel, *J. Therm. Anal. Calorim.* 76 (3) (2004) 883–893.
- [20] J.H. Sun, Y.F. Li, K. Hasegawa, A study of self-accelerating decomposition temperature SADT using reaction calorimetry, *J. Loss Prevent.* 14 (2001) 331–336.
- [21] O.P. Korobeinichev, S.S. Khlevnoi, Mass-spectrometer study of the thermal decomposition of nitroglycerine power at high temperatures, *Combust. Explos.* 6 (3) (1970) 352–353.
- [22] C.E. Kirby, N.P. Suh, Reaction near the burning surface of double-base propellants, *AIAA J.* 9 (2) (1971) 317–320.
- [23] Y.H. Yu, K. Hasegawa, Derivation of the self-accelerating decomposition temperature for self-reactive substances using isothermal calorimetry, *J. Hazard. Mater.* 45 (1996) 193–205.
- [24] J.H. Sun, et al., Catalytic effects of inorganic acids on the decomposition of ammonium nitrate, *J. Hazard. Mater.* 127 (2005) 204–210.
- [25] Z.Sh. Wang, *Energetic Material Conspectus*, Harbin Institute of Technology Press, Harbin, 2006.
- [26] Zh.L. Xiao, Sh.Q. Hu, X.Q. Wu, et al., *Safety and Environmental Protection Technology of Explosives & Propellants*, Beijing Institute of Technology Press, Beijing, 2006.
- [27] Q.H. Zhao, Sh.W. Zhang, Q.Sh. Li, Density function theory study on the mechanisms of decomposition of HONO elimination reactions of 1,3,3-trinitroazetidene, *T. Beijing I. Technol.* 26 (2) (2006) 166–170.
- [28] P. Chen, F.Q. Zhao, et al., Thermal decomposition kinetics of triethylene glycol dinitrate, *Chin. J. Chem.* 22 (2004) 1078–1082.
- [29] P. Chen, F.Q. Zhao, et al., Thermal decomposition characteristics of triethylene glycol dinitrate, *Chin. J. Initiators Pyrotech.* 3 (1993) 5–10.
- [30] D.R. Brian, B.B. Thomas, Thermal decomposition of energetic materials 82. Correlations of gaseous products with the composition of aliphatic nitrate esters, *Combust. Flame* 128 (2002) 181–190.
- [31] United Nations, Recommendations on the transport of dangerous goods, Manual of Tests and Criteria, third revised ed., 1999.
- [32] N.N. Semenov, *Some Problems in Chemical Kinetics and Reactivity*, Princeton University Press, 1959 (Chapter 8).
- [33] T. Kotoyori, Critical temperatures for the thermal explosion of liquid organic peroxides, *Process Saf. Prog.* 14 (1) (1995) 37–44.
- [34] Q.S. Wang, J.H. Sun, et al., Thermal stability evaluation of Black Powder, RDX, PETN and TNT, in: *Proceedings of 2005 International Autumn Seminar on Propellants, Explosives and Pyrotechnics*, 2005, pp. 235–240.