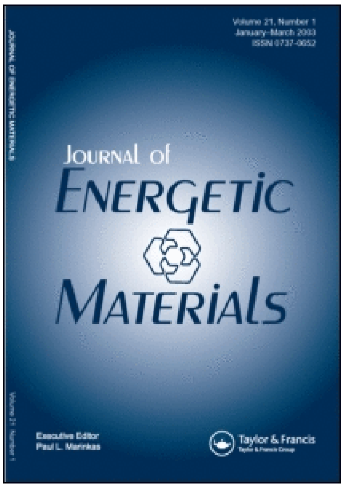

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# Combustion Mechanism of the Low Signature Propellant Containing 1,7-diazido-2,4,6-trinitrazaheptane(DATH)

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## ABSTRACT

The thermal decomposition behavior of the low signature (LS) propellant containing 1,7-diazido-2,4,6-trinitrazaheptane(DATH) is investigated by DSC, TG and DTG technique. Several analysis methods are used to study the physico-chemical structure of surface before and after combustion and the burning flame structure of this kind of propellant. Because DATH decomposes to produce a great quantity of $N_2$, the physico-chemical structure of burning surface of the propellant is obviously different from that of RDX-CMDB (Composite Modified Double-Base) propellant. It's mainly $N_2$ that gives rise to forming a lot of pores on the burning surface for its release. These pores can increase the burning rate because of extending the burning surface and increasing thermal-transfer intensity. In comparison with decomposition and combustion process of RDX-CMDB propellant, the propellant containing DATH creates the different decomposition products from the condensed phase to the fizz zone.

Keywords: Low signature (LS) propellant, Thermal decomposition, Burning surface, Burning rate, Combustion mechanism

## 1. INTRODUCTION

1,7-diazido-2,4,6-trinitrazaheptane(DATH)is an energetic oxidizer of propellants. There are rare research reports on thermal decomposition behavior and combustion characteristics of the propellant containing DATH. At present, many papers can be seen only that report the combustion characteristics of propellants containing the other azides, such as GAP、BAMO etc[1-9]. DATH was used to replace RDX in RDX-CMDB propellant in this paper. DATH is a kind of azidonitramine and has a great positive heat of formation. There are two moles $-N_3$ in

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a mole molecular of DATH. The thermal decomposition and combustion properties of the propellant are investigated by several analysis methods in our laboratory. The experimental results give us a lot of useful information for studying the combustion mechanism of this kind of LS propellant further.

## 2. EXPERIMENTAL

### 2.1 EXPERIMENTAL SAMPLES

The experimental samples are prepared by the solventless extrusion technique. The sample composition is shown in Table 1.

*Table 1 Composition of Sample (mass %)*

| Sample | binder | RDX | DATH | DINA | Pb salt | Cu salt | CB |
|---|---|---|---|---|---|---|---|
| 1 | 61.5 | 23.5 | 15 | — | — | — | — |
| 2 | 60.3 | 23.0 | 14.7 | — | 2.0 | — | — |
| 3 | 60.3 | 23.0 | 14.7 | — | — | 2.0 | — |
| 4 | 60.3 | 23.0 | 14.7 | — | — | — | 2.0 |
| 5 | 60.0 | 22.9 | 14.6 | — | 2.0 | 0.5 | — |
| 6 | 60.0 | 22.9 | 14.6 | — | 2.0 | — | 0.5 |
| 7 | 60.9 | 23.2 | 14.9 | — | — | 0.5 | 0.5 |
| 8 | 59.7 | 22.8 | 14.5 | — | 2.0 | 0.5 | 0.5 |
| 9 | 59.6 | 34.0 | — | 3.4 | 2.0 | 0.5 | 0.5 |

***Pb salt stands for Lead phthalate. Cu salt stands for Cupric adipate. CB is carbon black. DINA is N-nitro-dihydroxyethylamine-dinitrate.***

### 2.2 EXPERIMENTAL METHODS

TG and DSC experiments were carried out on a model TA 2000 instrument, TACO. USA. The operation conditions were as follows: the sample mass ,about 2.00 mg; heating rate, 10 K min$^{-1}$; reference sample, $\alpha$-$Al_2O_3$;atmosphere, a flowing rate of about 40 ml · min$^{-1}$ of $N_2$.
The photographs of combustion flame were obtained by the photographic camera through the view windows of the chamber. The chamber was filled with the flowing $N_2$. The size of propellant brand was 20mm×5mm×2mm. The curves of temperature profile were obtained by the micro-thermal-couple technology. The data acquisition system was HP 5430A Digital Oscilloscope. The personal computer was employed to analyze these data. Information of $-N_3$ group change before and after combustion could be gotten by using a Nicolet 60 SXR Fourier Transform Infrared Spectrometer (FTIR) with the in-situ cell at heating rate of 20℃/min,

which used to real-time follow the thermal decomposition process. JMS-5800 Scanning Electron Microscope (SEM: Japan Electronic Company) was used to research on the surface appearance before and after combustion.

## 3. EXPERIMENTAL RESULTS AND DISCUSSION

### 3.1 THERMAL DECOMPOSITION

We choose sample 1,sample 8 and sample 9 to carry out thermal decomposition research by DSC at 2MPa.The rates of heating are 5℃/min,10℃/min,20℃/min and 40℃/min respectively. The DSC curves of sample 1,sample 8 and sample 9 are Fig.1, Fig.2 and Fig.3 respectively.

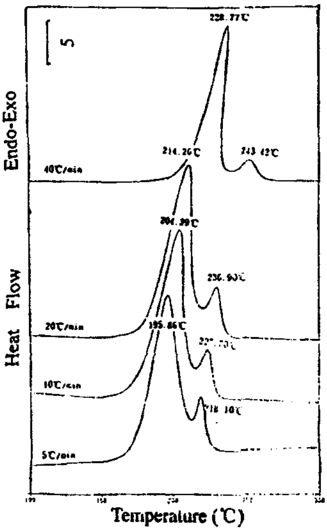


Fig.1 DSC curves of Sample 1

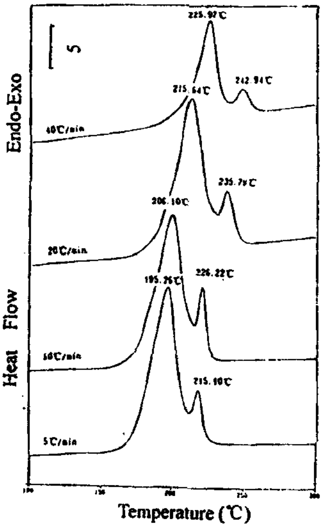


Fig.2 DSC curves of Sample 8

Analyzing these DSC curves, we discover that there are two decomposition peaks appearing on the DSC curves. And the decomposition peak temperatures of these samples increase with the increase of the rate of heating. And the peak shapes slope toward right. The fact follows a general rule. At the same time, with increasing the heating rate, the heat of decomposition reduces gradually. The distance between two decomposition peaks of sample 9 almost don't change. But that of sample 1 or sample 8 drastically reduces at a higher heating rate .The fact shows that the first decomposition process has a promotion effect on the second process for samples containing DATH.

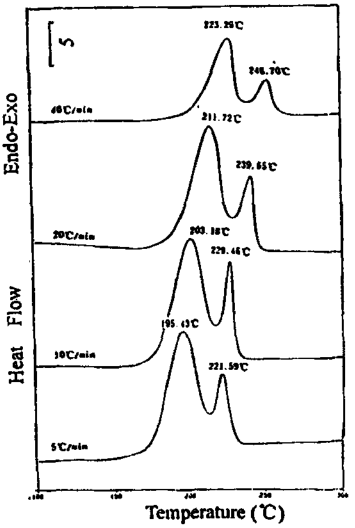


Fig.3 DSC curves of sample 9

In addition, the area of the first peak is bigger and that of the second one is smaller. We define the first decomposition peak temperature as Tm1. Tm1 stands for the decomposition peak temperature of binder. The second decomposition peak temperature is named as Tm2 that stands for the decomposition peak temperature of RDX. We think that the whole decomposition reaction process is mainly controlled by the first decomposition reaction because it releases a great deal of heat energy. Therefore, the first decomposition peak temperature is used to calculate the activation energy of decomposition reaction and evaluate the decomposition reactive degree if the reaction is easy or difficult.

*Table 2 Kinetics equations of sample decomposition*

| Decomposition peak | Sample 1 | Sample 8 | Sample 9 |
|---|---|---|---|
| $T_{m1}$ | $k=20.39e^{-14553/T}$<br>$\ln k=3.01-14533/T$ | $k=19.45e^{-14120/T}$<br>$\ln k=2.96-14120/T$ | $k=24.21e^{-16418/T}$<br>$\ln k=3.19-16418/T$ |

Kissinger method[10]is used to compute the kinetics data of the decomposition peak. The equations of kinetics are shown in Table 2. The results show that the activation energy of sample 8 is the smallest. But the activation energies of sample 1 is bigger and that of sample 9 is the biggest. In addition, the decomposition rate constant of sample 8 is bigger. So, we may conclude that sample 8 with catalysts decomposes easier than sample 1 without catalysts. And sample 8 and sample 1 with DATH decomposes easier than sample 9 without DATH. Therefore, both DATH and catalysts have a positive effect on the increase of the burning rate. At the same time, we consider that the catalysts change the activation energy of the first stage decomposition.

## 3.2 FLAME STRUCTURE

In a combustion chamber filled with $N_2$, tests of flame photo and temperature profile determination for nine samples are done under 2,4,and 6 MPa. By observing photos and analyzing curves, we may see the reaction of combustion surface becomes stronger and stronger with increasing pressure and the flame color changes from red-yellow to blue-white. There is a thinner dark zone in flame photos. The distance from flame to the combustion surface becomes smaller and smaller. The reason appearing these phenomena is that the test pressure is increased.

The combustion flames obviously exist certain thin dark zone under 2MPa.There are some heat-bright dots of different size and quantity on the burning surface for sample 4,sample 6 and sample 8 (See Fig. 4). In comparison with the sample components, we think that the size and quantity of heat-bright dots are directly proportional to additional carbon black (CB) content in these samples. CB plays an important role for forming these heat-bright dots. Sample 4 has 2 percent CB, so it has a lot of heat-bright dots. Pb/CB, Cu/CB and Pb/Cu/CB are composite catalysts used in sample 6,sample 7 and sample 8 respectively. The soot formed during combustion absorbs Pb、Cu or their oxides and they can mix and melt into sphere shape. The formation of heat-bright dots is due to releasing heat of the scission of $-N_3$ bonds to produce $\cdot C{\equiv}N+N_2$ and reduction of NO. But when the pressure is up to 4MPa,the bright dots disappear because of strong reaction in the combustion surface.

In addition, we discover some thin bright particle flow in the flame photos under 2MPa. One part is produced by spraying combustion of RDX particles. Such view also shows in reference [11]. Another is perhaps formed by organic pieces rising into flame with gas flow after DATH decomposition on the propellant burning surface.

Some facts in flame structure photos would be further explained from the temperature profile data of combustion wave. The slopes from the condensed phase to the flame zone increase gradually with increasing pressure from 2MPa to 6MPa.This shows that the surface temperature rises and the dark zone almost disappears and the distance from flame to the burning surface decreases with increasing pressure. Therefore, we consider that the reaction would be drastic under a high pressure.

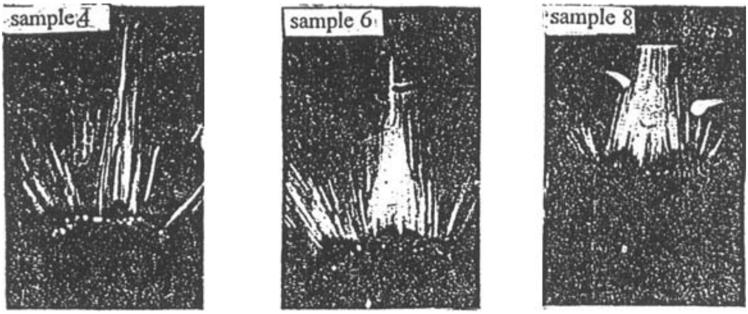


*Fig. 4 Photos of Flame Structure*

### 3.3 SURFACE PHYSICO-CHEMICAL STRUCTURE

We use sample 1,sample 8 and sample 9 to conduct the experiment.

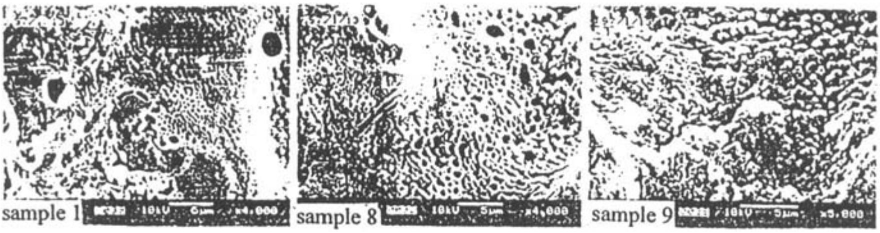
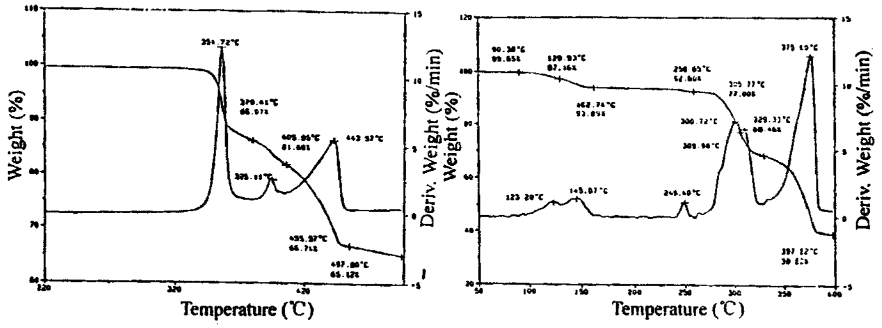


*Fig. 5 SEM photos after extinction*

Observed sample surface before combustion by SEM, the cross-section of sample 1 is obviously smooth and the binder keeps a good appearance. But that of sample 8 and sample 9 are coarse. We think that catalysts have an effect on the cross-link of binder. In addition, there are some RDX crystal particles appearing on the cross-section for all samples at a higher magnification. These particles may elucidate the spraying flow of RDX appearing in the flame photos under 2MPa. Analysed by FTIR, both sample 1 and sample 8 have two strong absorbing peak at 2100 cm$^{-1}$. But sample 9 has no the peak. We consider that the peak stands for $-N_3$ group when it appears in the samples.

Surfaces of three samples after extinction are like coral at a low magnification. But their surfaces are significantly different at a high magnification. The burning surface of sample 8 likes a bee nestle and has some dense small pores and these pores are very like small caves. Though some pores appearing also in sample 1,but the quantity of pores is less than that of sample 8.The surface of sample 9 looks like a solid block without almost any pore in a great area. Only are there some gaps among blocks. (See Fig. 5) We may suppose that the density of pores is strongly relate with the combustion reaction .The view can just explain the data of the burning rate.

By Infrared Photoaccousitic Spectroscopy, we may conclude that $-N_3$ group decomposes into -C≡N on the propellant surface and produces a lot of $N_2$ and $NO_2$. The result may elucidate that sample 1 and sample 8 have a lot of pores on the surface after extinguishing. And the result can further explain that $-N_3$ group on the burning surface decomposes completely and $-N_3$ of interior decomposes partly and that of the deepest zone don't almost decompose at all.



*(a) Pb salt* *(b) Cu salt*

*Fig. 6 TG/DTG curves of catalyst decomposition*

In addition, analyzing the surface composition of three samples by electron-probe method, we discover a lot of carbon. This proves that there is a tight bright carbon layer. At the same time, the surfaces of sample 8 and sample 9 accumulate a lot of Pb and Cu . This may explain the composition of heat-bright ball. Pb salt retains 65.12 percent residue after decomposition completely at 500℃ by TG. The content is accordant with the theory content after Pb salt into PbO finally. Cu salt still retains 38.8 percent after combustion. (See Fig. 6) The content is also accordant with the content of Cu salt into CuO. Therefore, we consider that Pb and Cu of the surface are their oxides.

## 5 CONCLUSION

(1) DATH added into propellants may change the reaction state of combustion surface. The reason is that DATH has a great positive heat of formation and $-N_3$ group can decomposes to produce a great deal of $N_2$ and heat energy.

(2) The release of $N_2$ creates a lot of small pores. The pores are useful to extend the burning surface and increase heat-transfer and improve the burning rate.

(3) DATH decomposes gradually from surface to interior. It's decomposition process would be supposed as follows:

$N_3$-R-$N_3$ (DATH) ------R''$(CN)_2$ + $N_2$ +$NO_2$+ Q (heat energy)

R''$(CN)_2$ ------ Organic pieces

(4) The physic-chemical structure of burning surface of the propellant is obviously different from that of RDX-CMDB. The difference focuses on the production of decomposition from the condensed phase to the fizz zone.

(5) Carbon black has an important role to form heat-bright dots. It is a bearer of Pb and Cu oxides.

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