CHARACTERIZATION OF 2-OXY-4,6-DINITRAMINE-S-TRIAZINE

by


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ABSTRACT

Physical and chemical characterization of 2-oxy-4,6-dinitramine-s-triazine (dinitroammeline-DNAM) as well as the evaluation of its potential as a clean additive in propellant compositions is presented. The selected base propellant is composed by phase stabilized ammonium nitrate (PSAN) as filler and hydroxyl terminated polybutadiene (HTPB) as binder in a 80/20 % (weight) composition.

The synthesis of DNAM was performed by nitration of 2,4,6-triamine-s-triazine (melamine). Chemical characterization was carried out using standard techniques. Density was estimated by Stine’s algorithm and measured by gas pycnometry. The study of the particle size distribution was made by means of laser diffraction. Oxygen bomb calorimeter and simultaneous thermal analysis (DSC/TGA) were used for thermochemical characterization.

The equilibrium thermodynamic properties of global combustion characteristics of PSAN/DNAM/HTPB were calculated using THOR and NASA-Lewis CET89 codes, in order to predict its performance and relevant energetic characteristics. Experimental tests were performed in a pressurized strand burner to measure and compare the combustion regression rate of a PSAN/DNAM/HTPB mixture related to the base PSAN/HTPB.

The obtained results show the contribution of DNAM in the combustion of the base PSAN/HTPB reactive mixture.

1. Introduction

Environmental conditions lead to the continuous development of energetic materials based in CHNO global compositions, free of Cl or F components. However, the development of completely new energetic is very risky and expensive, conditioned now by economic restrictions. In this work the above mentioned difficulty was avoided by using a known substance that as far as we are aware was never used in propellant formulations.

It is well known the greater interest of heteroaromatic nitrocompounds comparatively to the analogous nitroaromatic systems. The compound 2-oxy-4,6-dinitramine-s-triazine (dinitroammeline-DNAM) belongs to the first category and is reported to be isolated for the
first time by Cason (1947). Atkinson (1951) elucidated its structure and reported its partial characterization. It was not found in the literature any explicit application of DNAM since the early works.

Clean gas generators can be based in propellant compositions of PSAN/HTPB and these have been matter of study (Carvalheira, 1995; Korting et al., 1987; Strecker and Lind, 1979). Combustion products free of Cl or F components and low flame temperatures could be mentioned as some of the advantages. Unfortunately, there are a set of disadvantages due to the inherent properties of PSAN, such as high hygroscopicity and low burning rate of PSAN/HTPB based propellants. The particular aspect of the low burning rate might be overcome by means of the use of suitable additives. In this context, the present study is the start point of a systematic evaluation of the potential of DNAM as a clean additive in the above mentioned formulations.

2. DNAM Synthesis and Characterization

2.1 Synthesis Methodology

The synthesis of DNAM was performed according to a well-documented procedure (Atkinson, 1951) by the nitration of 2,4,6-triamine-s-triazine (melamine) with an acetonitrile mixture:

\[
\begin{align*}
\text{NH}_2 \quad \text{NH}_2 \quad \text{NH}_2 & \quad + \quad 3\text{HNO}_3 \\
\text{N} & \quad \text{N} & \quad \text{N} & \quad \xrightarrow{\text{Ac}_2\text{O}} \quad 0-5^\circ\text{C} \\
\text{NHNO}_2 & \quad \text{NHNO}_2 & \quad + \quad \text{NH}_4\text{NO}_3 & \quad + \quad \text{H}_2\text{O}
\end{align*}
\]

The purification was achieved by dissolving the crude product in a sodium bicarbonate solution, followed by filtration and subsequent acidification with HCl. The yield was ca. 50%. Elemental analysis was performed (Fisons EA1180) and the results are shown in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>%N</th>
<th>%C</th>
<th>%H</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{3}H\textsubscript{5}N\textsubscript{7}O\textsubscript{5}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>calc.</td>
<td>45.16</td>
<td>16.60</td>
<td>1.39</td>
</tr>
<tr>
<td>found</td>
<td>45.10</td>
<td>16.31</td>
<td>1.51</td>
</tr>
<tr>
<td></td>
<td>45.05</td>
<td>16.45</td>
<td>1.45</td>
</tr>
</tbody>
</table>
2.2 Spectral Characterization

In figure 1 the IR (Nicolet 750) spectrum of DNAM is presented. The presence of nitro groups is identified by the intense signals near 1600 and 1250 cm\(^{-1}\). The band around 3200 cm\(^{-1}\) is assigned to the monosubstituted amino group. This is also revealed by the absence of absorption in the region 1680-1640 cm\(^{-1}\) typical of nonsubstituted NH\(_2\) groups in this kind of systems. The predominance of keto form is clearly shown by the presence of the strong absorption near 1770 cm\(^{-1}\) due to the C=O group. Also, the signal around 760 cm\(^{-1}\) is typical when the triazine is in the iso form, i.e., with less then three double bonds in the ring and at least one double bond external to the ring (Colthup et al., 1975).

![IR spectrum of DNAM](image)

Fig. 1 - IR spectrum of DNAM.

2.3 Density and Particle Size Distribution

Density of DNAM was calculated using Stine's algorithm (Stine, 1881) and measured by means of gas (Helium) picnometry (AccuPyc 1330). The results are shown in Table 2.

<table>
<thead>
<tr>
<th></th>
<th>Calculated (g cm(^{-3}))</th>
<th>Measured (g cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Linear Nonlinear</td>
<td></td>
</tr>
<tr>
<td>Enol form</td>
<td>1.936 1.938</td>
<td>1.9410 ± 0.0007</td>
</tr>
<tr>
<td>Keto form</td>
<td>1.900 1.916</td>
<td></td>
</tr>
</tbody>
</table>
The calculation was made for the two possible tautomeric forms and considering for each one the data based on linear and nonlinear methods reported by Stine (1981). The best results obtained considering the enol structural formula is not consistent with the information revealed by the IR spectrum. Nevertheless, there is a very good agreement between the computed and observed densities for all cases. It should be noted also that density of DNAM is attractive in the energetic materials context.

The particle size distribution of DNAM was carried out by means of a laser diffraction technique with PIDS (Coulter LS130). The results are resumed in figure 2. This study revealed a monomodal distribution with particle size below 10 μm and median diameter (d50) of 2.5 μm.

![Particle size distribution of DNAM](image)

**Fig. 2 - Particle size distribution of DNAM.**

2.4 DSC/TGA and Calorimetry

As indicated by the DSC/TGA curves (*Rheometric Scientific STA 1500*) in figure 3, DNAM exhibits a sharp exothermic decomposition at 228-230 °C, with a considerable loss of weight. It is also apparent the stability of the compound in the temperature range below the decomposition temperature.

Heat of combustion of DNAM was measured in an oxygen bomb calorimeter (*Parr 1271*) and a value of 1663 ± 2.9 cal g⁻¹ was obtained. The value reported by Atkinson (1951) was 1673 cal g⁻¹.
3. Performance Calculations of Propellants

Theoretical calculations were performed in order to predict the global combustion characteristics of several propellant compositions based on PSAN/DNAM/HTPB mixtures. Two different computer codes were used. In both cases, calculations were performed for several propellants with binder contents in the range 10-20 % and considering, for each one, PSAN/DNAM solid loading ratios in the range 0/100-100/0 %. It should be mentioned that IPDI was included in the binder phase in a ratio HTPB/IPDI of 92.32/7.68 %.

The standard heat of formation of DNAM was estimated from the heat of combustion value. Relevant properties of the other reactants were found in the literature (Chase et al., 1985; Volk and Bathelt, 1994).

It should be realized that the thermodynamic computation codes assume the global contribution of any component. The problems arising from the endothermic phase transitions of PSAN and from dissociation and recombination during expansion are not taken into account.

3.1 THOR Code

The theoretical prediction of combustion products was performed using THOR code, based on theoretical work of Heuzé et al. (1985, 1989) and later modified by Campos (1991).
Several kinds of equations of state can be used, namely BKW, Boltzmann and JCZ3. This THOR code uses now a new EoS (Durães et al., 1995), with the same assumptions of a Boltzmann EoS, but based now on physical intermolecular potential of gas components instead of correlations from final experimental results. The selection of components are dependent of atomic initial composition. For a classical CHNO system it is assumed an equilibrium composition of CO₂, CO, H₂O, N₂, O₂, H₂, OH, NO, H, N, O, HCN, NH₃, NO₂, N₂O, CH₄ gases and two kinds of solid carbon (graphite and diamond). The solution of composition problems involves simultaneously:

- the thermodynamic equilibrium (thermal, mechanical and chemical equilibria), obtained with the mass and species balance, and the equilibrium condition \( G = G_{\text{min}} \) (P,T,x_i); previously described, applying to the condensed phase the model proposed by (Tanaka, 1983);

- the thermal equation of state (EoS);

- the energetic equation of state, related to the internal energy \( E = \sum x_i e_i(T) + \Delta e, e_i(T) \) being calculated from JANAF Thermochemical Tables (Chase, M. W., Jr. et al., 1985), and polynomial expressions of Gordon and McBride (1971);

- the combustion regime, being P constant for the isobar adiabatic combustion (equal initial and final total enthalpy \( H_b^{ib}=H_0^{ib} \)), the isochor adiabatic combustion (\( E_b^{ib}=E_0^{ib} \)).

Figure 4 shows the results of calculations employing the THOR code for the flame temperature as a function of the composition of PSAN/DNAM/HTPB mixtures. Because HTPB is a non-energetic binder, the expected increase in the flame temperature with the decrease of binder content is observed. In global terms, the highest temperature variation with the PSAN/DNAM ratio does not exceed 24 %. This value corresponds to a large variation in PSAN/DNAP ratio. In each successive increment for the PSAN/DNAM ratio plotted, the temperature variation is substantially lower then that value.

Figure 5 shows the composition of combustion products for a propellant with 20 % of HTPB and considering various PSAN/DNAM ratios. It could be observed that comparatively to the base PSAN/HTPB propellant the addition of DNAM does not affect the composition of the most pollutant products in a large extent. Other important fact is the absence of NOₓ species.
Fig. 4 - Flame temperature as a function of the composition of PSAN/DNAM/HTPB mixtures.

Fig. 5 - Composition of combustion products as a function of the PSAN/DNAM ratio in a propellant with 20% HTPB.
3.2 NASA - Lewis CET89 Code

The well known NASA-Lewis CET89 code (McBride, 1989) was used to compute the adiabatic flame temperature and the specific impulse. In the calculations it was assumed a combustion of the propellant in the combustion chamber at 7.0 MPa followed by an adiabatic expansion of combustion products along a convergent-divergent nozzle, with a pressure ratio of 70.0/1.0.

The adiabatic flame temperature as a function of the composition of PSAN/DNAM/HTPB mixtures obtained with this code is now presented in figure 6. In global terms, the evolution of the curves is similar to that one obtained using the THOR code. The highest temperature variation with the PSAN/DNAM ratio is also near 24%. However, the flame temperatures now achieved are relatively higher for the case of high binder contents. This could be explained mainly by differences in the applied numerical method of convergence and thermal EoS in these two codes.

![Diagram](image)

Fig. 6 - Flame temperature as a function of the composition of PSAN/DNAM/HTPB mixtures.

The specific impulse (figure 7) increases with the decrease of DNAM content for all binder load range. The largest variation is 11% and occurs for the composition with 10% of HTPB and for the extreme variation in the PSAN/DNAM ratio.
The calculated thermodynamic properties of global combustion characteristics, viewed as a whole, show a relevant effect. The calculated flame temperature and specific impulse decrease moderately with the increase of DNAM content in PSAN/DNAM/HTPB mixtures. A low specific impulse is not a determinant factor for gas generator purposes, while low flame temperatures are desirable in this kind of applications.

Figures 8 and 9 show respectively the variation of flame temperature and specific impulse with the equivalence ratio for several PSAN/DNAM and PSAN/DNAM/HTPB compositions. The flame temperature of DNAM is considerably higher than the flame temperature of PSAN. This fact suggests differences in burning characteristics of PSAN/DNAM/HTPB compared with the base PSAN/HTPB reactive system. However, the possible complete dissociation and carbon formation in combustion products must be taken into account.
Fig. 8 - Flame temperature as a function of the equivalence ratio for PSAN/DNAM/HTPB mixtures.

Fig. 9 - Specific impulse as a function of the equivalence ratio for PSAN/DNAM/HTPB mixtures.

Figures 8 and 9 also show the increase of the equivalence ratio with the increase of DNAM content. For keep the equivalence ratio in acceptable levels, the addition of DNAM to the PSAN/DNAM/HTPB global compositions implies a reduction of the binder content. In these circumstances, the possible loss of rheological and/or mechanical properties should be
considered. The fine particle size of DNAM might be an important factor to attenuate this difficulty.

4. Experimental Measurement of Combustion Regression Rate

The combustion characteristics of PSAN/DNAM/HTPB propellant were performed in a strand burner with inert atmosphere (N₂) within a pressure range 2-10 MPa, at ambient temperature. Two compositions were tested:

- PSAN(80%)/HTPB(20%);
- PSAN(62%)/DNAM(12%)/HTPB(20%),

both with a density near 96 % of the theoretical maximum density (this one 1.464 g cm⁻³ for PSAN/HTPB and 1.481 g cm⁻³ for PSAN/DNAM/HTPB).

The obtained results are resumed in figure 10. The correspondent fitting results for the Vieille's law model, \( r = ap^n \), are presented in Table 3.

![Graph showing the combustion regression rate of propellants tested.](image)

**Fig. 10 - Comparative results of the combustion regression rate of the propellants tested.**

<table>
<thead>
<tr>
<th>Propellant composition</th>
<th>( a )</th>
<th>( n )</th>
<th>Corr. coef.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSAN(80%)/HTPB(20%)</td>
<td>0.61</td>
<td>0.55</td>
<td>0.990</td>
</tr>
<tr>
<td>PSAN(62%)/DNAM(12%)/HTPB(20%)</td>
<td>0.69</td>
<td>0.55</td>
<td>0.998</td>
</tr>
</tbody>
</table>

Table 3 - Fitting results for the model \( r = ap^n \).
The obtained results show that in the pressure range considered the addition of DNAM does not change the pressure exponent and leads to an increment of the regression rate comparable to its mass content in the global formulation. This is in a good agreement with predicting calculation and the discussion made about the influence of DNAM in the burning characteristics of the PSAN/HTPB base composition.

5. Conclusion
The observed properties of DNAM like its chemical composition, density and particle size distribution as well as the thermal stability revealed an interesting substance candidate to be used as an additive in propellant formulations.

The calculated thermodynamic properties of global combustion characteristics predict a relevant effect by the addition of DNAM to a base composition formed by PSAN/DNAM. The calculated flame temperature and specific impulse decrease moderately with the increase of DNAM content in PSAN/DNAM/HTPB mixtures. The composition of combustion products indicates that we are in presence of a clean propellant, free of severe pollutants such as NOx and HCl.

The advantage of the addition of DNAM to PSAN/HTPB based propellant was also revealed by the observed influence on the burning characteristics of the tested mixtures. The acceptable value of the pressure exponent as well the increasing in the combustion regression rate suggests a deeper study of this reactive system, namely in respect to the ignition mechanism.

References


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