



Application of the Energetic Complex [Cu(TNBI)(NH₃)₂(H₂O)] in Heterogeneous Solid Rocket Propellants

**Rafał Bogusz,^{1*} Judyta Rećko,² Paulina Magnuszewska,¹
Rafał Lewczuk¹**

¹*Institute of Industrial Organic Chemistry,
Annopol 6, 03-236 Warsaw, Poland*

²*Military University of Technology,
Urbanowicza 2, 00-908 Warsaw, Poland*

**E-mail: bogusz@ipo.waw.pl*

Abstract: This paper presents results from the application of [Cu(TNBI)(NH₃)₂(H₂O)] (CuTNO) to heterogeneous solid rocket propellants based on HTPB/AP, replacing RDX. A series of different compositions of solid heterogeneous rocket propellants based on HTPB and ammonium perchlorate, containing CuTNO or RDX, were prepared and investigated. The ballistic parameters of the examined propellants were determined by combustion in a laboratory rocket motor (LRM). The ballistic properties were evaluated in the pressure range 4-10 MPa and it was found that the linear burning rate at 10 MPa increased by more than 20% for the CuTNO containing propellant, compared to the RDX-based composition. By linear regression of the $r = f(p)$ curves obtained, the burning laws for the investigated propellants were determined. It was found that the CuTNO additive increases the pressure coefficient by over 46%, compared to unmodified propellant. The determination of the sensitivities to friction and impact, the calorific value, hardness and decomposition temperature of the propellants obtained were also investigated.

Keywords: CuTNO, RDX, HTPB, heterogeneous solid rocket propellants

1 Introduction

In the technology of heterogeneous solid rocket propellants (HSRP), classic substances like HTPB as main binder element, ammonium perchlorate (AP) as

the oxidizer [1], aluminium powder as a metallic fuel [2], and high explosive materials (RDX, HMX, FOX-7) as energetic additives [3-5] are used. These compositions are investigated to enhance specific properties, such as linear burning rate, for new applications of this group of explosives. There are several ways of improving the parameters of such propellants. It is possible to use burning rate modifiers (catocene, butacene, nano-Fe₂O₃) [6-9], or to apply highly energetic binder compounds like NHTPB, BAMO, GAP *etc.* [10-12]. In the present work another possibility is presented, namely the application of a modern energetic complex with copper [Cu(TNBI)(NH₃)₂(H₂O)] (CuTNO). This is a derivative of 4,4',5,5'-tetranitro-1*H*,1'*H*-2,2'-biimidazole (TNBI), which can be obtained by a simple method [13]. It has been proven that TNBI and its salts are interesting energetic materials [14, 15]. We have concluded that the use of an oxygen-rich molecule containing copper, which could act as a catalyst in heterogeneous propellants, is justified. The structure of the CuTNO molecule is shown in Figure 1.

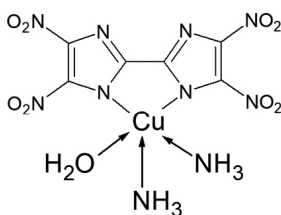


Figure 1. Structure of CuTNO

Copper complexes with energetic ligands have attracted considerable attention, since they have superior explosive performance and have been proposed as lead-free primary explosives or ingredients in low-smoke propellants [16-19]. Nevertheless the properties of CuTNO are specific to secondary explosives [20]. The compound is insensitive to friction, its sensitivity to impact is equal to 6.5 J and it decomposes above 230 °C during DTA/TG measurements. Taking into account these properties, it was decided to replace RDX with CuTNO in the HSRP composition.

The aim of this paper is to demonstrate how CuTNO influences on selected properties of a solid heterogeneous rocket propellant based on HTPB. The results were compared with an analogous RDX-based composition. In this study we report the impact of CuTNO on the sensitivity to mechanical stimuli, calorific value, hardness, decomposition temperature and linear burning rate of the examined propellants.

2 Experimental

2.1 Test methods

Research methods have been described in our previous paper [9]. For greater clarity they have been quoted below.

An adiabatic calorimeter IKA C 4000F was used for the measurement of the isochoric heat of combustion (calorific value, Q) of the propellants obtained. Its constant was determined using standard gunpowder with a known calorific value of 4922 J/g. The results obtained for the calorific values were the mean of two different measurements, differing from each other by a maximum of 25 J/g; the sample mass of the tested propellant was 5.8 g.

In order to determine the sensitivity to mechanical stimuli, the standard Kast hammer and Peters apparatus were used in accordance with the procedure described in more detail in [21].

To determine the Shore A hardness of the propellants, hardener testing equipment Zwick/Roell HPE type A was used. The size of the penetration of the indenter into the flat surface of the examined propellant, during 3 s under a pressure of 12.5 N, was measured and converted into Sh A. Six measurements were performed, with an accuracy of 0.1 Sh A, for each tested propellant, which were used to calculate the mean value.

The decomposition temperature of the investigated propellants was examined by two independent methods: Wood's alloy heating bath, described precisely in [22, 23], and differential thermal analysis (DTA). For the DTA measurements an OZM Research DTA 551-Rez apparatus was used; the weight of each sample was 30-40 mg, and the measurement was carried out in the range 30-450 °C.

To estimate the ballistic parameters of the investigated propellants, a laboratory rocket motor (LRM) [24] was used. As a basis for the calculation, the indirect method of linear burning rate determination was applied and has been described in [11]. Test samples of dimensions 100 mm × 50 mm × 25 mm were combusted at ambient temperature, using a nozzle with a throat diameter of 7 mm.

To estimate the density and the specific impulse of the investigated propellants, the ICT-Thermodynamic-Code (ICT-Code) software was used.

2.2 Propellant preparation

The CuTNO complex was obtained by reaction of *in situ* synthesized TNBI ammonium salt with Cu^{2+} cations and water, according to a previously published procedure [20].

Rubber HTPB 4P60C (ECO), ammonium perchlorate (IPI) - coarse and fine-grained, aluminium powder (Benda Lutz), RDX (NITROERG), and dimeryl diisocyanate (IPI) as the curing agent were used to prepare the samples. The formation of the propellant mass was performed at 60 °C, using a laboratory planetary mixer NETZSCH. The propellant slurries were casted into shaped molds and cured at 65 °C for 7 days. The compositions of the prepared propellants are presented in Table 1.

Table 1. Compositions of the prepared propellants

| Component | P1 [wt.%] | P2 [wt.%] | P3 [wt.%] |
|------------------------|--------------|--------------|--------------|
| HTPB | 11.46 | 11.46 | 11.46 |
| DDI | 2.14 | 2.14 | 2.14 |
| Additives ^a | 0.4 | 0.4 | 0.4 |
| AP | 70 | 61 | 61 |
| Al | 16 | 16 | 16 |
| RDX | - | 9 | - |
| CuTNO | - | - | 9 |

^a Catocene, Tepanol, Lecithin

3 Results and Discussion

3.1 Physicochemical properties of the propellants

Table 2 presents the calorific value, hardness, density and sensitivity to mechanical stimuli of the propellants.

Table 2. Physicochemical properties of the investigated propellants

| Parameter | P1 | P2 | P3 |
|------------------------------|-------|-------|-------|
| Calorific value [J/g] | 6429 | 6196 | 5721 |
| Hardness [Sh A] | 78.3 | 77.7 | 91.3 |
| Friction sensitivity [N] | 120 | 80 | 160 |
| Impact sensitivity [J] | 9.81 | 9.81 | 9.81 |
| Density [g/cm ³] | 1.744 | 1.734 | 1.744 |

As may be inferred from the above data, addition of high explosive material to the propellant compositions significantly decreases the calorific value. For the propellant P2 (containing RDX), the change in calorific value was 4% and

for the propellant P3 (containing CuTNO) it was 11%, in comparison with the propellant P1 (unmodified propellant). Thus it is clear that the CuTNO additive has a significant influence on the calorific value.

In the case of the hardness value, it was found that the CuTNO additive gave a significant improvement. It may be calculated that the hardness value obtained for the propellant P3 was over 16% higher than those of the propellants P1 and P2, which have similar values for this parameter. The significant increase in the hardness of P3 propellant is probably due to the presence of copper ions in the propellant composition. It may be assumed that copper ions, as for iron ions, catalyse the curing process of the propellant slurry, which has a direct impact on the hardness of the resultant propellant.

Interesting data was obtained from the friction sensitivity measurements. The addition of CuTNO to the propellant composition decreased the friction sensitivity in comparison to the propellant P1. This phenomenon is quite interesting for the addition of high explosives to solid propellants. A significant decrease in the friction sensitivity of the propellant P3 results from the fact that the friction sensitivity of pure CuTNO is equal to 360 N, therefore the addition of this material to the fuel composition will reduce the sensitivity to friction of the propellant obtained.

In the case of impact sensitivity, no correlation between these three propellants was observed.

Based on theoretical calculations, it was found that CuTNO does not reduce the density of the investigated propellant, because its density is similar to AP and higher than RDX.

3.2 Thermal analysis – decomposition temperature

Figure 2 shows the DTA curves of the obtained propellants. Table 3 presents the decomposition temperatures as determined by Wood's alloy heating bath and the DTA decomposition onset temperatures.

There are clear differences between the decomposition temperatures determined by both methods. The Wood's alloy heating bath measurement gave significantly lower decomposition temperatures than DTA analysis, over 58 °C for P1, 145 °C for P2 and 144 °C for P3. This phenomenon results from the multi-step character of the propellant decomposition process. In the DTA curves, peaks for decomposition, which belong to RDX (208 °C) and CuTNO (232 °C), are visible. These transformations are the first steps in the decomposition process in the cases of P2 and P3 propellants. Under the DTA measurement conditions, the energy emitted by these transformations is not sufficient to initiate full decomposition, but under the Wood's alloy heating bath measurement conditions, the emitted energy

is sufficient. For safety reasons, the decomposition temperatures obtained by the Wood's alloy heating bath measurement are correct and justified. Furthermore, in the DTA analyses no significant differences between the full-decomposition temperatures of the investigated propellants were observed.

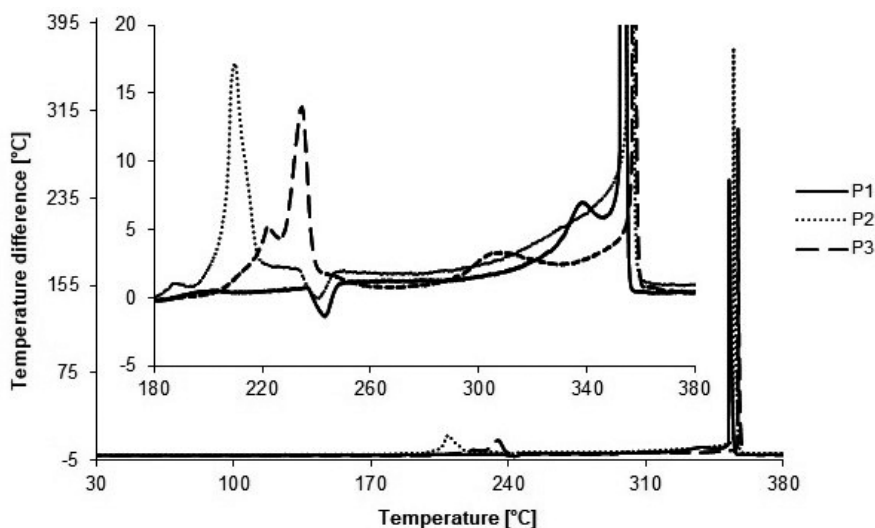


Figure 2. DTA curves of the investigated propellants

Table 3. Decomposition temperatures of the investigated propellants

| Propellant | Full-decomposition onset temperature by DTA [°C] | Decomposition temperature by Wood's alloy heating bath [°C] |
|------------|--|---|
| P1 | 352.3 | 294.1 |
| P2 | 354.9 | 209.6 |
| P3 | 356.8 | 212.8 |

3.3 Ballistic examinations

The main ballistic parameter describing an HSRP is the linear burning rate, r . In order to determine the dependence $r = f(p)$, propellant samples were combusted in the LRM. The indirect burning rate determination method, based on the LRM tests, was adopted. The pressure courses registered during combustion of the propellant samples are shown in Figure 3. The characteristic values of the combustion process obtained for each propellant are shown in Table 4.

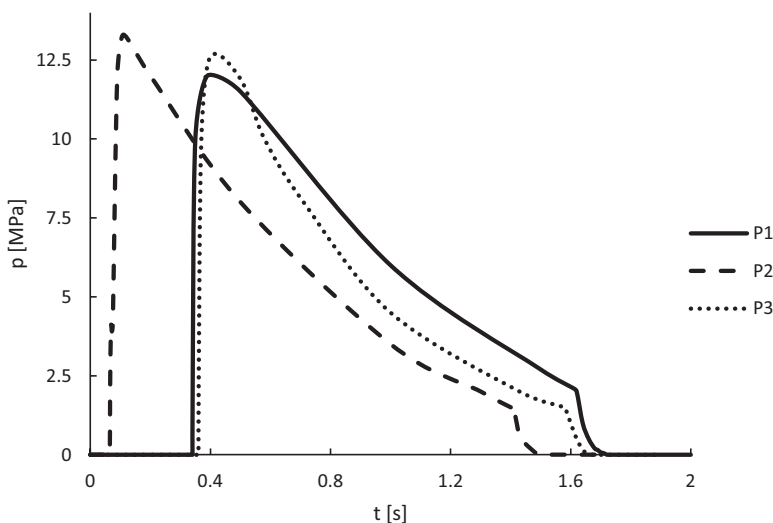


Figure 3. Propellants P1-P3 $p = f(t)$ curves

Table 4. Combustion time, P_{\max} , and specific impulse of the investigated propellants

| Parameter | P1 | P2 | P3 |
|---------------------|-------|-------|-------|
| Run time [s] | 1.27 | 1.34 | 1.23 |
| P_{\max} [MPa] | 12.0 | 13.3 | 12.6 |
| I_{sp} [s] | 265.0 | 265.5 | 260.9 |

For the data obtained, an increase in the maximum pressure in the combustion chamber for the high explosives-based propellants was observed. However, for the P3 composition, which was based on CuTNO, the maximum pressure was lower than for the P2 composition, which was based on RDX. This is probably related to the lower energy of CuTNO compared to RDX. This is reflected in the calorific value of the investigated propellants. However, CuTNO still exhibits the features of a highly energetic additive due to the higher values of the maximum pressure in the combustion chamber, in relation to the reference propellant P1. It was found that the maximum pressure in the combustion chamber increased in comparison with propellant P1, by 10.8% for propellant P2 and 5% for P3. In addition, it was calculated that the CuTNO-based propellant exhibits the lowest value of specific impulse. The CuTNO additive slightly reduced the specific impulse by 4.1 s, compared to propellant P1, and 4.6 s compared to propellant P2.

The calculation of the linear burning rate and its dependence on pressure were performed in accordance with the methodology presented in [11]. The Wolfram

Mathematica® 10 software, for numerical evaluation of the $p = f(t)$ characteristics obtained, was used. The $r = f(p)$ curves obtained for the investigated propellants are shown in Figure 4. The linear burning rates for the selected motor operating pressures are shown in Table 5.

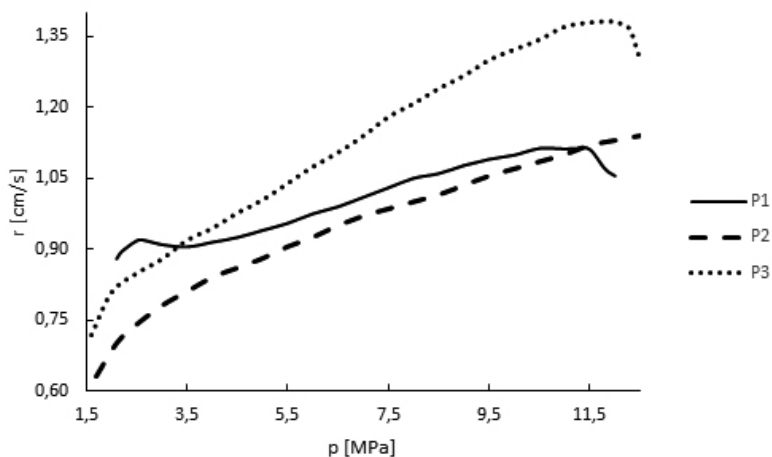


Figure 4. Propellants P1-P3 $r = f(p)$ curves

Table 5. Linear burning rate of the investigated propellants

| Propellant | Linear burning rate | | |
|------------|---------------------|-----------------|------------------|
| | 4 MPa [cm/s] | 7 MPa [cm/s] | 10 MPa [cm/s] |
| P1 | 0.91 | 1.01 | 1.10 |
| P2 | 0.83 | 0.97 | 1.07 |
| P3 | 0.95 | 1.15 | 1.33 |

The burning laws of the investigated propellants were determined by linear regression of the $r = f(p)$ curves obtained. The values of a , n , R^2 and the estimation ranges of the burning rate laws obtained are shown in Table 6.

Table 6. Burning laws for the investigated propellants

| Propellant | a | n | R^2 | Range [MPa] |
|------------|-------|-------|--------|-------------|
| P1 | 0.660 | 0.220 | 0.9924 | 4.5-11.5 |
| P2 | 0.565 | 0.278 | 0.9958 | 1.7-13.3 |
| P3 | 0.617 | 0.323 | 0.9882 | 1.6-12.0 |

Based on the data analysis it was found that propellant P2, based on RDX, represents the lowest linear burning rate value. In the higher pressure range (7-10 MPa), propellant P2 showed similar linear burning rate values to propellant P1. In the case of propellant P3, based on CuTNO, it was found that in all pressure ranges it showed the highest linear burning rate values. The significant increase in the burning rate of P3 propellant in all pressure ranges is probably due to the presence of copper ions in the propellant composition. It can be assumed that copper ions, as with iron ions, catalyse the ammonium perchlorate decomposition process, which has a direct impact on the burning rate. On this basis, it was found that, at a pressure of 7 MPa, the linear burning rate increased by 13.9% and 18.6% in comparison with propellants P1 and P2, respectively, and at 10 MPa, by 20.9% and 24.3%, respectively. Additionally, propellants P2 and P3 exhibit more stable combustion processes than propellant P1, which is reflected in the $r = f(p)$ curves of the investigated propellants. Furthermore, it was found that the addition of CuTNO to the propellant composition significantly increased the burning rate dependence on pressure. In comparison with propellant P1, the pressure coefficient in the burning law of propellant P3 was increased by over 46%, and by 16% in comparison with propellant P2. Such a high increase in the pressure coefficient value will enhance the sensitivity of CuTNO-based propellants to the pressure changes, in comparison with the other investigated propellant compositions.

4 Conclusions

This paper presents the possibility of the application of CuTNO in heterogeneous solid rocket propellants based on HTPB/AP. The studies conducted demonstrated the possibility of replacing classic high explosives materials, like RDX, widely used in technology of this kind of propellant, by CuTNO. During these studies, heterogeneous solid rocket propellants based on HTPB/AP with the addition of 9% CuTNO, or 9% RDX, and without any additions, were successfully prepared, casted and combusted.

During the measurement of their physicochemical properties, it was found that a high amount of CuTNO additive significantly decreased the propellant calorific value obtained, in comparison to compositions without any high explosive additive and the RDX based propellant. On the other hand, it was found that the addition of CuTNO improved the hardness and reduced the sensitivity to friction, in comparison with the other investigated propellants. Furthermore, it can be stated that the copper ions contained in CuTNO catalyse the curing process of the propellant slurry.

Thermal analysis has shown no negative aspects of the CuTNO additive. Comparison of the DTA curves of propellants with CuTNO and RDX has shown that both of these propellants are characterized by similar decomposition processes and thermal stability.

In the case of ballistic examinations, it was found that the CuTNO-based propellant exhibited higher linear burning rates than the other propellants investigated. This fact probably results from an influence of the copper ions on the ammonium perchlorate decomposition process, similar to that of iron ions. Additionally, the propellant based on CuTNO was characterized by a good LRM working time, despite exhibiting high linear burning rates. From the estimation of the burning laws of the investigated propellants, it was found that CuTNO has a negative influence on the pressure coefficient and can enhance the sensitivity to working pressure changes of CuTNO-based propellants. Based on the data obtained, in particular an enhancement of the linear burning rate, it can be expected that CuTNO could also be used as a burning rate modifier. Studies on this aspect of the application of CuTNO in heterogeneous solid rocket propellants will be progressed.

In conclusion, it can be stated that CuTNO can be used as a replacement for RDX in heterogeneous solid rocket propellants. The advantages of the application of CuTNO include lower friction sensitivity, higher hardness, density and linear burning rate compared to RDX. Nevertheless, the addition of CuTNO reduces the specific impulse and calorific value of a heterogeneous solid rocket propellant.

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