Central European Journal of Energetic Materials, **2014**, *11*(1), 3-13
ISSN 1733-7178

Biuret: a Potential Burning Rate Suppressant in Ammonium Chlorate(VII) Based Composite Propellants

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Abstract: Several composite propellant compositions containing various concentrations of biuret, a new burning rate suppressant, were formulated and studied to optimize the concentration of biuret in the composite propellant. Biuret was used here for the first time in a composite propellant as a burning rate suppressant. The theoretical properties of the compositions containing different concentrations of biuret were computed by using the NASA CEC-71 programme and the burning rate performances were evaluated. In addition, the sensitivity, thermal and mechanical properties of the compositions were also evaluated. The composition containing ammonium chlorate(VII) (AP) 65%, Al 15%, binder 20% and biuret 0-6% over the batch were prepared. The composition containing 6% biuret over the batch was insensitive to friction and impact. As the amount of biuret was increased, the energy, burning rate and sensitivity decreased, whilst the auto ignition temperature increased. The formulation containing 4% biuret over the batch was found to be the optimum with respect to energy, burning rate, pressure index, and sensitivity.

Keywords: burning rate suppressants, biuret, burning rate, HTPB, composite propellant

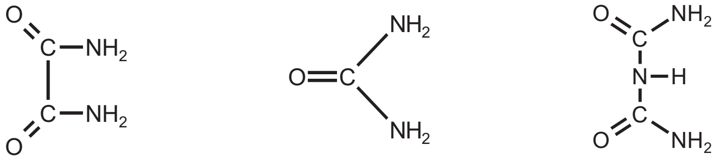
1 Introduction

The state of the art for composite propellant development is to have compositions with burning rates for varying conditions, such as a high burning rate for quick action and a low burning rate for idle purposes, so as to conserve the fuel. It is desirable to have propellants that will provide thrust when required and that will also conserve fuel when thrust is not needed [1].

The use of additives to reduce the propellant burning rate and pressure exponent has been known for many decades. The aim of the present research was to produce an AP/Al/HTPB based propellant with a substantially low burning rate and exponent that could be useable for tactical rocket motor applications. At the same time, several criteria were imposed on the propellant, including a non-toxic exhaust, material availability, and low cost of ingredients.

A burning rate suppressant is an additive that has an opposite effect to that of a catalyst, and has been used to decrease the burning rate for AP based composite propellants. Potential burning rate suppressants include oxamide, melamine, nitroguanidine, urea, calcium carbonate, calcium sulphate, ammonium chloride, and ammonium sulphate. Other suppressants which may be used in practice include dicyanoguanidine, chlorinated hydrocarbons, aluminum hydroxide, ammonium salts (sulphate, oxalate, phosphate), lithium fluoride, strontium carbonate, *N*-bromosuccinimide, hexabromocyclododecane, pentabromodiphenyl oxide, decabromodiphenyl oxide, fire master 836, tetrabromophthalatediol, triphenyl antimony, diammonium bitetrazole, 5-aminotetrazole, ammonium polyphosphate, and other flame retardants [2, 3].

Inorganic salts like sodium bicarbonate, sodium carbonate and calcium carbonate have burning rate retarding effects. These suppressants have been used in the formulation of nitrogen generating propellants [4]. Other additives which suppress the decomposition of sodium azide and decrease the combustion rate include insensitive explosives such as 3-nitro-1,2,4-triazol-5-one (NTO), 3-amino-5-nitro-1,2,4-triazole (ANTA) [5] and nitroguanidine. The product residues suppress the combustion rate of solid rocket propellants. Cyclic azines (diaminofurazan), dicyandiamide and diaminoglyoxime have also been proposed to contribute to burning rate suppression and to lowering of the pressure exponent.



(a) (b) (c)

Figure 1. (a) oxamide, (b) urea, (c) biuret.

In view of this, Ghorpade *et al.* [6] has performed detailed experimental studies on composite propellant formulations incorporating different burning rate suppressants, such as melamine, oxamide, urea and nitroguanidine. Of these ingredients, oxamide and melamine were found to be superior. However oxamide showed a higher pressure index. Consequently melamine was used for further studies.

In this study, oxamide and urea were used as burning rate suppressants because they have structural similarities. Based on this observation, biuret could be a potential burning rate suppressant. Figure 1 shows the structures of oxamide, urea and biuret.

All three compounds have an active amide group and liberate nitrogen compounds on combustion. Biuret is susceptible to decomposition due to the presence of the C-N-C grouping (C-C = 86 kcal/mole, C-N = 54 kcal/mole). Hence, biuret should be evaluated as a burning rate suppressant.

Biuret is a compound with the chemical formula $H_2NC(O)NHC(O)NH_2$. It is formed by the condensation of two molecules of urea. This white solid is soluble in hot water. It is reported that biuret is also used as a non-protein nitrogen source in ruminant feed, where it is converted into protein by gut micro-organisms. It is less favored than urea, due to its higher cost and lower digestibility, but this latter characteristic also slows down its digestion and so decreases the risk of ammonia toxicity.

The main objective of the present paper was to use biuret at varying concentrations as a burning rate suppressant in unique propellant formulations.

2 Materials and Methods

The binder, consisting of hydroxy terminated polybutadiene, (HTPB: OH value 40-50 mg/g, moisture 0.15%, from Orion Chemicals), was cured with toluene di-isocyanate (TDI: purity 99%, RI 1.565-1.567 at 30 °C; from Bayers). Dioctyl adipate (DOA: saponification value 303 ±3, moisture 0.5%, from Subhas Chemicals) was used as a plasticizer to increase processibility. The additive pyrogallol (melting point: 131-134 °C, from S.D. Fine) was used as a cross-linking agent. Biuret (purity 99%, melting point 193 °C, from Loba Chemicals) was used as a burning rate suppressant. The mixture of trimethylolpropane (OH value 1220, moisture 0.5%, purchased from Celenese) and butane-1,4-diol (OH value 1220, RI 1.444 ±0.002 at 30 °C, moisture 0.5%, purchased from Biaf) was used as an adduct in the composition. Two different sizes of ammonium chlorate(VII) were used in the propellant formulations. The first consisted of pure, research grade ammonium chlorate(VII) (purity 99%, density 1.95, from Tamilnadu chlorates) with an average particle size of 300 µm. The other size of ammonium chlorate(VII) was made by grinding ammonium chlorate(VII) (> 99% pure) in a fluid energy mill to an average particle size of 60 µm. Aluminum metal powder (from MEPCO) of average particle size 15 μm, was used as a metal fuel. The propellant formulation is given in Table 1. The propellant formulations were mixed in 10 kg batches using a vertical planetary mixer of 15 L capacity. During mixing, vacuum (2-3 tor) was applied at 55 °C, in order to remove air bubbles from the formulation prior to casting. The propellant mixture was cast under vacuum by slurry cast techniques [7]. The propellant was cured at 60 °C for 10-12 days in a water-jacketed oven. The base composition, without burning rate suppressant, was also processed in the same manner. The propellant formulations were subjected to various performance tests.

Table 1. Approximate propellant compositions

Ingredient	Weight (%)			
	Example 1	Example 2	Example 3	Example 4
HTPB	14.80	14.80	14.80	14.80
DOA	4.0	4.0	4.0	4.0
TDI	1.0	1.0	1.0	1.0
Pyrogallol	0.08	0.08	0.08	0.08
Adduct	0.12	0.12	0.12	0.12
AP	65	65	65	65
Al	15	15	15	15
Burning rate suppressant	Weight (% over the batch)			
	Example 1	Example 2	Example 3	Example 4
Biuret	0	2.0	4.0	6.0

The strand burning rates of the propellants were determined in the pressure range 5-9 MPa by employing an Acoustic Emission Technique [8, 9]. The methodology involved combustion of the strand (ignited by means of a Nichrome wire) of dimensions 100×6×6 mm in the nitrogen pressurized steel bomb. The acoustic signal generated and the perturbations caused by the propellant deflagration were transmitted through the water medium to a piezoelectric transducer (200 kHz) connected to an oscilloscope. The burning rates were computed from the time that was recorded for the trial conducted at each pressure for each sample. The standard deviation was of the order of 0.2%.

The densities of the biuret containing propellants were determined by a Metler density kit (density 1.432 g/cc, heat of formation -565.8 kJ/mol). Toluene was used as a liquid.

Density = (weight of the sample/weight of the sample in solvent)×specific gravity of the solvent (toluene).

The sensitivity to impact stimuli of the propellant compositions was determined with a fall hammer apparatus (2 kg drop weight) using the Bruceton Staircase method [10] and the results were given in terms of the statically obtained 50% probability of explosion (H_{50}). The friction sensitivity was measured on a Julius Peter apparatus by incrementally increasing the load from 0.2 to 36 kg, until there was ignition/explosion in five consecutive test samples.

The ignition temperatures were measured by a Julius Peters apparatus. The sample was heated uniformly at a constant rate (5 °C/min) in a Woods metal bath, until it exploded or ignited at the ignition temperature.

Thermal analysis of the propellants was carried out on a STA (Q-600,USA), Perkin Elmer Pyris Diamond DSC apparatus at a heating rate of 20 °C/min under a N_2 atmosphere (sample mass ~10 mg). Gaseous decomposition products were analyzed by a Bruker Equinox 55 hyphenated with TG**.**

The mechanical properties were obtained with an Instron device (Model TIC-1185, UK). The operating instrumental parameters were always maintained constant; gauge length 25 mm, cross head speed 50 mm/min. The stress and strain properties were determined using a dumbbell-shaped specimen as per specification ASTM-D-638.

3 Results and Discussion

Five different series of propellant compositions based on AP/HTPB/Al, with four different burning rate suppressants (melamine, oxamide, urea, picrate *etc*.), have already been published [11, 12]. The theoretical performance of the formulations containing biuret were computed using NASA CEC-71. Biuret was added at different concentration levels (2, 4, 6% over the batch) in three formulations and their theoretical performances were evaluated (see Table 2).

Table 2. Theoretical performance parameters of various propellants with different concentrations of biuret

No.	Theoretical data	Example 1 Base (a)	Example 2 (b)	Example 3 (c)	Example 4 (d)
1	Characteristic velocity (C*, m/s)	1502	1488	1480	1469
2	Flame temperature (T_f, K)	2633	2531	2466	2402
3	Specific impulse, (Isp, s)	245.7	242.2	239.4	236.6

(a) Base composition: AP (65%), Al (15%), binder (20%), burning rate suppressant (biuret)
(a), (b), (c), (d): 0, 2, 4, 6% over the batch, respectively.

From Table 2, it was observed that the flame temperature (T_f), C*, and specific impulse (Isp) decreased with increasing biuret concentration. The strand burning rate experiments were conducted in the pressure range of 5-9 MPa, and the base composition exhibited a burning rate of 4.4-5.6 mm/s (see Table 3). The addition of biuret leads to a 55-60% reduction in the burning rate of the propellant composition.

Table 3. Ballistic properties of various propellants with different concentrations of biuret

No.	Ballistic properties		Example 1 Base (a)	Example 2 (b)	Example 3 (c)	Example 4 (d)
1	Burning rate at in (mm/s)	5 MPa	4.39	2.85	2.65	2.58
		7 MPa	4.76	3.15	2.95	2.8
		9 MPa	5.61	3.6	3.4	3.25
2	‘n’ value (at 5-9 MPa)		0.41	0.39	0.42	0.38
3	Density (g/cm^3)		1.701	1.696	1.690	1.684

[Note: biuret density 1.432 g/cm^3]

The burning rate trend for various burning rate suppressants (10%) with different compositions* was as follows:

Burning rate suppressant:	Biuret	Melamine	Oxamide	Urea	Nitroguanidine	Base
Burning rate (mm/s at 7 MPa):	2.3	2.7	2.8	2.9	4.4	5.4
‘n’ value:	0.42	0.39	0.55	0.92	0.48	0.52

*composition: binder 20%, AP 60%, burning rate suppressant 10%, Al 10%

The burning rate and pressure exponent of biuret containing compositions were relatively low compared to the base composition and other burning rate suppressants [11]. As the concentration of the biuret was increased from 2 to 6% over the batch, the burning rate of the propellant decreased gradually from 2.85 to 2.58 mm/s at 5 MPa. There was approximately no effect of concentration on the pressure exponent of the propellant compositions (Table 3).

Biuret decomposes at a relatively low temperature and forms a large amount of gaseous products (containing nitrogenous compounds), which exert lower feed back to the deflagrating propellant surface, and hence decreases the burning rate. Additionally, the negative oxygen balance of these compounds is responsible for partially oxidized binder. Hence less energy is released in the combustion process (at the surface), which aids the lowering of the burning rate.

All of the propellant formulations containing biuret were insensitive to impact and friction compared to the base composition (see Table 4). The insensitiveness may be attributed to the negative oxygen balance of the burning rate suppressant (biuret) in contrast to AP.

Table 4. Sensitivity of various propellants with different concentrations of biuret

No.	Sensitivity parameter	Example 1 Base (a)	Example 2 (b)	Example 3 (c)	Example 4 (d)
1	Friction sensitivity(N)	160	192	240	288
2	Impact sensitivity (h_{50}) (J) F of I (J)	6.3 8.2	6.7 8.6	7.1 9.2	7.5 9.8
3	Ignition temperature (°C)	294	298	300	303

(a) Base composition: AP (65%), Al(15%), binder(20%), burning rate suppressant (biuret) (a), (b), (c), (d): 0, 2, 4, 6% over the batch, respectively.

Table 5 shows the DSC results of four compositions containing 0, 2, 4, 6% of biuret over the batch. As the concentration of biuret was increased, ΔH and the peak temperature decreased consistently. The gaseous products generated during the combustion of biuret probably absorb a large amount of heat causing a cooling effect in the matrix, and hence ΔH and the peak temperature are decreased.

Table 5. Thermal properties of various propellants with different concentrations of biuret

No.	Thermal properties at 20 °C/min	Example 1 Base (a)	Example 2 (b)	Example 3 (c)	Example 4 (d)
1	Peak temperature (°C)	399.6	373.5	365.7	356.6
2	ΔH (J/g)	-2666.6	-2521.6	-2117	-1780.6

(a) Base composition: AP (65%), Al (15%), binder (20%), burning rate suppressant (biuret) (a), (b), (c), (d): 0, 2, 4, 6% over the batch, respectively.

The Simultaneous Thermal Analysis (STA) results (Table 6) for the biuret incorporated propellant gave an exotherm with 7-8% reduction in T_{final} and T_{max} as compared to the base composition. In dynamic TGA, the biuret-based propellant composition exhibited 91.42% weight loss in the temperature range 280.1-361.4 °C, but the base composition gave 82.1% weight loss in the temperature range 281.6-391.5 °C. The weight loss appears to correspond to the decomposition of the matrix. Figures 2 and 3 represent comparative DTA and TGA traces of the propellant compositions with and without biuret.

Table 6. DTA and TGA thermal analysis results of various burning rate suppressants

No.	Composition	DTA		TGA	
		initial temp. ($T_{initial}$,°C)	max. temp. (T_{max},°C)	temperature (°C)	weight loss (%)
1	Base composition (a)	249.1	383.9	281.6-391.5	82.1
2	Base composition + 4% of biuret over the batch	247.8	354.9	280.1-361.4	91.4

(a) Base composition: AP (65%), Al (15%), binder (20%), burning rate suppressant (biuret) (0% over the batch).

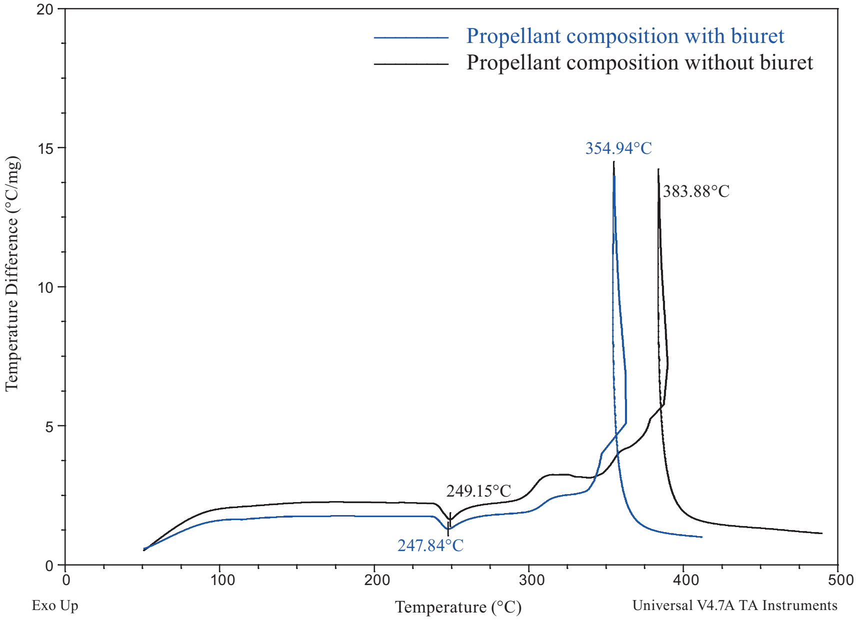


Figure 2. DTA trace of the propellant composition without biuret (B1) and with biuret (BIU).

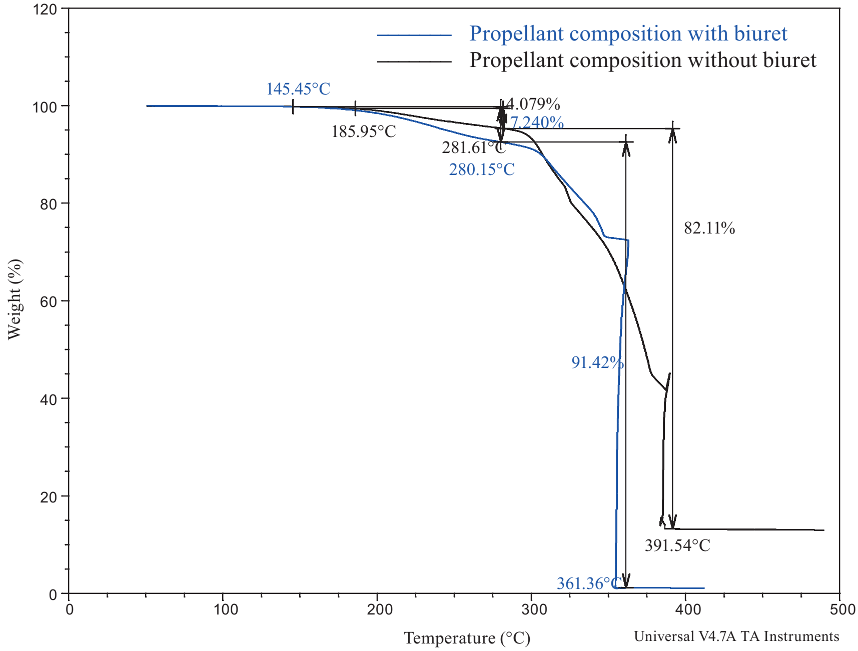


Figure 3. TGA result of the propellant compositions without biuret (B1) and with biuret (BIU).

The mechanical properties (see Table 7) were obtained with an Instron device (Model TIC- 1185, UK). The operating instrumental parameters were always maintained constant, with gauge length 25 mm, and cross head speed 50 mm/min. The stress and strain properties were determined using a dumbbell-shaped specimen, as per specification ASTM D 638 (Table 6).

Table 7. Mechanical properties of various propellant samples with different concentrations of biuret

No.	Mechanical properties	Example 1 Base (a)	Example 2 (b)	Example 3 (c)	Example 4 (d)
1	Tensile strength (kg/cm^2)	4.26	4.1	4.0	3.4
2	Percentage elongation (%)	26.8	20.7	18.4	17.4
3	Young's modulus (kg/cm^2)	34.7	39.2	44	50.1

(a) Base composition: AP (65%), Al (15%), binder (20%), burning rate suppressant (biuret)
(a), (b), (c), (d): 0, 2, 4, 6% over the batch, respectively.

4 Conclusions

This is the first report of using biuret as a burning rate suppressant in a composite propellant. Biuret lowered the burning rate and the ‘n’ value compared with propellants containing other burning rate suppressants. The concentration optimization has also been carried out. From these results, Example 3, *i.e.* the propellant formulation containing 4% biuret over the batch, gave an optimized product with respect to energy and burning rate. These compositions were more insensitive to friction and impact than the base composition. The DSC pattern suggested that the site of action of the suppressant is in the gas phase. Biuret based propellant gave a reduction in T_{final} and T_{max} values compared to the base composition. As the concentration of biuret was increased, the burning rate, friction and impact sensitivities decreased. A marginal change was observed in the mechanical properties. The decomposition at lower temperature indicates that the gaseous products formed during decomposition exert a lower feed back to the deflagrating propellant surface due to the low burning rate and negative oxygen balance of these compounds and are therefore responsible for partially oxidized binder. Hence less energy is released in the combustion process (at the surface), which supports the lowering of the burning rate. The formulation containing 4% biuret over the batch was found to be optimum with respect to energy, burning rate, pressure index and insensitivity.

Acknowledgements
The authors are thankful to Shri B. Bhattacharya, Director of H.E.M.R.L., for valuable suggestions, constant encouragement and permission to publish this work.

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