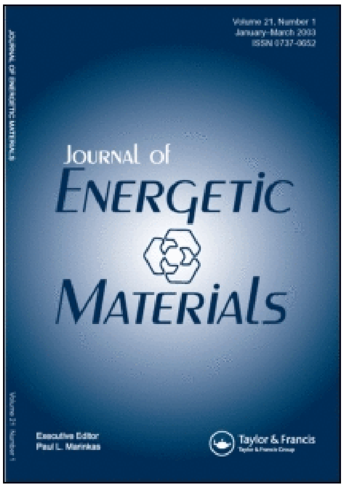

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"CLEAN BURNING" LOW FLAME TEMPERATURE SOLID GUN PROPELLANTS

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ABSTRACT

In an attempt to eliminate nitrogen oxides (NOx's) from the combustion and pyrolysis products of solid propellants, an investigation into the use of "De-NOx" agents was performed. The agents selected were all compounds which thermally decompose to generate amines; participation of amines in the thermal De-NOx process results in the reduction of nitrogen oxides to nitrogen. Of all the compounds screened, it was found that urea was the best suited for use as a De-NOx agent in solid gun propellants. Use of urea resulted in a significant decrease in NOx production. Furthermore, urea is thermally stable up to a temperature of 130° C, and is compatible with nitrocellulose-based formulations. Compared to neat JA2 (a double-base propellant), a JA2/urea formulation containing 10 wt-% urea generates 60% less NOx. Calculations indicate that the incorporation of 4% urea results in a 200° K decrease in flame temperature and a decrease in impetus and velocity of approximately 4% and 2%, respectively.

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INTRODUCTION

Incomplete combustion of solid gun propellants is a common occurance during the firing of both experimental and fielded gun systems. Included among the products of this phenomenon are nitrogen oxides and carbon monoxide. Carbon monoxide, CO, poses the most serious health hazard (1), and is found at such dangerously high levels that health agencies may impose restrictions on the number of test firings that be performed per day . Unfortunately, elimination of CO from gun propellant combustion products it not feasible from a ballistic standpoint. However, the corrosive nature of nitrogen oxides (NOx's) also make them a matter of concern for both users and environmental/health-related agencies. A. Snelson *et al.* (2) measured breech NOx concentrations that were 10^5 times greater than predicted by thermochemical calculations, indicating that the actual problem may be more serious than many users suspect. While it may be argued that bore evacuators protect tank crews against toxic combustion products, this is true only when the evacuators are functioning properly and when intact. It has been reported that a hole as small as 2 cm is sufficient to allow dangerously high levels of toxic gases into the crew compartment. It has been suggested that even intact evacuator systems do not keep tank compartments free of propellant combustion gases. Exposure of test crews to combustion gases is becoming increasingly more common as test site personnel resort to enclosed (muffled) bays to reduce noise levels near urban populations. At such sites, large fans must ventilate the test bay for several minutes to remove toxic vapors before testing can resume.

Solid residues resulting from incomplete combustion also pose significant safety and environmental concerns. For example, smoldering residues remaining after firing often result in significant quantities of smoke. This low pressure pyrolysis generates much larger quantities of NOx and other non-equilibrium gases than does high pressure combustion. Re-ignition of propellant residue in fielded tanks has been reported. Propellant residue in breeches is also said to be responsible for the creation of sealing problems.

As disscussed above, incomplete combustion of solid propellants can pose a significant hazard to the health and safety of military and civilian personnel. The work presented here, as well as that currently in progress, is intended to address and reduce this hazard by identifying solid propellant formulations which will burn more cleanly and more completely.

BACKGROUND

It has been known for some time that M30 gun propellant (composed of nitrocellulose, nitroguanidine and nitroglycerine) differs from other NC-based propellant in that its flame exhibits no "dark zone", i.e. no non-luminous zone (3-7). Dark zone chemistry is dominated by the chemistry of NO - more specifically, by the slow conversion of NO to N_2 (8). Much attention has been given to this chemistry because of its potential importance to delayed ignition (5,6). It was proposed by Anderson (9) that the absence of the dark zone in M30 might suggest that nitroguanidine was behaving as a "De-NOx agent", i.e. and species capable of reducing NOx to N_2. A proposed mechanism for the removal of NOx's by amines is described in Figure 1 (10).

De-NOx agents have been shown to be effective in eliminating NOx production in internal combustion engines and other devices. In these applications, the agents are ammonia- or amine-producing species which reduce NO to N_2. In nitrate ester- or nitramine-based solid gun and rocket propellants, NO is produced from the -NO_2 groups in the energetic oxidizer (e.g., RDX), polymer (e.g., nitrocellulose NC), or plasticizer (e.g., nitroglycerine, NG). The concept for the current work is based on the use of De-NOX agents in solid propellants to reduce NO to N_2 at or near the burning propellant surface; the increased near-surface energy release should also lead to more complete combustion (i.e. more equilibrium products and less solid residue) and reduction of other products of a toxic or carcinogenic nature. In addition to reducing NOx levels in the combustion products of solid gun propellants, burn rate modification by De-NOx agents is also possible. Previous attempts to "catalyze" the burning of solid propellants have made use of oxidizing agents (e.g PbO), rather than reducing agents (e.g NH_3). [Note: an exception to this has been found, Fifer and McBratney (11), and Fifer and Cole (12)] If De-NOx agents can effectively eliminate NOx from the combustion products of solid propellants, they may also serve as effective burning rate "catalysts", thereby simultaneously preventing pollution (by both NOx and heavy metals) and enhancing performance.

Based on this background information, an investigation into the effects of ammonia- and amine-generating compounds on solid propellant combustion and pyrolysis products was undertaken. In an examinination of the pyrolysis products of M30 (a triple-base propellant) and two “nitroguanidine-free” nitrocellulose-based propellants (M9 and M10, double- and single-base propellants, respectively), it was observed that M30 actually generates more NO than do the propellants without nitroguanidine. These results suggest that while nitroguanidine might participate in the elimination of NO under high pressure combustion conditions, it does not do so at atmospheric pressure. Results to be presented below indicate that while nitroguanidine does generate NH_3, it also generates significant quantities of NO and is therefore an unsuitable de-NOx agent.

The specific focus of the present work is on the use of urea as a De-NOx agent.

EXPERIMENTAL

Samples: Experimental quantities of a double-base, JA2-like solid propellant were fabricated by handmixing acetone solutions of JA2 with ground urea. Pyrolysis samples were prepared by casting films of the handmixed propellants on aluminum foil. Candidate De-NOx agents included triaminoguanidine nitrate (TAGN), nitroguanidine (NQ), triamino-trinitro-benzene (TATB), ammonium carbonate, and urea. Structures of these compounds are given in Figure 2.

Chromatographic Instrumentation: Analyses of pyrolysis products were conducted using a Hewlett Packard 5965 Gas Chromatograph ("GC") interfaced to a Hewlett Packard Model 5965A infrared detector, "IRD", and 5970 Mass Spectrometric Detector, "MSD" (only MS results are reported here). Chromatographic conditions: Quadrex capillary column 0.32 mm x 25 m x 3 μm OV-17 film; oven program: 50°C for 3 min, then 50°C to 200°C at 10 deg/min;

injector and interface chamber held at 200° C.

Pyrolysis experiments: Samples were placed in quartz tubes and held in place with plugs of glass wool. Tubes were inserted into a coil-type Pyroprobe (Chemical Data Systems, CDS, Model 122) which was connected via a heated CDS interface chamber to the splitless injector of the GC. The heated GC interface was continuously swept with helium carrier gas. Approximately 0.6 mg of sample was pyrolyzed for each analysis. All samples were pulse- pyrolyzed at 1000° C.

Thermal Analysis: Differential scanning calorimetry (DSC) was performed using a Mettler DSC 30 calorimeter interfaced to a Mettler TC10A processor. The heating rate was 10° C/min. Samples were placed in crimped aluminum pans with three pin holes punched through the cover. Analyses were run under a nitrogen atmosphere (20 mL/min).

Calculations: Blake (13) calculations were performed using a value of -80.227 kcal/g-mol for the heat of formation of urea, and "standard" library values for JA2 propellant.

RESULTS AND DISCUSSION

Screening runs of potential de-NOx agents were performed by pyrolyzing the materials at 1000° C. The primary basis for acceptance during screening runs was that the materials thermally decompose to generate ammonia or amines. Results of screening tests, as well as the melting (or decomposition) temperatures for the candidate De-NOx agents, are given in Table 1. Based on the information in Table 1, it was concluded that the energetic materials (TAGN, NQ, and TATB) were unsuitable as De-NOx agents because they generate significant quantities of NO. Ammonium carbonate was eliminated from further consideration because of its low decomposition temperature.

Figure 3 shows the experimental results for pyrolysis of JA2-like propellants containing urea. Levels of NO generated from pyrolysis of two different hand-mixes of JA2/urea propellants are shown, as well as results from Blake calculations for propellant with the same composition. The computations and experimental data show a trend of decreasing NO with increasing urea, although the actual experimental NO concentrations are much higher than the equilibrium predictions.

Figures 4 and 5 show impetus and flame temperatures, respectively, calculated using the Blake code. As expected, the impetus is observed to decrease as the percentage of urea in the formulation increases. The net change in impetus for a JA2-like propellant containing 4 wt-% urea is approximately 4% relative to neat JA2. The flame temperature of the JA2/urea propellant containing 4 wt-% urea is approximately 200°K lower than that of neat JA2. The decrease in projectile velocity for the same JA2/urea propellant is expected to be approximately 2% (considering that muzzle velocity can be approximated by the square root of the impetus).

The DSC thermograms presented in Figure 6 indicate that the JA2/urea formulation (7 wt-% urea) decomposes at approximately the same temperature as does neat JA2. This result indicates that JA2 and urea are chemically compatible. This is to say that urea will not act as a catalyst in the thermal decomposition of JA2 at these heating rates. Physical compatibility has yet to be determined.

CONCLUSION

Based on the results presented here, it is concluded that urea is an attractive De-NOx agent: it effectively reduces the level of NO generated by pyrolysis of JA2-like propellants, yet has little effect on performance when used at low levels of incorporation. Added benefits of the use of urea as a De-NOx agent include a) that urea has been reported to be a successful flash supressant (14), and b) that it results in flame temperature decreases that are expected to significantly extend the life of gun barrels. Results reported for the use of polyurethane additives in double-base propellants (15) suggest a similar flame temperature suppression and concomitant wear reduction.

Combined with the reduction in the production of corrosive NOx's, the reduction of flame temperature achieved by the use of urea in solid gun propellants should extend the life of gun barrels while at the same time improving air quality at R&D test centers, as well as in training and battlefield situations.

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TABLE I. Relative pyrolysis yields and melting/decomposition temperatures for several candidateDe-NOx agents.

Compound	Relative Pyrolysis Yield		Tm (°C)	Comments
	NH3*	NO*		
Ammonium Carbonate	329	0	58 (d)	good De-NOx agent, but hygroscopic
Urea	101**	0	133	good thermal stability, compatible with NC
TAGN	281	111	216 (d)	generates NO on pyrolysis
NQ	66	194	225-250 (d)	generates NO on pyrolysis
TATB	33	174	325 (d)	generates NO on pyrolysis

(d) Decomposes

* Pyrolysis at 1000° C. Peak area determined by pyrolysis/GC-MS; sample mass = 0.3 mg

** Urea also generated "large" pyrolysis products (e.g. vapor phase urea). It is expected that under combustion conditions, more NH_3 will be generated.

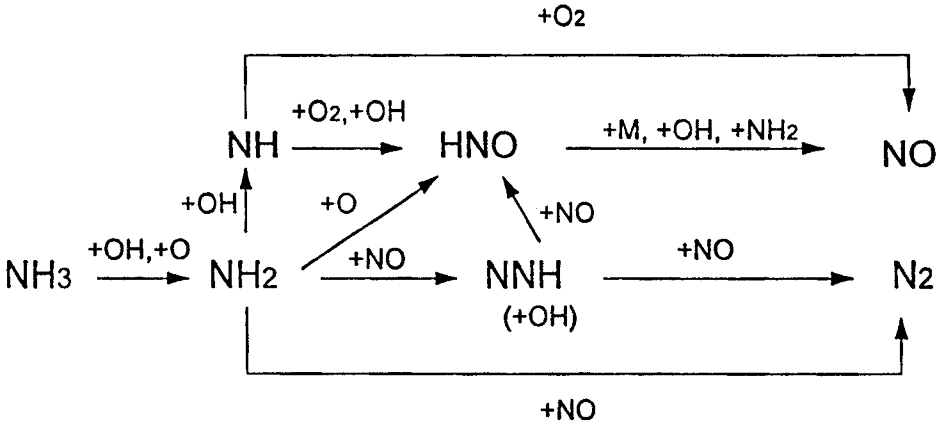
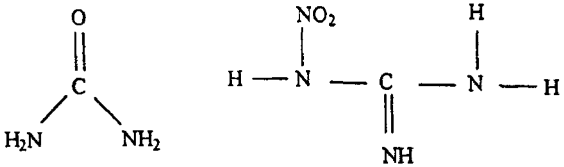


Figure 1: The thermal De-NOx process (10)

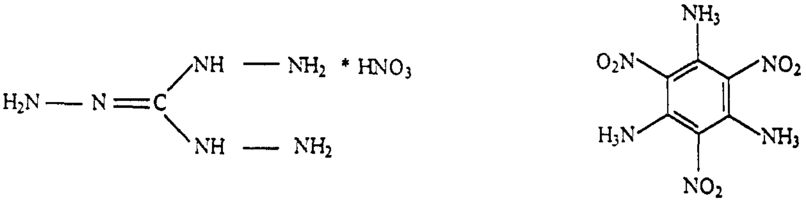
$(NH_4)_2CO_3$



Ammonium Carbonate

Urea

Nitroguanidine (NQ)



Triaminoguanidine Nitrate (TAGN)

Triamino-trinitro-benzene (TATB)

Figure 2: Structure of candidate De-NOx agents

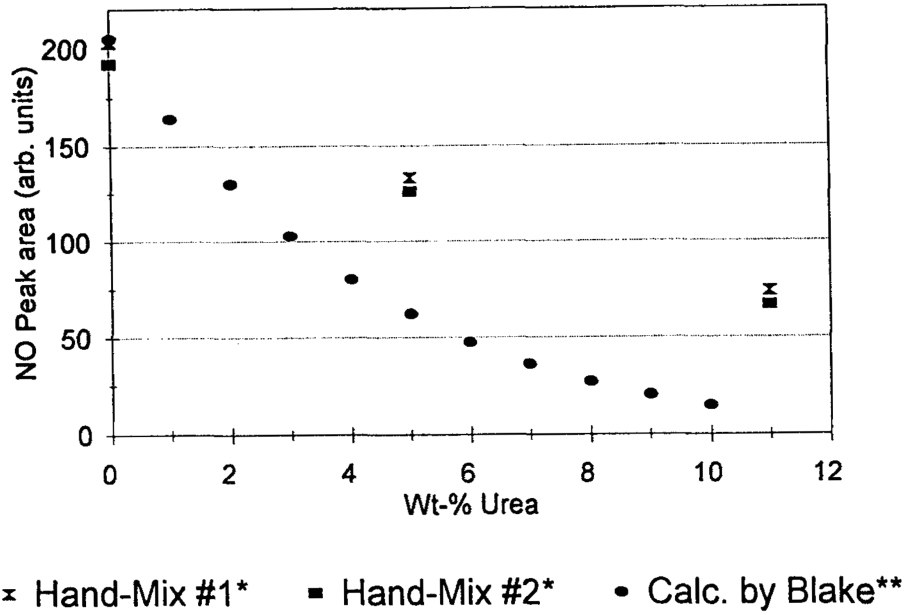


Figure 3: NO produced by JA2/Urea propellant; *) pyrolysis products, by GC-MS, scaled; **) equilibrium combustion products, scaled, 0.2 g/cc nominal gas phase density.

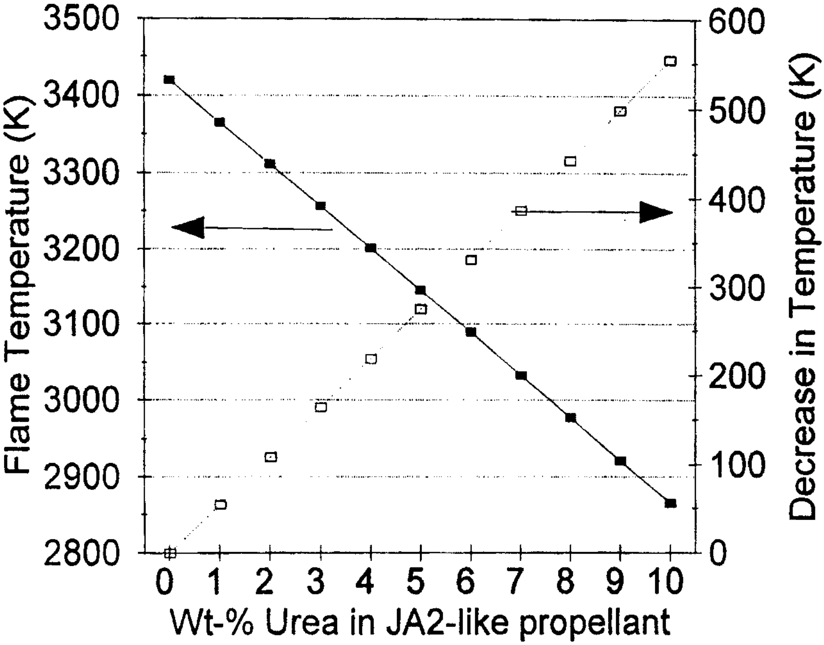


Figure 4: Calculated flame temperature for JA2/Urea propellant; from Blake calculations at 0.2 g/cc nominal gas phase density.

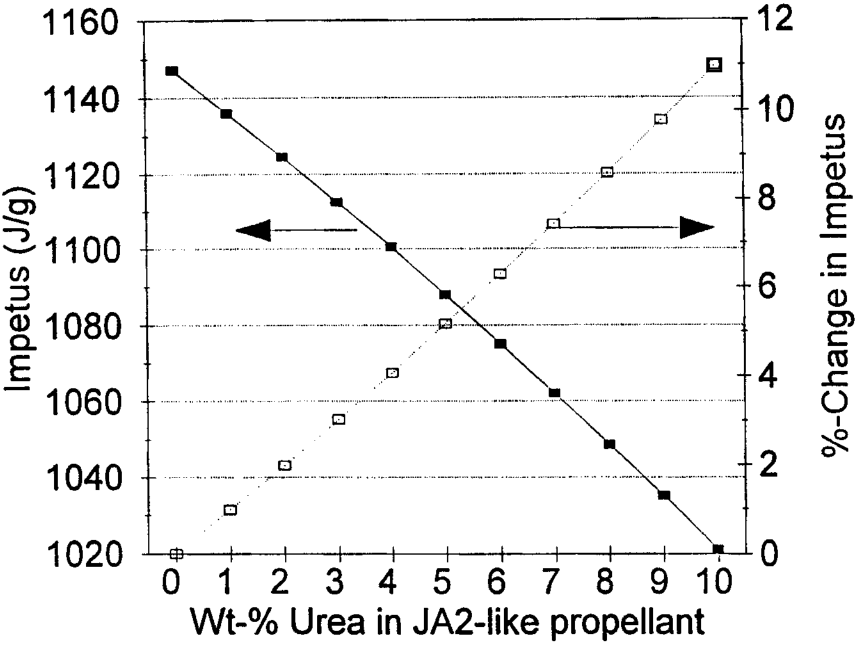


Figure 5: Calculated impetus for JA2/Urea propellant; from Blake calculations at 0.2 g/cc gas phase density.

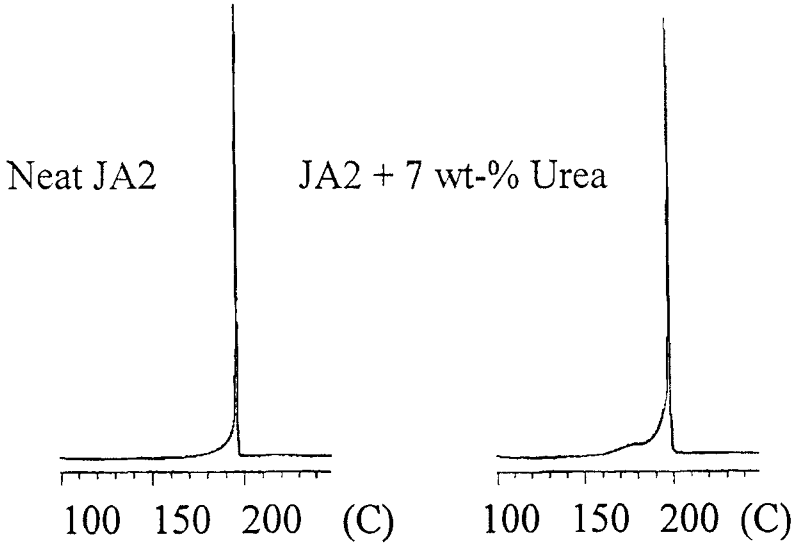


Figure 6: DSC thermograms for JA2 and JA2/Urea propellant. Little/no change in exotherm temperature observed, indicative of good compatibility.