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TITLE STUDY OF NEW MATERIALS FOR GUN PROPELLANT FORMULATIONS

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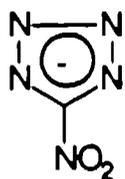
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STUDY OF NEW MATERIALS FOR GUN PROPELLANT FORMULATIONS

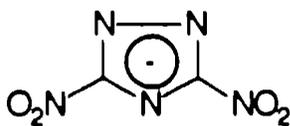
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As part of a joint effort of the U.S. Department of the Army and the U.S. Department of Energy, we are searching for new energetic materials to improve gun-propellant formulations. Theoretical calculations indicate that certain types of high nitrogen compounds produce lower average-molecular-weight gases than those with more carbon, and low average-molecular-weight by-products contribute to higher impetus. Therefore, our target compounds were chosen to contain only the elements C, H, N, and O, with a high percentage of nitrogen, be thermally stable and moderately insensitive to impact. Gun propellants containing RDX and the binder cellulose acetate butyrate (CAB) have proved to be less sensitive than nitrocellulose/nitroglycerine (NC/NG) based propellants to hot fragments.^{1,2} However, further reduction in reaction to shock, particularly a milder reaction to shaped-charge jets, is desirable. Replacing part of the RDX with an energetic material with a lower sensitivity may reduce the reaction of the propellant to this stimulus.

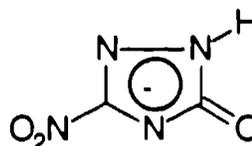
For many years, the synthesis effort of the Explosives Technology Group (M-1) at Los Alamos has centered around the preparation of new, energetic nitroheterocycles. We have found that many amine salts of nitroheterocycles are thermally stable and moderately insensitive to impact.³ To synthesize new materials with the desired properties for gun propellant formulations, several synthesis methods were studied and a variety of amine salts of 5-nitrotetrazole (NT), 3,5-dinitro-1,2,4-triazole (DNTr), and 3-nitro-1,2,4-triazol-5-one (NTO) were prepared. The structures of the anions are shown below.



NT



DNTr



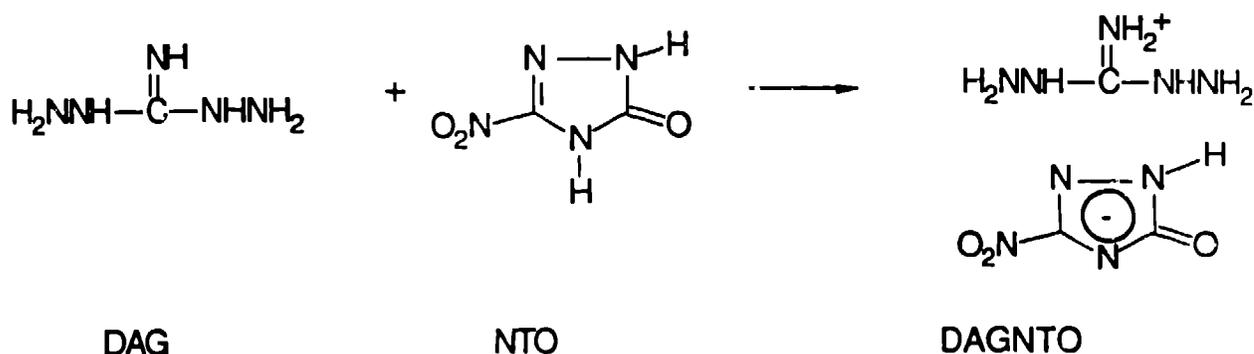
NTO

NTO is an explosive currently under development at Los Alamos as well as the Naval Surface Warfare Center and the Naval Weapons Center. It is soluble in water, has ERL Type 12 drop-weight-impact sensitivity > 260 cm, is acidic (pKa = 3.67), and forms stable salts with basic compounds.⁴ DNTr has a pKa of -0.6, and its ammonium salt (ADNTr) was studied as an eutectic with ammonium nitrate (AN).⁵ NT, also a strong acid, was studied as both the ammonium and ethylenediammonium salts in an eutectic with AN.⁶

Basically, all the salts were prepared by mixing an aqueous solution of the anion with an equivalent molar amount of the corresponding base or cation. The crude products were obtained by either evaporation of the water in a hood or in a rotary evaporator. Pure

salt compounds were obtained by recrystallization of the crude material from water or water/ethanol solution.

An example of the type of chemical reaction employed in this program is that used to prepare the diaminoguanidinium salt of NTO (DAGNTO) as shown below.



Certain chemical and physical properties of the prepared salts were determined. Also, thermal, impact, and spark sensitivities were measured. The thermal stability tests were differential thermal analysis (DTA), Henkin critical temperature, vacuum stability and pyrolysis. The results of some of these tests on the new compounds are shown in Table I. Data from RDX is also listed for comparison. It can be seen that they are all less sensitive to impact than RDX and the thermal stability of the salts are comparable to RDX. It is conceivable that catastrophic events from hot spall or metal jets into the propellant bed might be avoided by using a formulation containing one of these less sensitive propellants.

TABLE I. EXPLOSIVE PROPERTIES OF SALTS

<u>Compound</u>	<u>%N</u>	<u>DTA Exotherm (°C)</u>	<u>Impact Sensitivity (cm)</u>	<u>Spark Sensitivity (3-mil.)</u>
ENTO	44	250	No go	2.7
ANTO	48	190	No go	>1.0
HNT0	52	170	92	>1.0
GuNTO	52	260	No go	>1.0
AGNTO	55	200	No go	>1.0
DAGNTO	58	190	252	>1.0
TAGNTO	60	170	103	>1.0
ENT	58	216	42	1.7
GuNT	64	212	36	1.14
TAGNT	70	156	<15	>0.75
ADNT _r	48	200	58	0.86
DAGDNT _r	56	240	34	>1.0
TAGDNT _r	59	236	31	>1.0
DAGN	55	240	35	>1.0
TAGN	59	235	23	>1.0
RDX	38	205	22	0.2

To estimate the performance of these new compounds as gun propellants, we calculated the impetus and flame temperatures of these salts using the Blake thermodynamic code furnished by the Ballistic Research Laboratory of the US Army (BRL). The heats of formation (ΔH_f) of a new compound can be estimated from the ΔH_f of similar known compounds. But for best results, the ΔH_f of a compound is determined from the measured heat of combustion. The ΔH_f of all the salts were calculated from the heats of combustion measured by burning the compounds in a Parr combustion bomb under 30 atm oxygen pressure. High-nitrogen compounds often leave residues after burning because their burning temperatures are low. Whenever necessary, a standard (such as benzoic acid) was mixed with the sample to obtain a complete burn. The ΔH_f of the sample was then calculated after subtracting the heat of benzoic acid from the measured gross heat of combustion. To correct the heat of combustion from nitric acid formation, the bomb washings were titrated with standard sodium carbonate (0.0453 M) solution in all the runs. Table II includes the formula and the ΔH_f , which are the data input in the Blake calculations of the salts.

TABLE II. BLAKE CALCULATIONS OF SALTS

<u>Compound</u>	<u>Formula</u>	ΔH_f (a) (kcal/mole)	Impetus (J/g)	Flame Temp. (K)
ENTO	C ₆ H ₁₂ N ₁₀ O ₆	-112 ± 1	608	1638
ANTO	C ₂ H ₅ N ₅ O ₃	-66 ± 4	642	1706
HNTO	C ₂ H ₆ N ₆ O ₃	-38 ± 5	799	1988
GuNTO	C ₃ H ₇ N ₇ O ₃	-71 ± 3	531	1489
AGNTO	C ₃ H ₈ N ₈ O ₃	-43 ± 2	630	1644
DAGNTO	C ₃ H ₉ N ₉ O ₃	-21 ± 2	708	1768
TAGNTO	C ₃ H ₁₀ N ₁₀ O ₃	+14 ± 4	836	1980
ENT	C ₄ H ₁₀ N ₁₂ O ₄	+56 ± 3	960	2332
GuNT	C ₂ H ₆ N ₈ O ₂	+17 ± 2	802	2000
TAGNT	C ₂ H ₉ N ₁₁ O ₂	+94(calc)	1113	2531
ADNTr	C ₂ H ₄ N ₆ O ₄	0.6 ± 2.0	1205	3628
DAGDNTr	C ₃ H ₈ N ₁₀ O ₄	+35 ± 5	1069	2675
TAGDNTr	C ₃ H ₉ N ₁₁ O ₄	+59.8 ± 0.2	1142	2797
DAGN	CH ₈ N ₆ O ₃	-47	980	2253
TAGN	CH ₉ N ₇ O ₃	-11.5(b)	1160	2602
RDX	C ₃ H ₆ N ₆ O ₆	+14.7(b)	1386	4060

(a) Solid compounds at 298 K

(b) Literature value

If the compounds prepared were thermally stable and moderately insensitive to impact, their syntheses were scaled up to a quantity large enough for formulation with RDX and a binder, such as CAB/ATEC/NC/EC (see glossary).

After testing for compatibility of the ingredients in the new formulation, single-perforated propellant grains were prepared and burned in a closed pressure vessel to study the effect of the new component on the burning rate. The burning rate of the new formulation was then compared to that of a similar formulation without the new compound. Thus far, the three compounds used in the new formulations are ENT, ENTO, and ADNT.

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GLOSSARY

ADNTr - ammonium salt of 3,5-dinitro-1,2,4-triazole
AGNTO - aminoguanidinium salt of 3-nitro-1,2,4-triazol-5-one
ANT - ammonium salt of 5-nitrotetrazole
ANTO - ammonium salt of 3-nitro-1,2,4-triazol-5-one
ATEC - acetyl triethylcitrate
CAB - cellulose acetate butyrate
DAGN - diaminoguanidinium nitrate
DAGNTO - diaminoguanidinium salt of 3-nitro-1,2,4-triazol-5-one
DAGDNTr - diaminoguanidinium salt of 3,5-dinitro-1,2,4-triazole
EC - ethyl centralite
ENT - ethylenediammonium salt of 5-nitrotetrazole
ENTO - ethylenediammonium salt of 3-nitro-1,2,4-triazol-5-one
GuNT - guanidinium salt of 5-nitrotetrazole
GuNTO - guanidinium salt of 3-nitro-1,2,4-triazol-5-one
HNTO - hydrazinium salt of 3-nitro-1,2,4-triazol-5-one
NC - 12.6%N nitrocellulose
NTO - 3-nitro-1,2,4-triazol-5-one
RDX - hexahydro-1,3,5-trinitro-1,3,5-triazine
TAGDNTr - triaminoguanidinium salt of 3,5-dinitro-1,2,4-triazole
TAGN - triaminoguanidinium nitrate
TAGNT - triaminoguanidinium salt of 5-nitrotetrazole
TAGNTO - triaminoguanidinium salt of 3-nitro-1,2,4-triazol-5-one