Energetiska material med tillämpningar

Konferensbidrag jan - juni 2010

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Sammanfattning

Projekten Energetiska material med tillämpningar och Energetiska material - tekniköverföring bedriver verksamhet som är inriktad mot energetiska material med *låg känslighet* (IM) och energetiska material med *hög prestanda* (t.ex. burna vapen och undervattensstridsdelar). Verksamheten rör utveckling och framtagning av förbättrade energetiska material samt bedömning/experimentell utvärdering av hur dessa kan utnyttjas för verkans-, utskjutnings- och framdrivningsändamål.

Denna lägesrapport innehåller fem konferensbidrag som presenterats under första halvåret 2010. Två av dem presenterades vid 14th International Detonation Symposium i Idahoe, USA. Ett av dem har presenterats vid 2010 Space Propulsion Conference i San Sebastian, Spanien. Ett av dem fanns med vid 13th International Seminar on New Trends in Research of Energetic Materials, Pardubice, Tjeckien och det femte ska presenteras vid 41th International Annual Conference of ICT, Karlsruhe, Tyskland. De handlar om lågkänsliga explosivämnen och sprängämnen, om rökfria högpresterande raketkrut samt om nya rökfria oxidatorer med hög prestanda.

Nyckelord: lågkänslighet, hög prestanda, explosivämnen, sprängämnen, raketkrut, oxidatorer

Summary

The projects ”Energetiska material med tillämpningar” (Energetic materials and its applications) and “Energetiska material - tekniköverföring” (Energetic materials - transfer of technology) develop and evaluate energetic materials with low sensitivity (IM) and energetic materials with high performance within the fields of warheads, propulsion and launch.

This progress report contains five conference papers presented during 2010. Two of them were presented at the 14th International Detonation Symposium in Idahoe, USA. One of them was presented at the 2010 Space Propulsion Conference in San Sebastian, Spain. One of them was present at the 13th International Seminar on New Trends in Research of Energetic Materials, Pardubice, Czech Republic and the fifth will be presented at the 41th International Annual Conference of ICT, Karlsruhe, Germany.

Keywords: insensitive munition, high performance, explosives, propellants, oxidizers

Innehållsförteckning

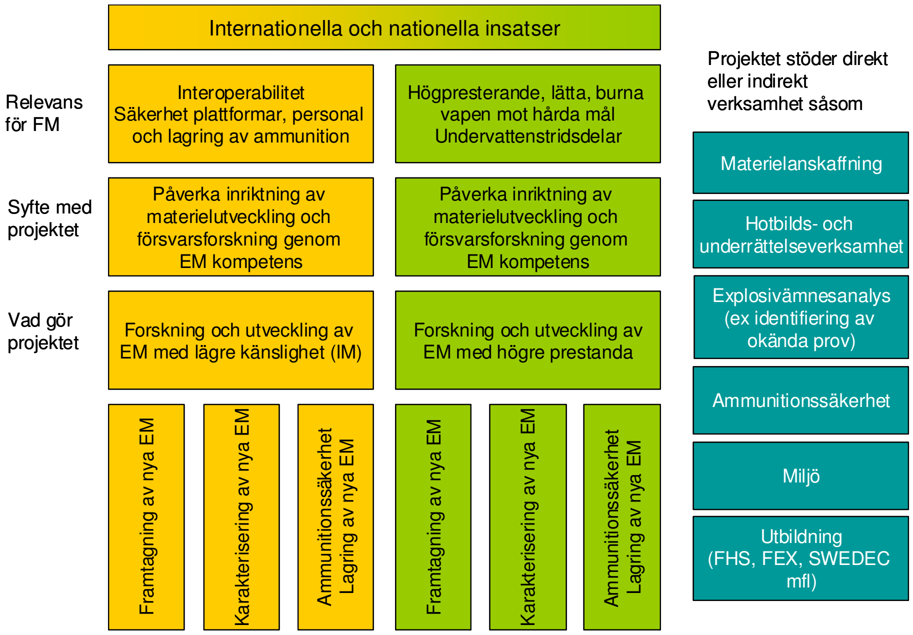
1 Inledning

Syftet med projekten ”Engergetiska material med tillämpningar” och ”Energetiska material - tekniköverföring” är att upprätthålla och utveckla kompetens för att kunna identifiera hot och möjligheter samt att vidareutveckla energetiska material mot högre TRL-nivåer. Projekten bidrar väsentligt till Sveriges internationellt framträdande roll inom explosivämnesområdet och gör att Sverige är med och påverkar internationell materielutveckling.

Projekten bedriver verksamhet som är inriktad mot energetiska material med *låg känslighet* (IM) och energetiska material med *hög prestanda* (ex. vis burna vapen och undervattensstridsdelar). Verksamheten rör utveckling och framtagning av förbättrade energetiska material samt bedömning och experimentell utvärdering av hur dessa kan utnyttjas för verkans-, utskjutnings- och framdrivningsändamål.

Direkt eller indirekt nytta för Försvarsmakten utgörs av stöd till underhåll, anskaffning och utveckling av materiel, samt teknisk underrättelseverksamhet. Exempel på detta stöd kan vara kunskap om och förmåga att utvärdera ammunitionsäkerhet, improviserade sprängladdningar (IED), ammunition som använts i ”out of area operations”, livslängd hos ammunition samt förutsättning för att ge utbildning.

IM, lätta/burna vapen och undervattensteknik är områden som Försvarsmakten visar speciellt intresse för just nu. Dessa områden är också högt prioriterade internationellt och därför är det möjligt att utväxla FM:s finansiering i hög grad. Projektet bedrivs därför till stor del i internationella samarbeten med EU/EDA, Frankrike, Tyskland och Singapore i syfte att utväxla de resurser som finns till förfogande inom området.



Figur 1. Översiktsbild - projektets verksamhetslinjer.

Denna lägesrapport innehåller fem konferensbidrag som presenterats under första halvåret 2010. Två av dem presenterades vid 14th International Detonation Symposium i Idahoe, USA. Ett av dem har presenterats vid 2010 Space Propulsion Conference i San Sebastian, Spanien. Ett av dem fanns med[1] vid 13th International Seminar on New Trends in Research of Energetic Materials, Pardubice, Tjeckien och det femte ska presenteras vid 41th International Annual Conference of ICT, Karlsruhe, Tyskland. De handlar om lågkänsliga explosivämnen och sprängämnen, om rökfria högpresterande raketkrut samt om nya rökfria oxidatorer med hög prestanda.

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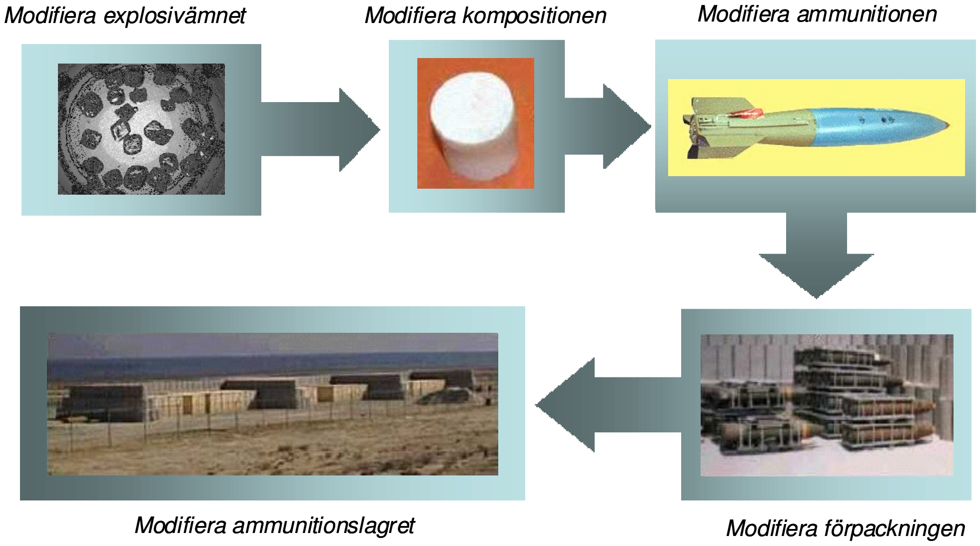
[1] Konferensbidraget var inskickat och fanns med vid NTREM i Pardubice, Tjeckien, men då alla flyg blev stoppade pga vulkanasksproblematiken så förhindrades FOIs medarbetare att presentera det.

2 Lågkänsliga energetiska material

Lågkänslig ammunition (Insensitive Munition - IM) blir allt viktigare för många nationer, inte minst för att man vill minska risken för och eventuella konsekvenser av om t.ex. ett ammunitionslager eller -transport utsätts för ett attentat eller en olycka. Andra mål för IM-utvecklingen är att begränsa den skada som kan drabba personal och plattformar och att undvika att en liten incident eskalerar till en katastrof. Det finns även ekonomiska fördelar att vinna genom användning av IM, bl.a. att transport- och lagringskapaciteten kan ökas, säkerhetsområden runt ammunitionslager kan minskas och bevakning av dessa lager kan minimeras.

IM är ofta förknippat med en högre tillverkningskostnad vilket inom artilleri länge setts som ett problem. Vid tillverkning av dyrare system, såsom robotsystem, utgör den extra kostnaden för IM dock en mindre del. Ser man till de totala ekonomiska aspekterna av tillverkning, logistik, säkerhet och användning är dock IM en god investering.

IM är ett helhetskoncept där IM-status uppnås för ett fullständigt ammunitionsobjekt inklusive sin förpackning. Denna helhetssyn gör det möjligt att uppnå IM-målen på flera olika sätt (Figur 2). Man kan använda mindre känsliga energetiska material, konstruera ammunitionen så att den ej detonerar vid höga påfrestningar och använda skyddande förpackningar. Det är oftast nödvändigt att använda en kombination av dessa metoder. Inom projektet ”Energetiska material med tillämpningar” arbetar vi framförallt med att modifiera det energetiska materialet (eller explosivämnet) och i viss mån med att modifiera kompositionen så att den blir lågkänslig (se även kapitel 2.2).



Figur 2. Olika sätt att uppnå IM.

2.1 Lågkänsliga explosivämnen

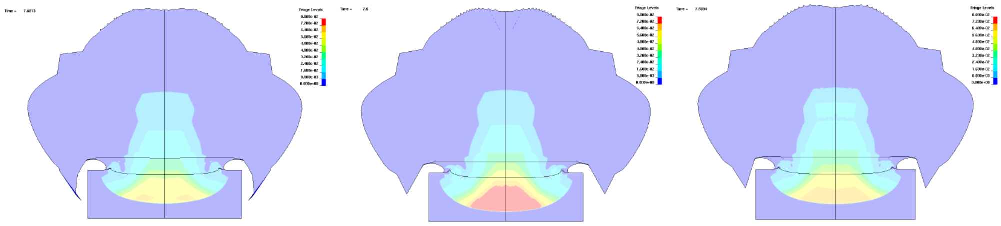
SNPE är genom EURENCO Europas ledande tillverkare av explosivämnen för olika applikationer. FOI har ett långsiktigt samarbete med SNPE:s forskningscentrum CRB, för framtagande av nya energetiska molekyler. Det nuvarande samarbetet är inriktat mot att hitta lågkänsliga molekyler med hög prestanda.

I det första konferensbidraget (Bilaga 1) jämförs fyra olika syntesvägar till 4-amino-3,5-dinitropyrazol. Det är ett explosivämne med god termisk stabilitet och acceptabel känslighet. För att kunna undersöka dess potential mer detaljerat har en av syntesvägarna skalats upp till 200 g-skala. Bidraget var tänkt att presenteras den 21-23 april vid 13th International Seminar on New Trends in Research of Energetic Materials, Pardubice, Tjeckien. Då vulkanaska stoppade alla flyg från Sverige till Tjeckien förhindrades dock FOIs medarbetare att presentera bidraget. Bidraget finns dock i Bilaga 1.

2.2 Lågkänsliga boostersprängämnen

FOI har länge haft samarbete med Eurenco Bofors inom tillverkning av explosivämnen och har på senare tid inlett samarbeten inom utveckling av energetiska kompositioner. Syftet är att ta fram kompositioner som i sig är lågkänsliga för att minska arbetet med att i efterhand modifiera hylsan eller förpackningen till ammunitionen. Även om IM omfattar hela ammunitionsobjektet i sin förpackning eller förvaringssituation, är den absolut säkraste lösningen att använda ett sprängämne med låg känslighet.

Under 2009 och 2010 har vi haft ett samarbete inom utveckling av lågkänsliga boostersprängämnen. Inledande resultat av detta samarbete har visat att man kan utveckla en boosterkomposition baserad på FOX-7 som har samma prestanda som hexotol, men med lägre känslighet. Dessa resultat kommer att presenteras den 29 juni - 2 juli vid 41th International Annual Conference of ICT, Karlsruhe, Tyskland. Temat för konferensen är energetiska material med låg känslighet, hög prestanda och minimal miljöpåverkan. Bidraget finns i Bilaga 2.

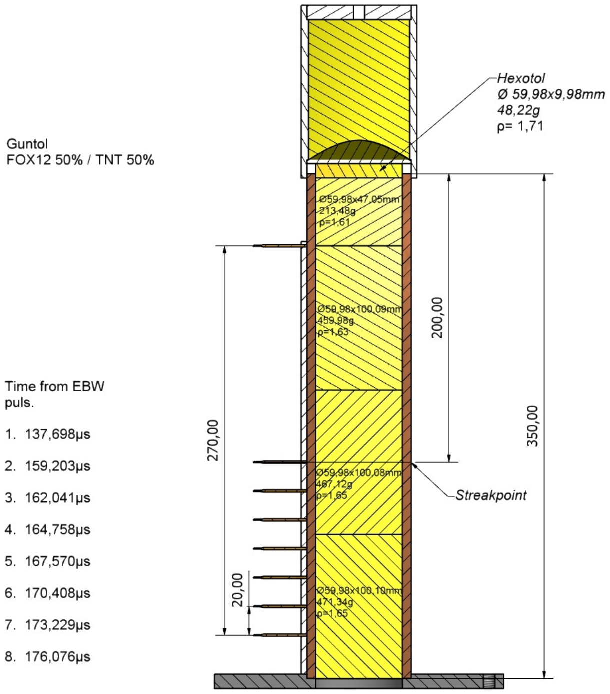


Figur 3. Utvärdering av tre olika boosterkompositioner med hjälp av beräkningar (tryck beräknat 7.5 µs efter initiering av boosterladdningen). Röd färg = 80 GPa; Blå färg = 0 GPa. Hexotol 60/40 (vänster), FOX-7/Viton 95.5/4.5 (mitten) och FOX-7/Viton 82/18 (höger).

2.3 Lågkänsliga gjutna sprängämnen

Lågkänsliga sprängämnen baserade på trotyl och det lågkänsliga explosivämnet N-guanidinureadinitramid (GUDN eller FOX-12) är under utveckling tillsammans med EURENCO Bofors, Karlskoga. Målet är att dessa sprängämnen ska bli tillräckligt lågkänsliga för att kunna IM-kvalificeras. FOI deltar i arbetet genom att bl.a. utvärdera dessa sprängämnens känslighet och prestanda med hjälp av large-scale gap test och cylindertest.

Resultat från känslighetsprovningen visar att Guntol, ett smältgjutet sprängämne baserat på 50/50 GUDN och trotyl, har mycket låg stötvågskänslighet. Cylindertest visade att aluminium-innehållande Guntol har en prestanda motsvarande HNS. Resultatet presenterades i ett konferensbidrag den 11-16 april vid 14th International Detonation Symposium i Idahoe, USA. Bidraget finns i Bilaga 3.



Figur 4. Schematisk bild på cylindertestladdningen.

3 Rökfria energetiska material med hög prestanda

Allt sedan man började använda svartkrut vid krigsföring har rök varit ett problem, då man röjt sin egen position eller genom att sikten försvårats. Än idag försöker man att begränsa eller eliminera rök från vapen. Särskilt gäller detta för kortträckviddiga PV-robotar. Vid användande av rökfritt krut minskar risken att skytten, eller utskjutningsplattformen upptäckts och därmed minskar risken att bli bekämpad. Även en robot blir svårare att upptäcka vilket gör det svårare att bekämpa den och ger kortare tid för att aktivera olika skyddsåtgärder. Rökfria krut medger även möjlighet att styra roboten med optiska metoder. Tidigare skedde detta visuellt (Rb 56 Bill) men i moderna robotar sker optisk styrning med hjälp av laser. Det är dock fortfarande viktigt att skytten kan följa målet visuellt, dels för att kunna se hur målet agerar, men även för att kunna bedöma vilken verkan egen eld har uppnått. På senare tid har man uppmärksammat vikten av att kunna bekämpa mål från begränsade utrymmen, vilket är särskilt viktigt vid strid i urban miljö. I detta fall är det angeläget att roboten inte producerar giftig eller irriterande rök som kan skada skytten.

De idag använda kruten till PV-robotar är oftast baserade på nitrocellulosa, så kallat dubbelbaskrut,. Ett problem med dessa typer av krut är att de har måttliga prestanda och dåliga lågtemperaturegenskaper (en PV-robot bör kunna användas ned till -40°C). Då krutet är relativt styvt går det ej att limma direkt mot raketmotorhylsan, vilket försvårar designen av motorn. I dubbelbaskrut använder man även giftiga blytillsatser för att få önskade brinnegenskaper. Användandet av sådana blytillsatser kan komma att förbjudas i framtiden.

Kompositkrut är en kruttyp som har betydligt bättre specifik impuls än dubbelbaskrut och väsentligt bättre mekaniska egenskaper. Dagens dominerande kompositkrut för raketer består av ammoniumperklorat, AP, fördelat i en elastisk bindemedelsmatris. En nackdel med AP-krut är dock att det produceras stora mängder rök vid förbränningen, Figur 5. En av trenderna inom området energetiska material är att utveckla rökfria kompositkrut som har samma, eller högre prestanda än dagen rykande AP-krut.

Genom att använda kompositkrut med hög prestanda har man visat att storleken för en PV-robotstridsdel kan ökas väsentligt [2] Alternativt kan robotens vikt minskas, vilket är särskilt viktigt för handburna system. Den stora utmaningen är att ersätta AP med en oxidator som inte genererar någon rök, utan att minska den specifika impulsen.

Figur 5. Förbränningsexperiment med rykande ammoniumpereklorat-baserat kompositkrut (t.v.) och rökfritt ammoniumdinitramid-baserat kompositkrut (t.h.).

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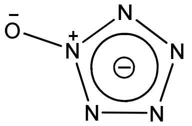
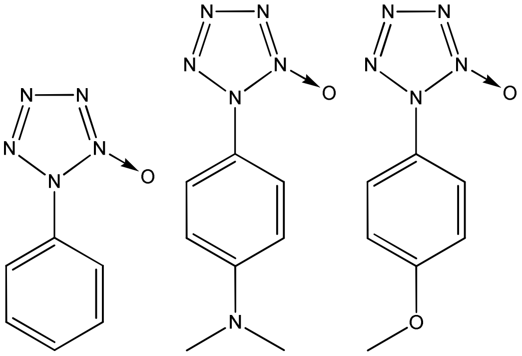
[2] B. Eiderfors, S. Olsson, Möjliga prestandaförbättringar med nya rökfria krut i kortträckviddiga PV-robotar, Teknisk rapport, FOI-R--2050--SE, Stockholm, 2006.

3.1 Rökfria oxidatorer

Inom samarbetet med CRB, Frankrike, pågår arbete med att utvärdera kväve-syreföreningar (N_xO_y). Dessa skulle kunna bli användbara, i form av salter, som oxidatorer i rökfritt kompositkrut med mycket hög prestanda. Inom projektet har därför beräkningar på kväve-syreföreningar gjorts. Beräkningarna visar att en av de undersökta föreningarna, N-oxy-pentazolatjonen (Figur 6), är stabil och att den skulle kunna syntetiseras från flera olika startmaterial (Figur 7).



Figur 6. N-oxy-pentazolatjon.



Figur 7. Möjliga startmaterial till N-oxy-pentazolatjonen.

Resultat från beräkningarna presenterades den 11-16 april vid 14th International Detonation Symposium i Idahoe, USA. Bidraget finns i Bilaga 4.

3.2 Rökfria kompositkrut

Arbetet med att utveckla ett rökfritt raketkrut med hög prestanda till burna PV-vapen har på senare tid gjort att vi lyckats framställa rökfria ADN-baserade krut med goda prestanda. Batcher upp till 3,75 kg av ADN/GAP-krut har tillverkats och vid provning uppvisar krutet en hög brinnhastighet och en tryckexponent mellan 0,4 och 0,5.

Resultaten redovisades 3-6 maj vid 2010 Space Propulsion Conference i San Sebastian, Spanien. Denna konferens räknas som en av de större konferenserna inom framdrivning. Bidraget finns i Bilaga 5.

4 Bilagor

Bilaga 1 - Four syntheses of 4-amino-3,5-dinitropyrazole

Bilaga 2 - Characterization of compositions based on new low sensitive energetic materials

Bilaga 3 - Extremely low sensitivity melt castable explosives based on FOX-12

Bilaga 4 - High performance green solid propellants based on ADN

Bilaga 5 - New high energy oxidizers: A QM study

Four syntheses of 4-amino-3,5-dinitropyrazole

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Abstract:

In this paper, syntheses of 4-amino-3,5-dinitropyrazole from four different starting materials are described. The starting materials are 4-nitropyrazole, 4-nitro-3,5-dimethylpyrazole, 3,5-dinitropyrazole and 4-chloropyrazole, respectively. They are compared in terms of yield, number of steps, price of starting materials and suitability for scale-up into pilot scale production. The overall yield, calculated from commercially available starting materials, ranged from 21 % in the case of synthesis via 3,5-dinitropyrazole up to 46 % for the on starting from 4-chloropyrazole. The cheapest starting material was 3,5-dimethylaminopyrazole and the most expensive 4-chloropyrazole. With numerous factors taken into account, the latter was chosen for a pilot scale study and the product could be produced in batches of 200g.

Keywords: energetic materials; 4-amino-3,5-dinitropyrazole;synthesis; pilot plant scale

1 Introduction

Nitroaromatics, such as picric acid and 2,4,6-trinitrotoluene (TNT), have been used as explosives throughout the last century. Nonaromatic explosives, mainly cyclic nitramines such as 1,3,5-triaza-1,3,5-trinitrocyclohexane (RDX) and 1,3,5,7-tetraaza-1,3,5,7-tetranitro-cyclooctane (HMX) are also in use. The different classes of compound have their advantages and drawbacks, respectively. Compared to the nitramines, TNT has relatively low sensitivity to mechanic stimuli and thus to involuntary detonation, but relatively low oxygen content and heat of formation, which are important factors in the force of an explosive. RDX and HMX

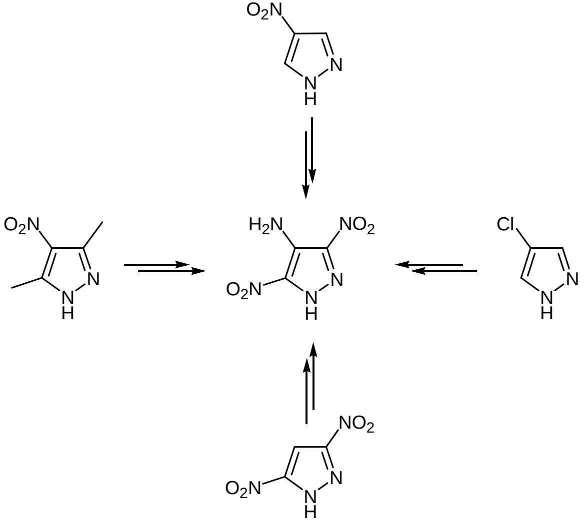

Figure 1: A schematic view of the four syntheses of 4-amino-3,5-dinitropyrazole

have higher energy and oxygen content, thanks to the carbons being exchanged for nitrogen, but also higher sensitivity.

The combination of higher energy content and lower sensitivity is often desired. The former can be calculated[1,2], whereas the latter is difficult to predict. However, there are some features that seem to have a beneficial effect. One such is alternating electron donating groups and nitro groups, which can be found in energetic materials with low sensitivity, *e.g.* 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) and 1,1-diamino-2,2-dinitroethylene (DADNE, FOX-7)[3]. 5-Nitro-1,2,4-triazol-3-one (NTO) is also a highly insensitive explosive, but it has no electron donating groups in its structure. Though, it has strong intermolecular hydrogen bonding, which appears to increase the stability towards thermal and mechanical stimuli. The hydrogen bonding gives the compounds a graphitelike crystal structure, where the infinite sheets, being held together by hydrogen bonds within the layers, can slide on each other without any bond breaking. The hydrogen bonding thus seems to have a stabilising effect from the supermolecular point of view[4].

The above factors directed our attention towards nitropyrazoles, which have favourable properties, such as high thermal stability and high energetic potential. Furthermore, they can be substituted in no less than four positions, *i.e.* on the three carbons and also on one of the nitrogens, which allows a large variety of derivatives.

This work deals with 4-amino-3,5-dinitropyrazole, which is an example of a pyrazole with alternating nitro and amino groups, which forms infinite sheets[5]. Protected 4-amino-3,5-dinitropyrazole was first prepared by Vinogradov *et al.*[6] in a synthesis with six steps and later presented as such by Shevelev[7] *et al.* Schmidt *et al.*[5] presented a shorter synthesis in 1996, which used vicarious nucleophilic substitution of hydrogen in 3,5-dinitropyrazole. This last step of this elegant synthesis involves the fairly toxic reagent trimethylhydrazinium iodide (TMHI). Another drawback is the tedious synthesis of the starting material 3,5-dinitropyrazole, which includes four steps and was described by Jansen *et al.* in 1973[8]. The high thermal stability and moderate sensitivity to impact of 4-amino-3,5-dinitropyrazole makes it an interesting candidate as a new energetic material. To allow a full evaluation of a substance, the synthesis should be possible to perform in at least multigram and preferably in kilogram scale. This made us look deeper into new, more efficient and straightforward synthetic pathways.

2 Results and discussion

2.1 4-Amino-3,5-dinitropyrazole *via* 3,5-dinitropyrazole

One of the major drawbacks in Schmidt's synthesis[5] is the use of the toxic 1,1,1-trimethylhydrazinium iodide (TMHI). Therefore, other vicarious nucleophilic substitution (VNS) reagents were evaluated. One first attempt with hydroxylamine in methanol failed. However, the combination of 4-amino-1,2,4-triazole and potassium *tert*-butoxide in anhydrous DMSO produced the desired product in 82 % yield, cf. Figure 2. 4-Amino-1,2,4-triazole has two advantages in comparison with TMHI. It is commercially available and considerably less toxic than the chemicals involved in the production of TMHI.

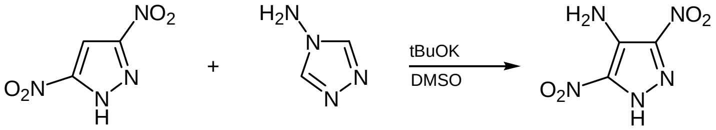

Figure 2: Synthesis 1, 4-amino-3,5-dinitropyrazole via VNS

This reaction worked efficiently with higher yield (82 %) than the previously published procedure[5] (67 %) and provided a pure DMSO solvate of the desired product. This synthesis has five steps starting from pyrazole. In our hands, the published procedure[8,9] with minor modifications, produced 3,5-dinitropyrazole in 27 % from pyrazole. This resulted in an overall yield of 21 %.

2.2 4-Amino-3,5-dinitropyrazole *via* 4-nitropyrazole

To reduce the number of steps in the synthesis, another route was envisaged. The reduction and protection is a one-pot procedure. Counting this as one step resulted in four-step procedure starting from pyrazole, *i.e.* one step less than Schmidt's synthesis, *vide supra*. This synthesis is outlined in Figure 3. The nitration of pyrazole into 4-nitropyrazole was quantitative. The reduction in aqueous, basic sodium dithionite solution to afford 4-aminopyrazole, protected as a carbamate, had a yield of 60 %. This reaction produced an isomeric mixture. However, nitration resulted in one single product, which was very hygroscopic, in 95 % yield.

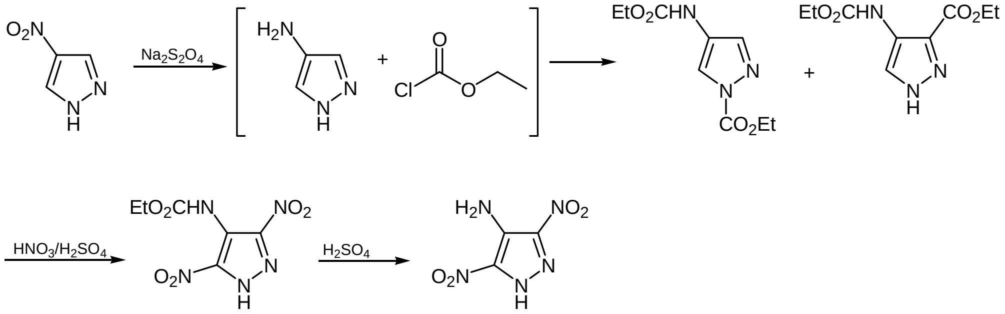

Figure 3: Synthesis 2, 4-amino-3,5-dinitropyrazole from 4-nitropyrazole

The removal of carbamates, by the use of different methods[10-15], has been described in the literature. The hydrolysis was first attempted in refluxing 40 % aqueous potassium hydroxide solution and then 35 % hydrochloric acid. In the basic solution, the conversion is a few percent after 72 hours' refluxing. To avoid the risk of nitro group substitution by chloride ions, the carbamate was heated in 60 % sulphuric acid overnight to remove the protective group. Recrystallisation of the extracted product from water produced the hydrate of the desired product in 70 % yield. The overall yield of this procedure was 40 %.

2.3 4-Amino-3,5-dinitropyrazole from 3,5-dimethylpyrazole

The synthesis *via* decarboxylation-nitration outlined below, cf. Figure 4, had more steps than the ones already described, *vide supra*, but id has the advantage to use the inexpensive and commercially available 3,5-dimethylpyrazole as its starting material. This compound was readily nitrated in mixed acids at ambient temperature to give corresponding 4-nitro derivative, which can be oxidized into 4-nitropyrazole-3,5-dicarboxylic acid[16] in 60 % yield. The latter compound was reduced with sodium dithionite to 4-aminopyrazole-3,5-dicarboxylic acid[17].

The 4-aminopyrazole-3,5-dicarboxylic acid was subjected to nitration by mixed acids with the idea to get the desired product. A similar approach was used in the synthesis of 2,6-diamino-3,5-dinitropyridazine[18]. To prevent *N*-nitration, diazotisation and other by-reactions, the exocyclic amino group was protected as a carbamate, which allowed nitration in mixed acids, cf. Figure 4.

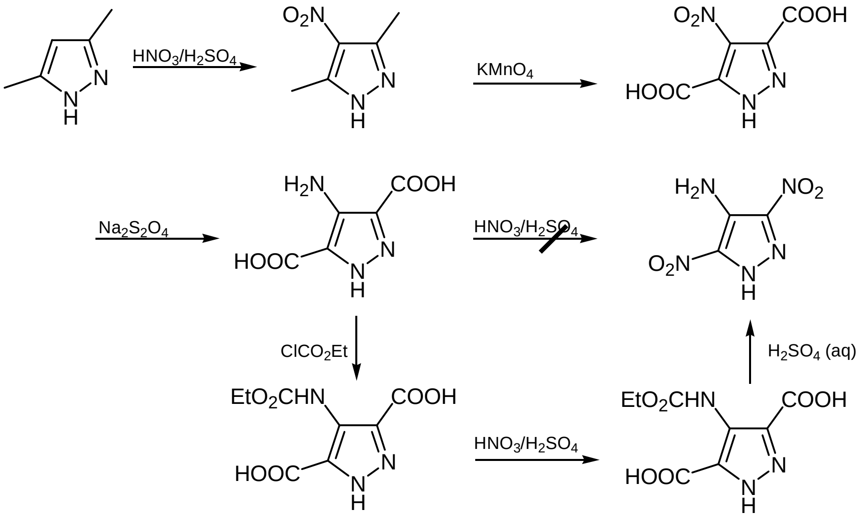

Figure 4: Synthesis 3, protected 4-amino-3,5-dinitropyrazole from 4-nitro-3,5-dimethylpyrazole

One problem encountered in this synthetic sequence is the high solubility of the intermediate carboxylic acid. Oxidation of 4-nitro-3,5-dimethylpyrazole proceed in 60 % yield, when the product was isolated in pure form. The oxidation is carried out in basic potassium permanganate solution. After the completion of the reaction, the manganese dioxide was removed by filtration. The filtrate was concentrated and neutralised, which resulted in precipitation of the product in yields as described above, *vide supra*. However, further concentration of this filtrated provided more, but impure product. The major impurity was potassium chloride, which did not disturb the following step. The yield of 4-ethylcarbethoxyamino-3,5-dicarboxypyrazole from 4-nitro-3,5-dimethylpyrazole was 72 % (two steps), which is considerably higher than it would have been with isolation of the intermediate. The nitration-decarboxylation into protected 4-amino-3,5-dinitropyrazole took place in mixed acids in quantitative yield. Since this procedure resulted in the same intermediate as described above, the hydrolytic removal of the protective group was performed in the same way, *vide supra*. The overall yield from 3,5-dimethylpyrazole to 4-amino-3,5-dinitropyrazole was 37 %, which can be considered as excellent, considering the number of steps in the reaction.

2.4 4-Amino-3,5-dinitropyrazole from 4-chloropyrazole

In another attempt to reduce the number of steps, a synthesis starting from 4-halopyrazoles was outlined, cf. Figure 5.

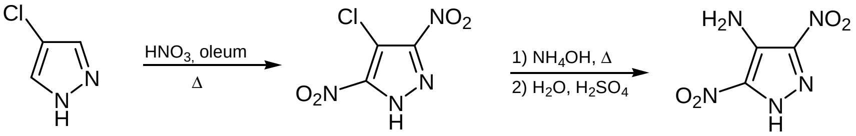

Figure 5: Synthesis of 4-amino-3,5-dinitropyrazole from 4-chloropyrazoles

One example of synthesis of dinitropyrazoles in a single step was reported by Coburn[19] in his studies on nitration of 1-methyl-4-substituted pyrazoles, cf. Figure 5. This can be contrasted by the exclusive formation of 4-nitropyrazole upon nitration of pyrazole itself[20,9,8].

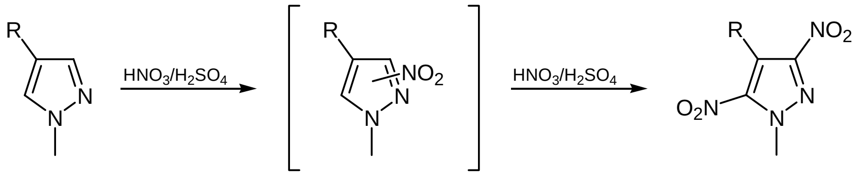

Figure 6: Dinitration of substituted pyrazoles

Perevalov[21] *et al.* studied the product distribution in the nitration of 1-methyl-4-bromo- and 1-methyl-4-chloropyrazole, respectively, cf. Figure 6. It was shown that the bromo compound underwent dehalogenation-nitration in position 4 to different extents depending on the reaction condition. The 4-chloro compound, on the other hand, did not undergo any such by-reaction. Therefore, nitration of 1*H*-4-chloropyrazole was evaluated, which yielded 4-chloro-3,5-dinitropyrazole in 71 % yield

The aromatic, nucleophilic substitution of 4-chloro-3,5-dinitropyrazole with aqueous ammonia into 4-amino-3,5-dinitropyrazole took place in a close vessel at high temperature. The reaction produced the ammonium salt of 4-amino-3,5-dinitropyrazole. Recrystallisation from acidic water yielded the product, which was the hydrate of 4-amino-3,5-dinitropyrazole. After azeotropic removal of the crystal water, the yield was 65 % from 4-chloro-3,5-dinitropyrazole. The yield could be increased by concentration of the mother liquor or repetitive recrystallisation of new product in the same mother liquor. Though, this was not examined. The overall yield of this procedure was 46 % from 4-chloropyrazole.

2.5 Comparison of the different syntheses

The choice of starting point will greatly influence any comparison of the different syntheses of 4-amino-3,5-dinitropyrazole. Our choice was to start from a commercially available starting material. Therefore, pyrazole is considered the starting point for the two first syntheses, 3,5-dimethylpyrazole in the third and 4-chloropyrazole in the last, *vide supra*. The advantages and disadvantages of the different syntheses are shown in Table 1 and they are then compared below.

The longest synthesis by these means is synthesis 3, *i.e.* the one starting from 3,5-dimethylpyrazole with six steps. Syntheses 1 and 2, both starting from pyrazole, have five and four steps, respectively. The shortest is the synthesis 4, starting from 4-chloropyrazole with only two steps.

The overall yields of the different procedure ranged from 21 % in the synthesis 1 via 3,5-dinitropyrazole up to 46 % in synthesis 4 from 4-chloropyrazole. On this basis, only synthesis 1 *via* 3,5-dinitropyrazole can be discarded. The other three procedures, all have yields between 37 and 46 %. This little difference means that other factors must be used in the selection of a procedure suitable for scale-up. Two such factors, besides the number of steps outlined above, are choice of solvents and production of waste. DMSO is generally a difficult solvent to purify, since it freely miscible with water and must be anhydrous in many reactions. This renders it less favoured by the industry. This is the main obstacle of the synthetic step from 3,5-dinitropyrazole to 4-amino-3,5-dinitropyrazole used in the first procedure. Sodium dithionite is used in synthesis 2 and 3. This reagent has to be used in large excess and cannot be easily reused or recycled. This reagent can thus only be used in small scale. Synthesis 3 includes an oxidation with potassium permanganate, which produces large amounts of waste. The only procedure using suitable solvents and not producing excessive waste is synthesis 4, starting from 4-chloropyrazole.

Table 1: A brief comparison of the different synthetic procedures

Synthesis 1. Via 3,5-dinitropyrazole, cf. Figure 2.	*Synthesis 2. Via 4-nitropyrazole, cf. Figure 3*
High yield in the last step Moderate production of waste Five steps DMSO required in the last step Low overall yield Quite expensive starting material	Excellent yield in two out of four steps Moderate production of waste No organic solvents required Four steps Moderate overall yield Quite expensive starting material
Synthesis 3. From 3,5-dimethyl-pyrazole, cf. Figure 4.	*Synthesis 4. From 4-chloropyrazole, cf. Figure 5.*
Cheap starting material No organic solvents Moderate overall yield Six steps High production of waste	Two steps Little production of waste Scale-up possible Moderate overall yield Expensive starting material

This procedure was successfully scaled up to small pilot scale. The limiting factor in this case was the size of our pressure reactor. Nonetheless, 200 g of 4-amino-3,5-dinitropyrazole could be produced in one single batch.

Some attention must be given to the price of the starting materials. Pyrazole as such is quite an expensive starting material, even though it is readily commercially available. In comparison, the price of 3,5-dimethylpyrazole amounts to one quarter of that of pyrazole. 4-Chloropyrazole, on the other hand, costs approximately twice as much as pyrazole itself. The comparison was made for lab scale quantities.

2.6 Conclusions

Four different syntheses of 4-amino-3,5-dinitropyrazole were developed and compared in terms of overall yield, number of steps, production of waste and price of the starting materials. One of them, namely the nitration of 4-chloropyrazole followed by aromatic nucleophilic substitution with ammonia, was successfully transferred into small pilot plant scale. Batches of up to 200 g of the desired product could be obtained.

Acknowledgments

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Characterization of Compositions based on New Low Sensitive Energetic Materials

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Abstract

FOX-7 and FOX-12 are new energetic materials with high to TNT equivalent performance and low to extremely low sensitivity. FOX-7 and FOX-12 are produced as regular products at Eurenco Bofors AB in Sweden since 10 years. The need for IM solutions has initiated a collaborative project between Eurenco Bofors AB and FOI, Swedish Defence Research Agency, Sweden. The aim is to develop and perform characterization of new insensitive compositions based on FOX-7 and/or FOX-12. The work performed includes finding of suitable binders, and investigation of the influence of crystal shape and particle sizes on the composition regarding press density and sensitivity. The characterization includes insensitivity tests, performance calculations and shock initiation simulations. Based on these results it will be possible to suggest the proper composition for a specific IM application. The initiation test showed that the GUNTOL composition was initiated at a thickness of 10.5 mm PMMA disks, which in turn was used to simulate the initiation of GUNTOL. The results show that a FOX-7 booster can contain as much as 18 wt% of binder and can still have the same initiation ability as a Hexotol booster of the same dimension.

Introduction

The necessity of IM (Insensitive Munitions) has become of out most importance since the defense forces needs safer or insensitive ammunition to minimize the risk of detonation. Most UN countries have IM policies and IM regulations enforced by law. The purpose of IM is to reduce the risk of response to accident or attack, to reduce collateral damage to personnel and equipment, and to reduce the risk of a minor incident escalating into a catastrophic event. Other benefits of IM are increased transportation capability, simplified storage, i.e. larger amounts of munitions can be stored and the safeguard and the safety distance around the storage can also be reduced.

Therefore a collaborative project has started between Eurenco Bofors AB and FOI, Swedish Defence Research Agency, Sweden. The aim is to develop and perform characterization of new insensitive compositions based on FOX-7 and/or FOX-12. FOX-7 and FOX-12 are produced as regular products at Eurenco Bofors AB in Sweden since 10 years.

The work performed includes finding of suitable binders, and investigation of the influence of crystal shape and particle sizes on the composition regarding press density and sensitivity. The characterization includes insensitivity tests, performance calculations and shock initiation simulations. Based on these results it will be possible to suggest a suitable composition for specific IM applications.

GUNTOL has earlier proven to be a very low sensitive composition and it has passed a full scale

IM test according to STANAG 4544. The test was performed on a 155 HEER shell filled with 9 kg of GUNTOL. The results are shown in Table 1 and Figure 1 below.

Table 1 Results from full scale IM-test according to STANAG 4544.

Test number	Test	Result	
1	Slow Cook-Off	V	(combustion)
2	Bomlet	V	(combustion)
3	RPG-7	IV	(deflagration)
4	Sympathetic Detonation	IV/III	(deflagration or explosion)

I=Detonation, II= Partial detonation, III= Eplosion, IV= Deflagration, V= Combustion

Figure 1. Donor and acceptor 15 cm apart (left). Witness plate with two detonations of acceptor consisting of TNT (middle). Witness plate with no detonation of acceptor consiting of GUNTOL (right)

The GUNTOL compostion also responds very well in the Bullet Impact test according to STANAG 4241, with a Type V reaction (combustion) as result. The Gurney energy of GUNTOL compositions vary between 2.1-2.3 km/s, which equals a performance of PBXN-110 (2.2 km/s). The gap value from SSGT (Small Scale Gap Test) value is below 3 mm, to be compared with a value of TATB of 7 mm, 15 mm for PBXN-110 and 20-25 mm for conventional melt cast Octol or Hexotol.

There are several factors that influence the IM properties of a product application and it is not only the composition that is regarded as IM, but the whole concept from energetic material to composition, to design of the ammunition, to casing and storage. The aim is to pass several different IM tests for each individual aspect of the application, but in the end it is the complete test results that will determine if a product is IM or not. However, it is of immense interest to consider low sensitive energetic materials and compositions, as these will give the largest impact on the IM properties.

The energetic materials sensitivity is influenced by factors, such as crystal shape, particle size, lattice irregularities and purity. Purity is mainly responsible for how even the lattice structure is. For every impurity that is built into the crystal a lattice disorder arises and weakens the crystal. Impurities therefore give the crystal different properties, everything from instability, crystal shape to discoloration. Instability, especially towards heat, long time storage and sensitivity to shock results in the largest problems. But as always it is the concentration level and type of impurities that count. Sometimes different agents are introduced to a system to attain a certain crystal modification of the shape.

When designing a formulation, it is important that the crystals can tightly pack together, in order to reach the highest density achievable of the theoretical value. The crystal shape defines how well the crystals can be packed, a spherical form is most preferable and a cubical shape is the second best. Other forms such as flakes and needles are not very favorable in order to reach a high packing density, particularly in pressed compositions. But the shape of the crystal is not enough, a perfect crystal distribution is necessary to attain a perfect packing of the crystals. Between the larger particles void forms and these have to be filled with smaller particles, which in turn create even smaller voids that have to be filled and so on. If all the voids are filled with crystals of right size there is no space left for porosity. Anything that disturbs the high density and makes it decrease will have a sensitizing effect on energetic materials and on compositions as well, because these voids may give rise to hot spots where a detonation easily can start and propagate.

Energetic materials are mixed with binders and other materials, in order to either enhance the performance and/or to decrease the sensitivity of compositions. To achieve low vulnerability for compositions new challenges arise, as one can choose to press a formulation, melt cast or cure cast. Every method has its advantages and disadvantages. We have chosen to work with a pressed composition, because it has lower costs due to shorter manufacturing time and contains less hazardous ingredients. However porosity is one of the most significant things that control the sensitivity of a formulation towards impact. If the porosity is high, about 3% and above, the shock sensitivity is high. If the binder is not evenly distributed on the crystal, voids and cracks can appear in the pressed product and these will further increase the sensitivity as the mechanical strength weakens.

If to much pressure is used during the press operation, the crystals might be severely damaged this will also increase the sensitivity, as lattice irregularities, e.g. tension lines forms in the crystal structure. Tension lines will transfer a shock wave and a detonation can occur instead of no reaction or deflagration. When the composition is intact the energy generated from a shock wave will be evenly spread in the crystals and the media that surrounds them and thus the composition will not detonate.

The aim of this work is to find a formulation based on a low sensitive energetic material such as FOX-7 that can be pressed into a high density and low porosity composition, with good mechanical properties. This paper presents work where the shock sensitivity of a melt casted GUNTOL-composition has been determined. The shock sensitivity data have then been used to predict the amount of energy that a FOX-7 booster would need in order to initiate the GUNTOL-composition. Finally, FOX-7 based formulations has been produced and tested with respect to sensitivity towards shock.

Experimental

Materials

The material used for initiation testing was GUNTOL (No. 34104, Batch No 20097027) provided by Eurenco Bofors, Sweden. The composition was based on 45 % (wt) of N-guanylurea dinitramide (GUDN) and 55% (wt) of TNT (Type 251 with HNS). Each sample had a weight of approx. 0.6 kg.

In the FOX-7 based formulations different FOX-7 classes with different crystal size distribution (Figure 2-4) from Eurenco Bofors AB were used. The following classes were used:

NSF 110	20-40 µm	article number 34084 (precipitated)
NSF 130	100-200 µm	article number 34096 (precipitated)
NSF 140	250-350 µm	article number 34097 (precipitated)

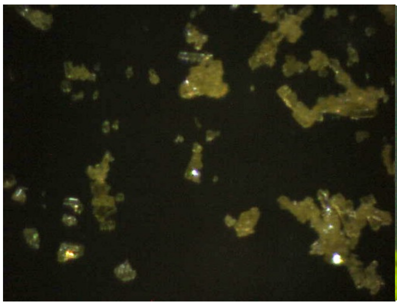

Figure 2. NSF 110 20-40 µm, 200x

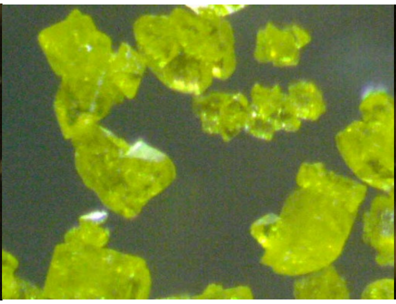

Figure 3. NSF 130 100-200 µm, 200x

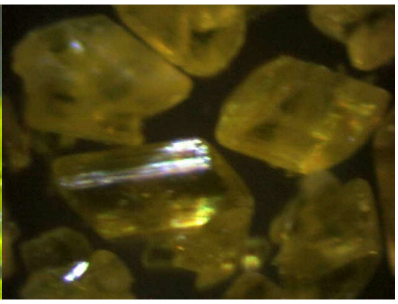

Figure 4. NSF 140 250-350 µm, 200x

Binders used in the pressed formulations were HyTemp and Viton.

Initiation test method

The shock sensitivity of GUNTOL was estimated by detonating a donor explosive billet of Hexotol (60 wt% RDX, 40 wt% TNT) and attenuating the shock wave by a layer of PMMA. The donor explosive had a diameter of 42 mm, thickness 20 mm and density of 1.6 g/cm^3. The charge weight was 44.4 g.

A standard NONEL blasting cap was used as detonator. PMMA disks having a thickness of 1.5 mm were used. The sample tube was a PMMA tube 100 x 64 x 3 mm. The witness plate was a 120 x 120 x 10 mm mild steel sheet. The setup is schematically drawn in Figure 5.

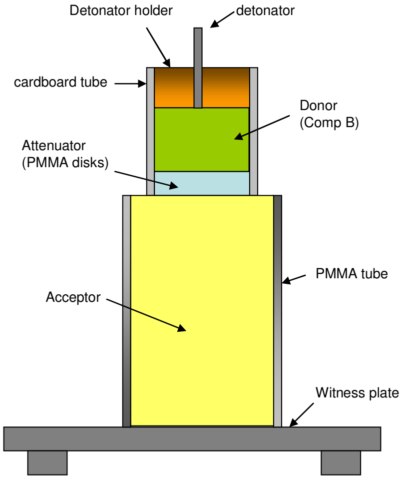

Figure 5. Setup of initiation test

Shock initiation simulations

To estimate the shock energy and brisance needed to initiate a GUNTOL charge a rough Ignition & Growth model was derived from this single experiment.

The Ignition and Growth model for shock initiation of HE consists of three elements, an EOS for the unreacted explosive, an EOS for the reaction products and a pressure dependent reaction rate law describing the conversion from unreacted HE to reaction products. In this study we used a JWL EOS for the reaction products with parameters for GUDN/TNT 50/50 given in reference 1. The unreacted EOS was not calculated, instead we used the same EOS as previous investigators have used for CompB [2]. The reaction rate law consists in its general form of three terms, an ignition term, a growth term and a completion term. In this study we used a simplified two-term form, omitting the completion term. Furthermore, we fixed all parameters in the two-term reaction rate model to reasonable values, except for the amplitude of the growth term, *G*, which was varied to match our experiment. The assumed form of reaction rate law was

$$\frac{df}{dt} = 44(1-f)^{0.222}(\mu - 0.01)^4 + G(1-f)^{0.222} f^{0.667} p^2$$

where ρ is the density, p the pressure, f the burn fraction and $\mu = \rho/\rho_0 - 1$. The initiation experiment was simulated using the finite element code LS-DYNA v. 971 in a 2D axisymmetric Lagrangian setting. A programmed burn model was used for the booster and the Ignition and Growth model for the acceptor charge. The mesh size was 0.125 mm. The *G*-parameter in the growth term was varied to get a critical gap thickness of 10 mm. The so obtained parameters for the Ignition and Growth model are presented in Table 2.

Table 2. Ignition and growth parameters for GUDN/TNT 55/45 at density 1.652 g/cc.

Product JWL EOS[1]		Reactant JWL EOS[2]		Rate law	
A (Mbar)	4.025	A (Mbar)	1479	G ($ms^{-1}Mbar^{-2}$)	135
B (Mbar)	0.05376	B (Mbar)	-0.05261		
R_1	4.2	R_1	12.0		
R_2	1.8	R_2	1.2		
ω	0.34	ω	0.912		
E_0 (Mbar)	0.074	T_0 (K)	298		
c_v (Mbar/K)	1.0e-5	c_v (Mbar/K)	2.487e-5		

[1] Data for GuDN/TNT 50/50 from reference 1.
[2] Data for CompB from reference 2.

This Ignition and Growth model was then used to evaluate different booster compositions based on FOX-7. The objective was to find a composition that has low sensitivity and at least as good initiation ability as hexotol. The base compositions consisted of 95.5 % FOX-7 and 4.5 % Viton. The amount of binder were then decreased, assuming a pressing density of 97 % of TMD, to a level where the explosive marginally initiated the GUNTOL acceptor charge after being attenuated by the 10 mm thick PMMA-disk. The performance and EOS of the booster composition was calculated using the thermo-chemical program Cheetah v. 2.0 and the BKWC-library.

Results and Discussion

Initiation test

Initiation test was performed on GUNTOL and the setup is shown in Figure 6. A line-up of the witness plates from the study is shown in Figure 7. The up and down series resulted in an 50% probability to detonation at approx. 7 FOI-cards, Table 3. Both negative and positive results were obtained with 7 FOI-cards. 7 FOI-cards are equal to a 10.5 mm PMMA attenuator. The result has been used to evaluate the energy needed to initiate a GUNTOL charge.

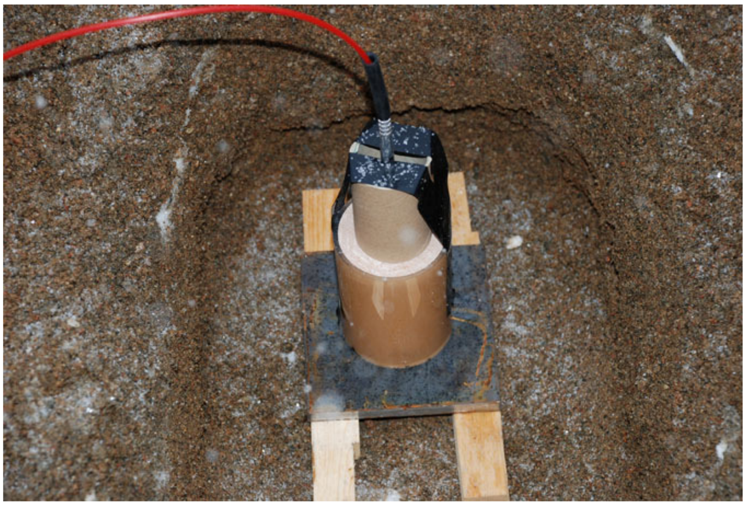

Figure 6. Initiation test setup with witness plate, PMMA tube with GUNTOL. Booster with detonator on top. The PMMA cards are not shown (placed inside the paper tube).

Figure 7. Witness plates from test series: test 1 to 5 (top row from left to right) and test 6 to 10 (bottom row from left to right).

Table 3. Initiation test series with results.

Test	FOI-Cards[a] (No.)	Result
1	None	Positive (+)
2	None	Positive (+)
3	4	Positive (+)
4	15	Negative (-)
5	8	Negative (-)
6	6	Positive (+)
7	7	Negative (-)
8	6	Positive (+)
9	7	Positive (+)
10	7	Negative (-)

a) One FOI-card has a thickness of 1.5 mm which corresponds to 6 US-cards (0.25 mm each).

Shock initiation simulations

The results are presented in Table 4 together with the results from the initiation simulations. The numerical simulations indicates that as much as 18 wt% of binder can be used and still achieve the same initiation ability as a hexotol booster of the same dimension.

Table 4. Calculated JWL for different fractions of HE/binder assuming a pressing density of 97 % of theoretical maximal density. Also included is an estimate of initiation ability of the compositions calculated using the IG-model in LS-DYNA.

Composition	FOX-7/Viton 95.5/4.5 wt%	FOX-7/Viton 88/12 wt%	FOX-7/Viton 85/15 wt%	FOX-7/Viton 82/18 wt%
ρ (g/cc)	1.818	1.824	1.823	1.822
D (m/s)	8362	7986	7825	7661
P_{CJ} (GPa)	29.23	26.68	25.56	24.47
A (GPa)	1118	1073	1034	1210
B (GPa)	10.26	10.70	10.52	15.48
R_1	5.0	5.08	5.09	5.49
R_2	1.1	1.12	1.13	1.33
ω	0.38	0.37	0.36	0.39
E_0 (kJ/cc)	8.951	8.555	8.363	8.101
Initiation ability	go	go	go	marginal

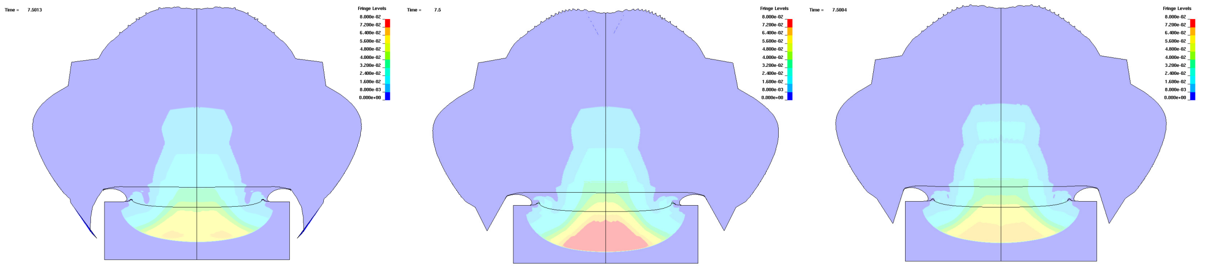

Figure 8. Calculated pressure (in Mbar) in the GUNTOL acceptor charge 7.5 μs after initiation of the booster (donor) charge. Red colour corresponds to 80 kbar (8 GPa) and blue colour to zero pressure. The booster charges were hexotol 60/40 (left), FOX-7/Viton 95.5/4.5 (centre) and FOX-7/Viton 82/18 (right).

Formulation

The main purpose of the formulation work was to investigate how FOX-7 particle shape and crystal size distribution influence a composition based on different binders. One part of the work was to find a suitable binder. We have chosen to work with pressed compositions, because they have lower cost due to shorter manufacturing time and contain less hazardous ingredients. The work has focused on press density, porosity and shock sensitivity. Shock sensitivity was determined by SSWGT Small Scale Water Gap Test according to STANAG 4488. The work is still ongoing and all the tests have not yet been performed.

Several binders have been tested in formulations, with a FOX-7 content of 95% and higher. The press density has reached values above 98% of the theoretical density of the composition, with a porosity of less than 2 %.

The appearance of the formulations differs a lot depending on which type of binder that was used. Figure 9-10 show pictures on the different formulations.

In Composition no 1 the individual granulates are larger than in Composition no 2. The granulates of Composition no 1 also have a rounded shape, with the FOX-7 crystals imbedded in the spheres, and they are opaque. The Composition no 2 granules look more like agglomerates of crystals and it is still possible to se the original crystal shape of FOX-7. The granules of Composition no 2 are clear to slightly opaque. The granules were produced with a solvent/non solvent slurry method.

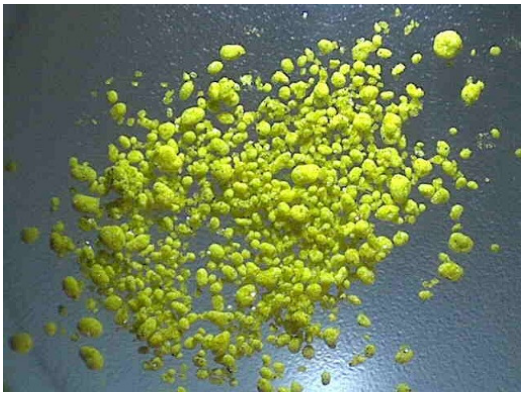

Figure 9. Composition nr 1 with binder type: Hytemp, 10x

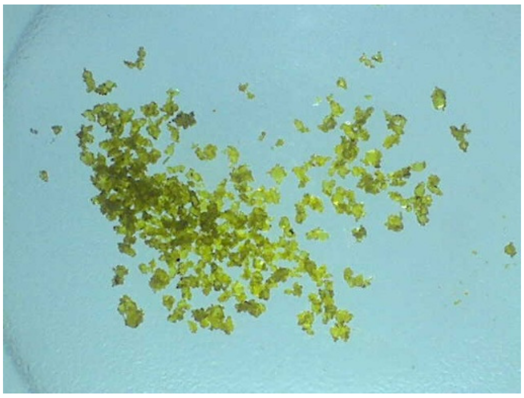

Figure 10. Composition 2 with binder type: Viton, 10 x.

Initial test results from SSWGT show that the porosity due to the different crystal size distribution has had the largest impact on the shock sensitivity and not the type or amount of binder. Probably when the perfect crystal size distribution in the composition has been accomplished the type of binder and amount will contribute with a larger effect upon the shock sensitivity that is a decreased sensitivity towards shock.

Conclusions

The initiation test of the GUNTOL-composition resulted in a critical PMMA thickness of 10.5 mm, This result was used to simulate the energy needed to initiate the GUNTOL-composition. The initiation simulations showed that a FOX-7 based booster composition with 18 wt% of binder can be used and still achieve the same initiation ability as a hexotol booster of the same dimension.

Further on, initial SSWGT tests show that the porosity, due to the different crystal size distributions in the FOX-7 compositions, had the largest impact on the shock sensitivity and not the type or amount of binder.

Our conclusion is that it is possible to produce an IM concept based on GUNTOL and FOX-7, whereas GUNTOL is used in the main charge and a FOX-7 based composition as a booster.

Acknowledgements

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Extremely Low Sensitivity Melt Castable Explosives Based On FOX-12

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Abstract. N-guanylurea-dinitramide (FOX-12 or GuDN) is a new energetic material with extremely low sensitivity and good potential for use as a propellant or IM explosive. This paper reports its use as a low sensitivity ingredient in melt castable formulations. The performance is evaluated by detonation velocity measurements and by cylinder expansion measurements. The sensitivity was evaluated by large scale gap tests. Three different explosives were tested; melt cast GUNTOL (50/50 wt% FOX-12/TNT), GUNTONAL1 (42.5/42.5/15 wt% FOX-12/TNT/Al-H2) and GUNTONAL2 (42.5/42.5/15 wt% FOX-12/TNT/Al-A100).

Introduction

The present development of energetic materials for military purposes is motivated by the need for 1) increased performance, 2) increased safety, and 3) custom or "tailored" capabilities. Several factors affect the development either directly or indirectly. The most important of these are the increased use of insensitive munitions (IM), the need for higher performance and other specific capabilities, environmental issues, standardization issues and increased systems integration. Requirements for and use of IM have increased following several accidents involving hundreds of fatalities, such as the fire on the US carrier Forrestal and the loss of the UK destroyer Sheffield where the ammunition carried on board the ships was mainly responsible for the violent development of the events. The need for different types of IM-solutions is imminent with the increasing number of international operations our Swedish forces take part in. It is also a very important part of the interoperability questions we have with our partners on the international arena.

One of the purpose of the ongoing research on energetic materials in Sweden is to produce more powerful, safer and environmentally friendlier explosives that fit into the new action plan of the defence forces. One line of research is towards compositions with lower sensitivity, which improves the safety of ammunition. A problem with lower sensitivity energetic materials in munitions has been that insensitivity almost always has meant lower performance.

In the search of new and safer high explosives a number of low sensitive molecules have been identified (e.g. TATB, NTO and FOX-7). At FOI we developed a new very insensitive compound, N-guanylurea-dinitramide (FOX-12 or GuDN), that could be of use for LOVA propellant as well in melt-cast and PBX high explosive formulations. N-guanylurea-dinitramide, se Figure 1, is a novel energetic material with extremely low sensitivity and good potential for use as a propellant or IM explosive[1,2].

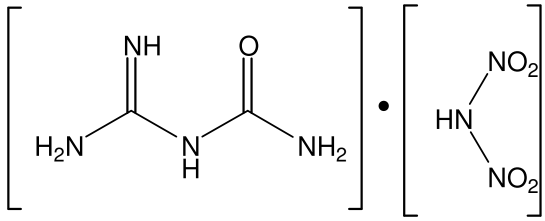

Fig. 1. FOX-12 (N-guanylurea-dinitramide).

This paper reports its use as a low sensitivity ingredient in melt castable formulations. The shock sensitivity was evaluated by the NOL large scale gap tests. The performance is evaluated by detonation velocity measurements and by cylinder expansion measurements.

Large Scale Gap Test

The shock sensitivity of GuDN/TNT 50/50 was evaluated by large scale gap tests. In the tests a donor explosive is used to generate a shock wave that is attenuated by an inert buffer and transmitted to the tested explosive, the acceptor. A witness plate is positioned below the acceptor charge to determine whether the shock stimulus is strong enough to initiate the acceptor explosive to detonation or not.

Test Method

A modified version of method 1041 in MIL-STD-1751A[3], NOL Large Scale Gap Test (LSGT) Method[4], was used in the tests. The main modifications were the size and composition of the donor charge. A NONEL blasting cap was used as detonator. The donor charge (97 g) was made of hexogen (RDX, NSH 49) containing 3% of wax and pressed to a density of 1.6 g/cm^3. The donor charge had a diameter of 42 mm and a thickness of 43.8 mm. The attenuator was made of stacked layers of PMMA disks (cards) of thickness 1.5 mm. The explosive material to the acceptor charges used in this study was provided by EURENCO Bofors, Art no. 34104, batch 20097027. GUNTOL 50/50 contains 50 % GUDN and 50 % TNT (Type 251 with HNS). The charges were cast by Nammo LIAB AB and machined to fit the sample tube. The LSGT tube was a mild steel seamless tube of height 140 mm, outer diameter 42.2 mm and wall thickness 3.2 mm. The witness plate was a 120 x 120 x 10 mm mild steel sheet, separated from the acceptor charge by a small air gap. The set up is schematically drawn in Figure 2.

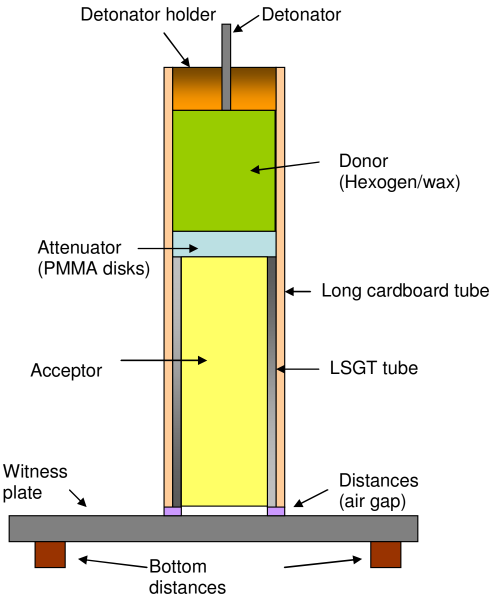

Fig. 2. The LSGT set up.

Results

The results from the LSGT are listed in Table 1. The explosives did punch a hole in the witness plate at 15 FOI-cards, but not every time (two out of four). The 50 % point was therefore found to be at 15 FOI-cards, i.e. 22.5 mm PMMA. At 16 FOI-cards the results were all negative.

A line-up of the witness plates is shown in Figure 3. The difference between a negative and positive result is clearly seen. Intact witness plates correspond to negative results while holes correspond to positive results.

Table 1 LSGT results

Shot	Density (g/cm^3)	# cards[a]	Result
1	1.63	15	-
2	1.62	10	+
3	1.63	13	+
4	1.63	14	+
5	1.66	15	-
6	1.69	14	+
7	1.62	15	+
8	1.69	16	-
9	1.63	15	+
10	1.63	16	-

a) Each card has a thickness of 1.5 mm.

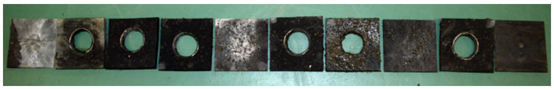

Fig. 3 Witness plates, from left to right, shot 1 to 10.

To compare our result with published NOL LSGT results for other HE that uses 160.6 g pentolite donor charges, it is necessary to convert the results from gap thickness, or number of card, to pressure in the PMMA stack at that thickness. 2D axi-symmetric simulations of our test were performed using LS-DYNA v. 971. Cheetah v. 2.0 was used to calculate a JWL equation of state for the RDX/wax donor. The shock hugoniot for PMMA, $u_s = 2.561\,\text{m/s} + 1.595 u_p$, were taken from ref 4. The calculated peak pressure in the shock wave after traveling 22.5 mm in the PMMA buffer was 62 kbar (6.2 GPa). This is very close to the result for the standard NOL LSGT with a 2 by 2 inch thick pentolite donor which generates a peak pressure of 61.5 kbar at that thickness[4].

Cylinder tests

The cylinder test is a standard experiment to evaluate the metal accelerating performance of a HE and the classical method to calibrate equation of states of the reaction products. Cylinder tests have been performed on guntol (50 wt% FOX-12 and 50 w% TNT) and two aluminized guntol-based compositions with different aluminum qualities (H2 and A100)

Charge Descriptions

Three different explosives were tested; melt cast guntol (50/50 wt% FOX-12/TNT), guntonal 1 (42.5/42.5/15 wt% FOX-12/TNT/Al-H2) and guntonal 2 (42.5/42.5/15 wt% FOX-12/TNT/Al-A100) provided by Eurenco in Karlskoga. A full-wall copper cylinder, (length 350 mm, inner diameter 60 mm, wall thickness 6 mm) filled with the investigated HE was used. A plane wave lens initiated the charge. Each charge consisted of several stacked cylinders of HE which were machined on its surface to tight-fit into the cylinder and minimize air gaps between the cylinders. The average density of each cylinder was obtained by measuring their height, diameter and weight. The highest density cylinders were positioned close to the slit position. The charge geometry for the guntol shot is shown in Figure 4, the other shots were similar.

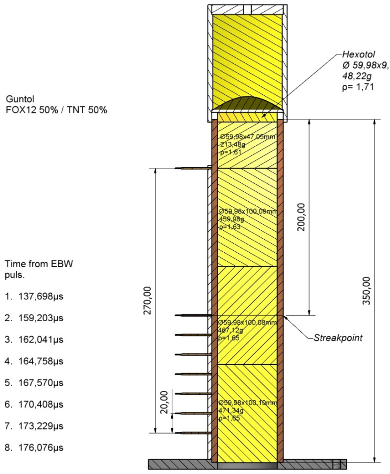

Fig. 4. Cylinder test charge.

Experiments

All three experiments were conducted with the same set-up. The description and presentation here is for guntol but the other experiments were done in the same way.

The detonation velocity was deduced by measuring the detonation front arrival time to 7 piezzo-pin transducers at 20 mm spacing over a length of 120 mm along the cylinder axis. An additional pin was placed close to the initiation point to obtain an average velocity over a longer distance. The cylinder wall motion at a position 200 mm downwards on the cylinder was measured by back-illuminating the cylinder with a argon flash bomb and collecting the transmitted light through a 50 µm thin slit which was recorded by a Cordin rotating mirror camera, model 116, used in streak mode, see Figure 5 and Figure 6. The selected streak speed was 4 mm/µs. The streak image was scanned in an optical flatbed scanner in transmission mode. The scanning resolution was 1600 dpi, giving a time resolution of 3.97 ns/pixel and a displacement resolution of 38 µm/pixel. The edge between the expanding cylinder and air was extracted by image processing and the radial displacement velocity was calculated with digital Savitzky-Golay filters[5].

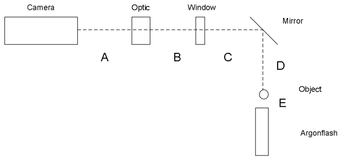

Fig. 5. Schematic drawing of the cylinder wall displacement measurement.

Fig. 6. Photo of experimental set-up showing the argon flash bomb located behind the HE-filled copper cylinder.

Results

The detonation velocities were obtained by linear regression of the measured arrival times. The estimated detonation velocity is slightly lower when all 8 pins are included in the analysis than when only the 7 pins around the slit are included in the analysis. This is probably due to the lower density, and hence lower detonation velocity, of the HE-cylinders closer to the initiation point. Detonation velocities were also calculated using the thermo-chemical software Cheetah, version 2.0, using the BKWC-library. For the aluminized explosives calculations were done both assuming instantaneous and no aluminum reaction respectively. The results are presented in Table 2. The recorded cylinder wall expansions at the slit position are presented in Figure 7.

Table 2. Detonation velocities for the tested HE. Measured detonation velocities using data only from pins around the slit and from all pins (values in brackets) respectively. Calculated velocities are assuming instantaneous and no aluminum reaction (values in brackets) respectively.

Composition	**Density (g/cm^3)**	**Meas. D (m/s)**	**Calc. D (m/s)**
FOX-12	1.66	7 870	7 810
FOX-12/TNT (50/50)	1.652	7 120 (7 040)	7 330
FOX-12/TNT /Al-H2	1.795	7 160 (7 130)	7 160 (7 450)
FOX-12/TNT /Al-A100	1.771	6 920 (6 900)	7 080 (7 340)

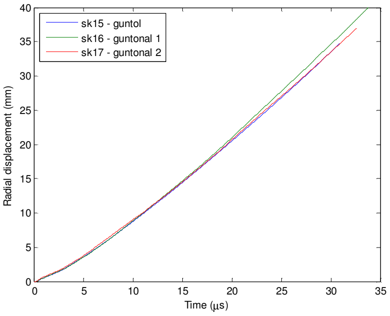

Fig. 7. Radial cylinder wall displacements for GuDN/TNT (blue), GuDN/TNT/Al-H2 (green) and GuDN/TNT/Al-A100 (red) respectively.

JWL-parameters

The Jones-Wilkins-Lee (JWL) equation of state (EOS) is a very popular EOS for HE and is implemented in most hydro codes. It is known to reproduce cylinder wall motions in cylinder tests very well for most HE. The JWL EOS has the form

$$p = A\left(1-\frac{\omega}{R_1 v}\right)e^{-R_1 v} + B\left(1-\frac{\omega}{R_2 v}\right)e^{-R_2 v} + \frac{\omega E}{v}$$

where $v = V/V_0 = \rho_0/\rho$ is the dimensionless specific volume, E is internal energy per initial volume unit (i.e. specific internal energy multiplied by initial density, $E = \rho_0 e$) and A, B, R_1, R_2 and ω are material parameters.

JWL-parameters were calibrated for FOX-12/TNT and FOX-12/TNT/Al-H2 using the measured detonation velocities and wall expansion histories. In the parameter fitting the total detonation energy E_0 and the polytropic exponent ω were fixed to the Cheetah-calculated values and the detonation velocity to the measured value. This leaves three free parameters to vary.

The cylinder test was simulated using the HI-Dyna2D code and the radial displacement and velocity were sampled by the dynacyl-routine. The JWL-parameters where adjusted to get a good agreement between the measured and calculated cylinder expansion under the constraint that the measured detonation velocity should be reproduced exactly. For the FOX-12/TNT/Al-H2 formulation it was necessary to lower the detonation energy slightly to get good agreement with the measured cylinder expansion. The new parameters are presented in Table 3 and 4 together with the Cheetah calculated parameters. The measured and calculated radial displacements and velocities using the Cheetah calculated and calibrated JWL-parameters respectively are shown in Figure 8 and 9.

Table 3. JWL-parameters for FOX-2/TNT 50/50 wt% at density 1.652 g/cm^3 calculated using Cheetah 2.0 with BKWC-library and fitted to measured detonation velocity and cylinder streak record.

	D (m/s)	**P_{CJ} (GPa)**	**A (GPa)**	**B (GPa)**	**R_1**	**R_2**	Fel! Objekt kan inte skapas genom redigering av fältkoder.	**E_0 (kJ/cm^3)**
Cheetah 2.0 BKWC	7 335	20.95	719.2	6.550	4.91	1.09	0.34	7.443
Fit to exp. data	7 120	22.11	402.5	5.376	4.2	1.8	0.34	7.4

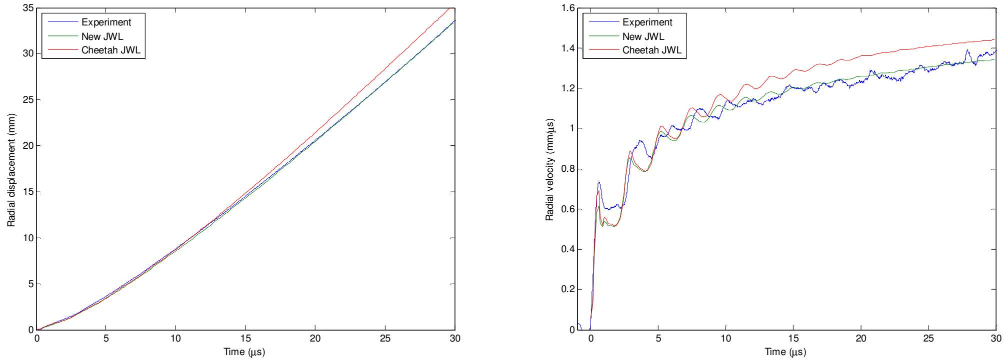

Fig. 8. Radial wall displacement (left) and velocity (right) history for GuDN/TNT from experiment (blue) and Dyna2D-simulations using Cheetah calculated JWL-parameters (red) and recalibrated JWL-parameters (green) respectively.

Table 4. JWL-parameters for FOX-12/TNT/Al-H2 42.5/42.5/15 wt% at density 1.795 g/cm^3 calculated using Cheetah 2.0 with BKWC-library assuming 100, 20 and 0 % Al-reaction respectively. Also shown are parameters fitted to measured detonation velocity and cylinder streak record.

	D (m/s)	**P_{CJ} (GPa)**	**A (GPa)**	**B (GPa)**	**R_1**	**R_2**	Fel! Objekt kan inte skapas genom redigering av fältkoder.	**E_0 (kJ/cm^3)**
Cheetah 0% Al	7 451	20.99	1228	6.01	5.38	1.11	0.28	7.131
Cheetah 20% Al	7 431	21.43	1165	7.15	5.36	1.08	0.25	7.965
Cheetah 100% Al	7 158	22.49	709.5	8.513	4.94	1.04	0.27	10.80
Fit to exp. Data	7 160	23.47	493.5	1.811	4.30	1.70	0.27	10.00

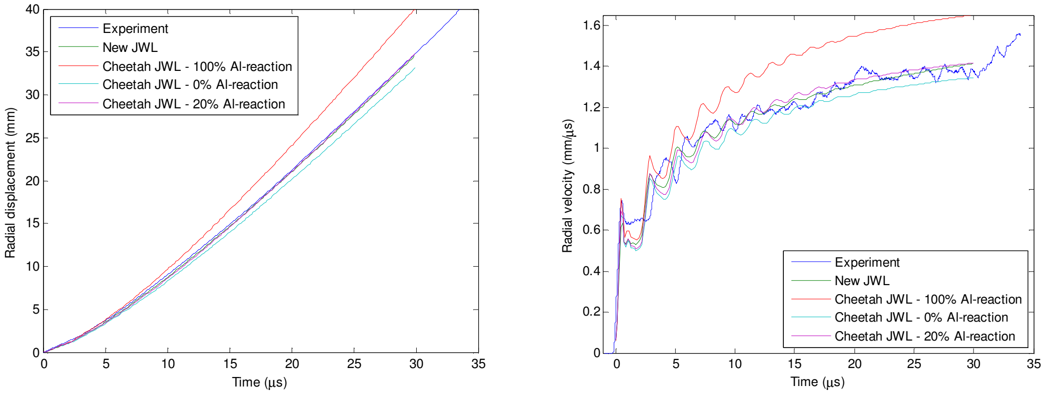

Fig. 9. Radial wall displacement (left) and velocity (right) history for FOX-12/TNT/Al-H2 from experiment (blue) and Dyna2D-simulations using Cheetah calculated JWL-parameters assuming different aluminum reaction extent and recalibrated JWL-parameters (green) respectively.

Discussions and Conclusions

The shock sensitivity of guntol as measured by LSGT was lower than most available melt cast low-cost main warhead fills. The minimum initiation pressures for some selected HE are compared in Table 5. Our set up for the LSGT was somewhat different from the standard NOL LSGT but numerical simulations showed that the peak pressure at the critical thickness was almost identical to the standard test.

Table 5. Comparison of shock sensitivity as measured by LSGT for selected HE.

HE	**Density (g/cm^3)**	**50 % point pressure (kbar)**
Guntol (50/50)[1]	1.63	62
TATB[2]	1.82	66.1
H-6 (cast)[2]	1.75	21.5
TNT (cast)[2]	1.58-1.61	21.2-54.1
Comp B[2]	1.69-1.70	16.9-20.5

[1] FOI LSGT as described in Sec. 2.

[2] NOL LSGT results from Ref. 3.

The calculated detonation velocities were slightly higher than the measured values, the difference being greatest for guntol and the aluminized compositions assuming no aluminum reaction. This is an expected behavior since the tested explosives are non-ideal and size effects are present in the experiments that reduce the detonation velocities compared to the infinite size values. The calculations are based on the CJ-theory which assumes one-dimensional flow corresponding to infinite sized cylinders. It has been proposed[6] that for most aluminized explosives only a small fraction of the aluminum burn in the reaction zone, defined as the region between the detonation front and the sonic plane, even for very large charges. This effect is due to the mole reducing effect of aluminum burning and is explained by the eigenvalue detonation model. Hence, the infinite size detonation velocities are probably closer to the calculations assuming no or little aluminum reaction. The aluminum will however burn behind the sonic plane and the JWL-parameters and detonation energies will be wrong if aluminum reactions are not included. The calculated wall expansion using Cheetah JWL-parameters assuming 20% Al-reaction gives rather good agreement with the experimental results. The remaining aluminum will probably burn at a later time, increasing the performance in blast and UNDEX applications. This calls for the need to include the afterburning of additional fuel, such as aluminum, in the hydro code models.

The metal accelerating performance, as measured by the radial wall velocity, of the three tested *explosives were quite similar*. The aluminized formulation with H2 Al-particles had a slightly better performance than the other two. For other applications, e.g. blast effects and underwater explosions, the aluminized explosives are probably superior. The metal accelerating performances of the formulations are similar to HNS, better than TNT but less than CompB.

Acknowledgment

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High Performance Green Solid Propellants Based on ADN

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Abstract

State of the art solid propellants are based on the oxidizer ammonium perchlorate (AP). Unfortunately, AP has negative impacts on the environment and on personal health. Possible substitutes are thus of interest. One material that has the potential to replace AP is ammonium dinitramide (ADN). This paper presents recent achievements in the development of ADN-based solid propellants.

Introduction

Solid propellants for space applications are today widely used in large boosters for launchers and, to some extent, for in-space propulsion. Propellants for these applications are based on the oxidizer ammonium perchlorate (AP), NH_4ClO_4, and aluminum powder embedded in a polymer binder matrix. AP is in many ways an excellent oxidizer due to its relative low hazardness and the possibility to tailor its ballistic properties. However, AP has negative impacts on the environment and on personal health.

Perchlorate anions (ClO_4^-) has been found in drinking water supplies throughout the southwestern United States [1]. At high enough concentrations, perchlorate can affect thyroid gland functions, where it is mistakenly taken up in place of iodide. Based on current information, perchlorate may be a problem for water supplies in some regions of the US [1].

Recently the US Department of Defense organized workshop on advanced strategy for environmentally sustainable energetics identified AP as one of the key environmental, safety, and occupational health issues [2]. Apart from impacting the thyroid activity in humans, AP forms vast amount of hydrochloric acid on combustion. For instance the space shuttle and the Ariane 5, generates 580 and 270 tons of concentrated hydrochloric acid respectively per launch.

Possible substitutes to AP are thus of interest, but useful alternatives are rare. One material that has the potential to replace AP is ammonium dinitramide (ADN). The structure of ADN is shown in Figure 1. Calculations show that ADN-based solid propellants can achieve performance equal to or higher than that of the conventional AP-based propellants [3].

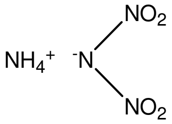

Figure 1. Structure of ADN.

Due to their large size, launcher boosters may not be the first application for such a new developed propellant. Smaller and less cost sensitive applications seem to be a better choice. ADN-based solid propellants are thus more likely to initially be used for in-space propulsion applications.

Today the majority of spacecrafts use liquid propulsion systems. Liquid rockets provide high performance and adjustable thrust, but they are complex, costly and use toxic propellants such as hydrazine, mono-methyl hydrazine (MMH) and nitrogen tetroxide (NTO).

When adjustable thrust is not required, solid propellants possess benefits such as storability, compactness and simplicity. No propellant delivery system is required which enables a huge improvement in reliability and cost. One disadvantage is however their relatively low specific impulse. Despite this, solid propellant rocket motors have been used to propel spacecrafts in numerous missions since first used in the upper stage of the first U.S. Satellite Explorer I in 1958. More recently solid propellant rocket motors are considered to be used for the ascend module in the Mars sample return mission [4]. Replacing the AP-based propellants in such applications with ADN will provide higher performance and lower environmental impact.

The development of ADN-based propellants in Sweden is driven by military needs for high performance minimum-smoke propellants for tactical missile applications. Thus non aluminized formulations are currently developed. For space applications, where there are no minimum smoke requirements, aluminium powder are likely to be included to increase the specific impulse.

Performance

To perform a correct performance comparison between different propellants the complete propulsion system must be taken into account. This is a complex task and requires a specific spacecraft to be studied. In this case only the theoretical vacuum specific impulses were calculated for different ADN-based solid propellants and for the liquid bi-propellant combination NTO/MMH. The calculations were performed using the NASA CEA 600 computer program [5, 6]. An infinite area combustor and shifted equilibrium during expansion were assumed. Typical combustion chamber pressure for solid rocket motors (70 bar) and liquid rocket engines (10 bar) were used and the nozzle area expansion ratio were in all cases equal to 50.

The binder considered in combination with ADN was polyglycidylazide (GAP). GAP was chosen because it:

- is compatible with ADN
- improves performance
- provides good ballistic properties in combination with ADN.

The thermochemical inputs used in the calculations are shown in Table 1.

Table 1. Input for the thermochemical calculations[a].

Material	Formula	ρ (g/cm^3)	ΔH_f (kJ/mol)
ADN[b]	$NH_4N(NO_2)_2$	1.81	-148
Al	Al	2.70	0
GAP	$C_3H_5N_3O$	1.29	+114
MMH	CH_6N_2	0.87	+54
NTO	N_2O_4	1.45	-20

a) all data from the ICT – Database [7] unless otherwise stated.
b) data from Östmark et al. [8].

The maximum solid loading in a propellant is generally limited by the viscosity of the uncured propellant slurry and must be low enough to allow casting. To obtain realistic results the maximum solid loading was in this case limited to 80%. The mixing ratio for the liquid bi-propellant combination NTO/MMH was two to one, similarly as used in the AESTUS rocket engine[i]. The results from the thermochemical calculations are shown in Table 2.

Table 2. Results from the thermochemical calculations.

Propellant	Mixture	I_{sp} (s)	ρ (g/cm^3)	$\rho \cdot I_{sp}$ (gs/cm^3)
ADN/GAP	70/30	301	1.61	485
ADN/GAP	80/20	313	1.67	523
ADN/Al/GAP	70/10/20	327	1.73	566
ADN/Al/GAP	65/15/20	332	1.76	584
ADN/Al/GAP	60/20/20	335	1.78	596
NTO/MMH	2/1	340	1.19	405

The results show that the theoretical specific impulse for ADN/Al/GAP with 20% Al approaches that of NTO/MMH. At a solid loading of 80%, the ADN-based propellants have densities 40 to 50% higher compared to NTO/MMH. This implies that the density specific impulses ($\rho \cdot I_{sp}$) are about 30 to almost 50% higher for the ADN-based propellants compared to NTO/MMH. Propellants with high Al-content is known to have lower performance than predicted due to Al particle agglomeration and two phase flow. Taking this into account ADN-based propellants still seems competitive due to their high densities.

Propellant formulation

The ADN used was procured from EURENCO Bofors in Sweden, which has been producing dinitramides on a pilot plant scale since 1996. To obtain a castable propellant formulation with low viscosity and high solid loading, particles with minimum spatial extension are required. For this reason spherical particles are preferred. The particle shape of ADN as received from EURENCO is needle shaped and thus not suitable for formulation.

At FOI a method to produce spherical ADN particles, prills, have been developed [9]. The prills are produced by spraying molten ADN through a nozzle. In the nozzle the molten ADN is atomized to form droplets which then solidify to the desired prills seen in Figure 2.

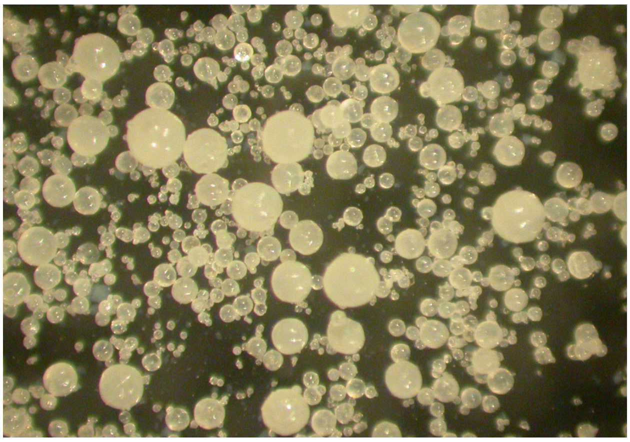
Figure 2. Spray prilled ADN.

The particle size can be controlled to some extent by varying spray nozzle size and pressure. Typical particle size distributions for the fine and coarse prills produced are shown in Table 3, Figure 3 and in Figure 4.

Table 3. Typical particle size distributions of prilled ADN.

Grade	d_{10} (µm)	d_{50} (µm)	d_{90} (µm)
Fine	30	60	120
Coarse	30	200	400

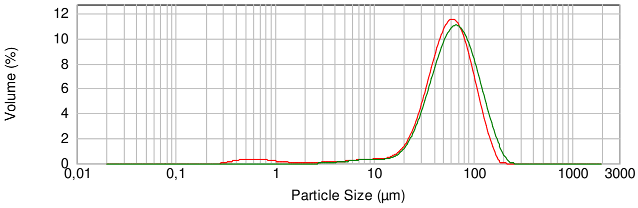

Figure 3. Particle size distribution of fine ADN prills.

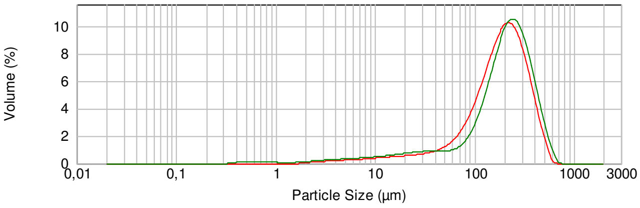

Figure 4. Particle size distribution of coarse ADN prills.

Currently the prills are produced using up to 250 g of ADN per batch. However, with modifications the method can be run continuously making the technology suitable for industrial production. Fumed silica (Cab-O-Sil) is added to the prilled material as an anti-caking agent. Without any anti-caking agent, the prilled ADN cakes after a short time of storage, even at dry conditions.

The prills and the as-received ADN were characterized with respect to particle density, tap density, melting point and purity. The results are shown in Table 4.

Table 4. Typical properties of as-received ADN and coarse prills [10].

	As received	Prilled
Amount Cab-O-Sil (%)	--	0.5
Particle density (g/cm^3)	1.81	1.79
Tap density (g/cm^3)	0.86	1.11
Melting point (°C)	93.2	92.5
Nitrate content (%)	0.03	0.08

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[i] http://cs.astrium.eads.net/sp/LauncherPropulsion/Aestus-Rocket-Engine.html

From the results in Table 4 it can be seen that the particle density decreases by 1%, but the tap density of the prilled material increases by 30%. The decrease in density might be due to inclusions in the particles formed during the spraying process. The increased tap density is important to obtain high solid loading.

The somewhat higher nitrate content in the prilled material is probably due to degradation of ADN during the prilling. The increased nitrate content might be responsible for the change in melting point.

The GAP used was obtained from EURENCO France (Lot: 76S04 [11]). Two types of propellants have been developed, one with 68% coarse, and the other with 70% coarse and fine prilled ADN. The relatively low solid loadings were chosen to ensure low viscosity and hence good quality of the casted propellants. Based on our experience, it is now clear that the solid loading can be increased.

Batches up to 3.75 kg have been mixed using an IKA HKV 5 high performance kneader and samples for characterization and motor testing have successfully been produced.

The thermal stability of ADN/GAP-based propellants was measured using a heat flow calorimeter. According to STANAG 4582 [12], the heat flow should not exceed 63.1 µW/g at 75°C during 19 days. Figure 5 show the result from the testing of the propellant containing 70% ADN. As seen the propellant has an excellent thermal stability with a heat flow well below the acceptance limit.

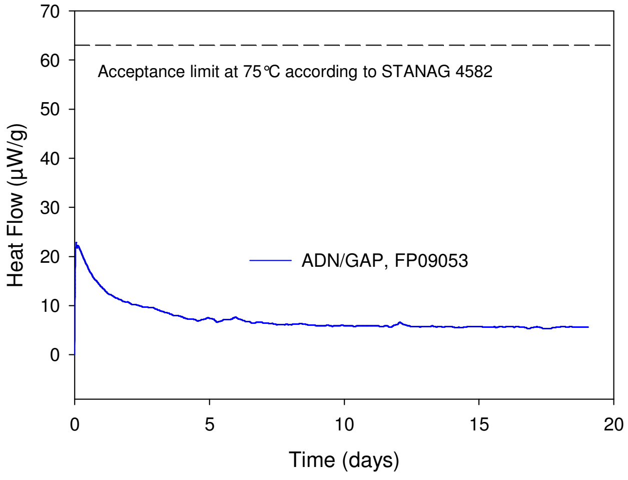

Figure 5. Thermal stability at 75°C of an ADN/GAP-propellant containing 70% ADN.

Ballistic testing

The burn rate was determined using a strand burner. The results were evaluated using Eq. 1,

$$r = ap^n \tag{1}$$

where p is the combustion pressure, in MPa, and r is the measured burning rate in mm/s. The pressure exponent, n, and the burning rate constant, a, where determined by linear regression analysis of the data in a log-log diagram. The results are shown in Figure 6 and Table 5.

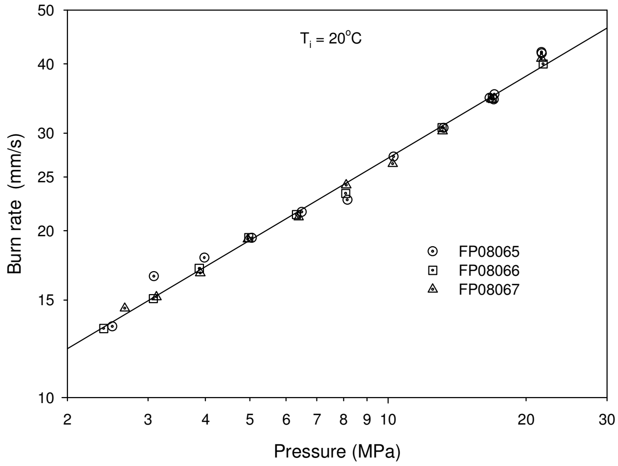

Figure 6. Burn rate as a function of pressure. Propellant: 68% ADN in a GAP-based binder.

Table 5. Evaluated constants in Eq. 1 and burn rate at 5 and 10 MPa.

Amount ADN	a	n	$R^{2\,a}$	r_5 (mm/s)	r_{10} (mm/s)
68%	8.7	0.49	0.993	19	27

a) R^2 is the linear correlations coefficient.

The burn rate is high and the burn rate exponent, n, is 0.49 in the examined pressure interval. The propellant containing 70% ADN had a somewhat lower pressure exponent and a higher burn rate at low pressures. This propellant was used for casting grains for motor testing. Four 400 g grains were casted and test fired, Figure 7.

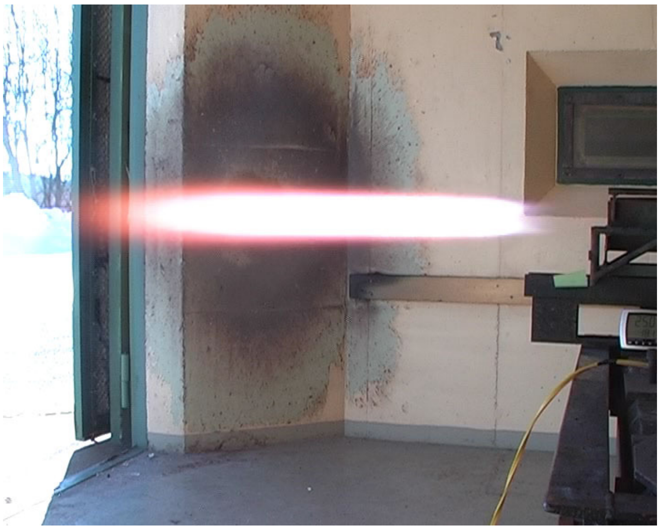

Figure 7. Test firing of a 400 g ADN/GAP grain containing 70% ADN.

Recently, three 3 kg case bonded grains were casted in steel cartridges, Figure 8. A HTPB-based insulation material was used between the steel cartridge and the propellant. Some minor machining was needed after casting but the propellant was easy to machine yielding a smooth surface. The 3 kg grains will be fired during May 2010 in order to determine the specific impulse.

Figure 8. Case bonded 3 kg grain cartridges for motor testing.

Conclusions

ADN based propellants provides higher specific impulse compared to AP. For space applications they are first likely to be used for in-space propulsion. The theoretical specific impulse for ADN/Al/GAP with 20% Al approaches that of NTO/MMH and has a 50% higher density.

To obtain castable propellant formulations with low viscosity and high solid loading spherical particles are needed. Such ADN particles, called prills, can be produced by spraying molten ADN through a nozzle. By this method the tap density increases by 30%. Adding 0.5% fumed silica prevents the prills from caking. The spray prilling method seems suitable for industrial production.

Batches up to 3.75 kg of an ADN/GAP-propellant containing 70% bimodal ADN have been mixed. The low viscosity of the propellant shows that the solid loading can be increased.

Strand burner experiments shows that ADN/GAP-based propellants have a high burn rate and a pressure exponent between 0.4 and 0.5. Test firing of 400 g grains have been performed. 3 kg case bonded grains were casted as well. They will be fired during May 2010.

Acknowledgment

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New High Energy Oxidizers: A QM study

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Abstract. A quantum mechanical study of a new class of high energy oxidizers has been done using high level density functional theory(DFT). The stability of two novel high energy oxidizer with potentially higher performance than ADN, 1-oxido-pentazolate and 1,3-dioxido-pentazolate has been studied. The 1-oxido-pentazolate ion has a barrier towards decomposition to N_3^- and N_2O of 36.4 kcal/mole and towards N_2 and N_2O^- of 27 kcal/mole. This compared to the decomposition barrier of the pentazolate ions at 25.6 kcal/mole, indicates that the 1-oxido-pentazolate ion is at least as stable as the pentazolate ion. The stability of possible starting materials, e.g. 2-phenyl-2H-pentazole-4-oxide, and synthetic routs has also been studied.

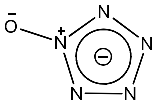
Introduction

For decades the oxidizer Ammonium Perchlorate (NH_4ClO_4) or AP has been used as an oxidizer for propellants and underwater (UW) explosives and not without reason. It has many favorable characteristics, like proper burning characteristics, cheap, good impact and friction properties. However, un-reacted ammonium perchlorate ending up in soil [1] and water [2] is a growing concern. When used in solid propellant its combustion products are corrosive and harmful for health and environment. Stricter regulations on the presence of the AP in the environment, most notably in (ground) water are currently being proposed. As such the replacement for this oxidizer has become a high priority, in some cases even top priority. One obvious candidate is Ammonium Dinitramide (ADN)[3-6] which currently is evaluation for potential use in both propellant and underwater applications.

In the search for oxidizers with even higher performance, polynitrogen and high nitrogen compounds have in recent years received considerable interest as potential candidates for high energy density materials (HEDMs). A large number of QM studies have been presented on N_x and N_xO_y compounds (see Chapter 8 and 9 in reference 7 and references here in). In many cases the barrier towards decomposition is very low, e.g. for *cyclic*-N_4O 2.0 kcal/mole[8] , which makes then nearly unusable as oxidizers. A break-through in the quest for polynitrogen compounds came in 1998 with the successful synthesis off the novel V-shaped N_5^+ ion[9, 10], the first new stable all-nitrogen compound in more than 100 years. Christe and coworkers have since reported the preparation and isolation of several N_5^+ salts[11-13]. This recent breakthrough has prompted the search for new all-nitrogen and high nitrogen compounds. Calculations have shown that *cyclo*-$N_5(D_{5h})$ is the most stable isomer of N_5^- toward fragmentation to

N_3^- and N_2, with a barrier of around 25.6 kcal/mol in the gas phase [12].

The formation of *cyclo*-N_5^- (D_{5h}) from arylpentazoles in mass spectrometry experiments has recently been reported[11, 13, 14]. Indirect proof of an electrochemical synthetic rout has also been presented[15]. It is also known that n-oxy ring systems are more stable than pure nitrogen rings[16]. This and the existence of the pentazolate ion and a potential electrochemical synthetic rout for it makes it interesting to look into the novel n-oxy-pentazolat compounds, I and II, as new oxidizers.



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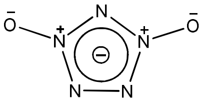
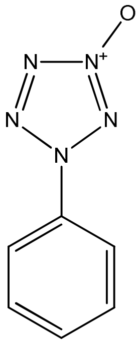


II

This paper presents a QM study of two novel high energy oxidizer with potentially higher performance than ADN, 1-oxidopentazolate (I) and 1,3-dioxidopentazolate (II). Stability of potential starting materials starting material (III - V) for the synthesis of compound I and reactivity compared to that off arylpentazoles and the pentazolate ion is also included. An electrochemical synthetic rout is also proposed.



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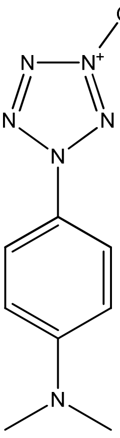

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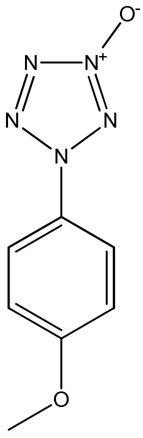

V

Computational Details

The stability of n-oxy-pentazolates and aryl-pentazole-oxides has been studied using high-level density functional theory (DFT). Stationary points, transition states, and minima were fully optimized at B3LYP/6-31+G(d) and at the B3LYP/6-311+G(d) level of theory. Vibrational frequency analysis (at the same level of theory) was used to characterize the stationary points (all-real frequencies for local stable structure; one-imaginary frequency for transition structure) and to determining the zero-point energy (ZPE) corrections. For transition states, intrinsic reaction coordinate (IRC) calculations were used to confirm the pathways connecting reactants and products. All calculations were performed using Gaussian 09W[17] program packages. The electrostatic potentials (ESP) were evaluated at the B3LYP/6-31+G(d) level of theory and the molecular surfaces was defined by the 0.001 au contour of the electron density. The electrostatic potential is in contrast to most other molecular descriptors, such as atomic charges, a real physical property that is rigorously defined and can be evaluated experimentally as well as theoretically. The electrostatic potential has been used extensively to analyze chemical reactivity and molecular interaction tendencies.

Results

Stable structures as indicated by frequency analyses (all-real frequencies) were obtained for I-V. In order to calculate the stability of I and III, the transition states (TS) for the elimination of N_2O and N_2 was determined, see Figure 1 and 2 and Table 1. The decomposition path for I, see Figure 3, can be seen as a ring opening followed by an elimination of the N_2O molecule, this in contrast to the symmetric elimination of N_2 from the *cyclic*-N_5^- system. The second decomposition path for I is the symmetric elimination of N_2. In Figure 5 is shown a proposed synthetic path for 1-oxidopentazolate. The proposed synthesis route is an oxidation of arylpentazoles followed by an electrochemical induce bond cleavage reaction[15].

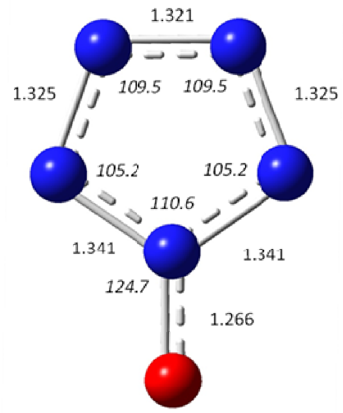

Fig. 1. Geometrical parameters of the structure for the N_5O^- species at the B3LYP/6-311+G(d) level of theory (bond length in angstrom, angels in degree)

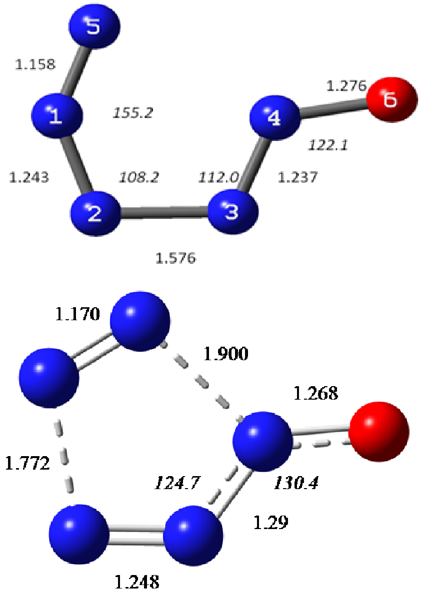

Fig. 2. Geometrical parameters of transition structures for the N_5O^- species towards N_2O elimination (TS1, top) and towards N2 elimination (TS2, bottom) at the B3LYP/6-311+G(d) level of theory. Bond length in angstrom and angels in degrees.

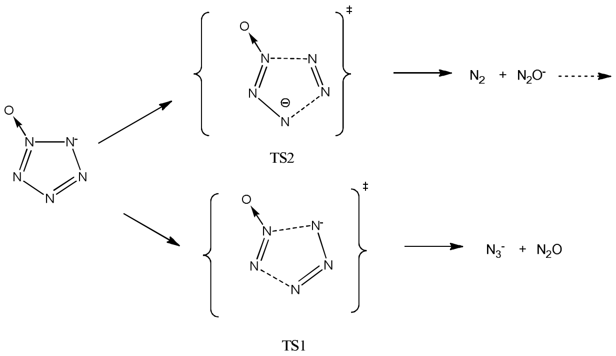

Fig 3. Decomposition paths for N_5O^-

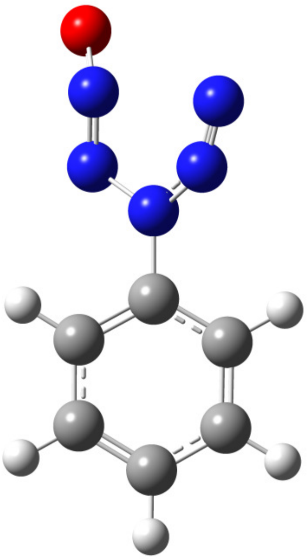

Fig. 4. Transition state structure for the elimination of N_2O from 2-phenyl-2H-pentazole-4-oxide at the B3LYP/6-31+G(d) level of theory.

In Figure 5 some of the possible competing decomposition reactions are also indicated, e.g. reaction 2-4 (R2-R4). No transition state for an elimination of N_2 was found bus should be further investigated. An overview of aryl-pentazole synthesis can be found in the review by Huisgen[18] and reference herein.

Table 1. Energy Barriers toward decomposition for Phenyl-pentazole-4-oxide at B3LYP/6-31+G(d) and at the B3LYP/6-311+G(d) level of theory. All values in kcal/mole. Definition of Energies: = electronic + zero point energy; = + ΔΔH , where ΔΔH is the enthalpy correction; = + ΔΔG , where ΔΔG is the free energy correction. The entropy and enthalpy correction are calculated at 298.15 and 1atm.

	B3LYP/6-31+G(d)			**B3LYP/6-311+G(2df)**		
TS1 for N_5O^-	39.4	40.1	38.7	36.4	37.2	35.5
TS2 for N_5O^-	27.4	28.1	26.7			
TS N_5^- -N_2	26.5	26.8	26.6			
TS:R1	25.6	25.7	24.4			
TS:R2	19.4	19.9	18.6		18.0	16.5
TS:R3	48.8					
TS:R4	No TS was found (to be further investigated)					

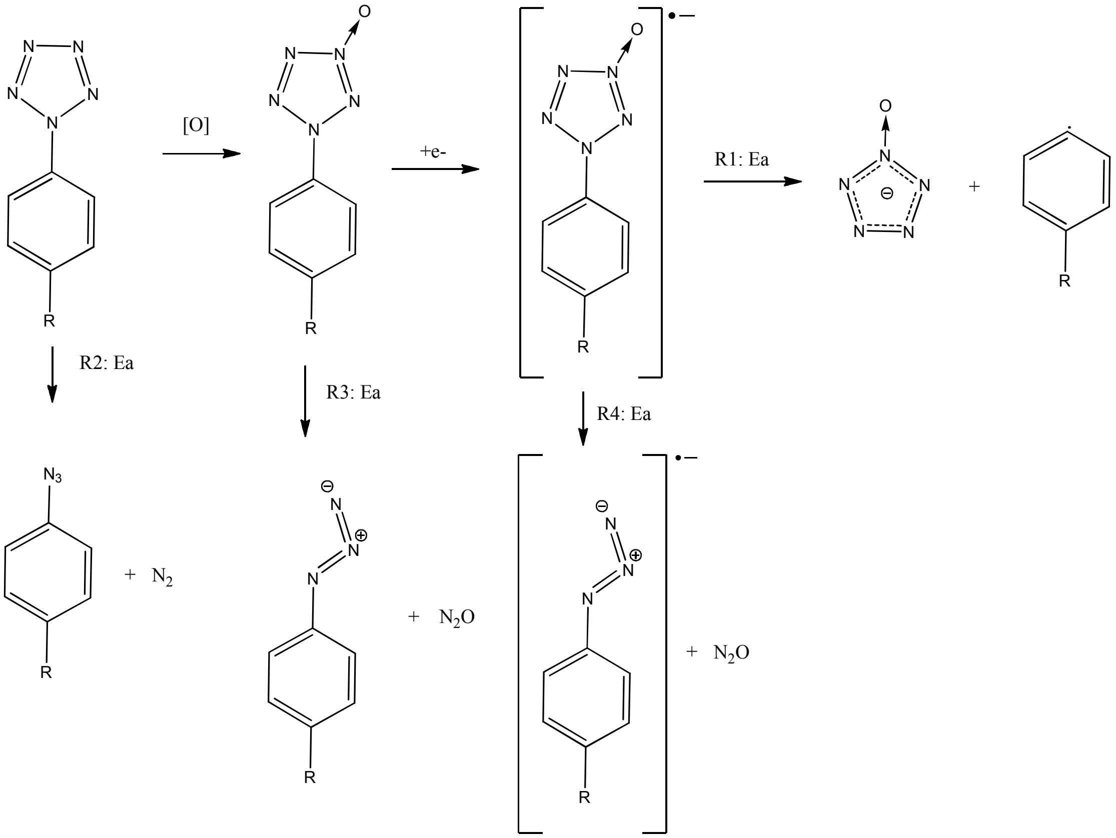

Fig. 5. Proposed Synthetic path for 1-oxidopentazolate.

Conclusions

The n-oxy-pentazolate anion has, using QM calculations, shown to be stable. It has a barrier towards decomposition to N_3^- and N_2O of 36.4 kcal/mole, this is 10.8 kcal/mole higher than the decomposition barrier of the pentazolate ions 25.6 kcal/mole[19]. The barrier towards decomposition to N_2 and N_2O^- is 26.7 kcal/mole. These values indicate, since the pentazolate ion has been detected, that bulk N_5O^- salts could be manageable on a preparative scale if suitable starting material (III, IV or V) could be synthesized. The 2-phenyl-2H-pentazole-4-oxide is surprisingly stable versus elimination of N_2O, $\Delta E=48.8$ kcal/mol. This can be compared with the stability for elimination of N_2 from phenyl-pentazole, 16.5 kcal/mol. The increased stability on the Phenyl-pentazole-oxide also strengthens the conclusion of that n-oxy-functionality increases the stability of cyclic nitrogen compounds. According to the QM calculations, the proposed synthetic route seems to be viable, the main question is if it is possibly to do a n-oxidation of t the Aryl-pentazoles, which are known to be very unstable at normal temperatures[20].

The QM calculation presented in this paper support the existence of the novel n-oxy-pentazolat compounds as new oxidizers and shows that they could probably be synthesizes for real measurements and tests.

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