

ACDA6020 Presentation technical summary and reflection

Additives in Nitrocellulose Based Gun Propellants: Performance, Chemical stability and the environment

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Introduction

Propellants are materials that convert stored chemical energy into kinetic energy. They achieve this through the evolution of hot expanding gasses, which do work to a projectile. This technical summary reflects specifically on propellants used in gun systems with a bore of 20mm or greater. Propellants are split into several subcategories, and this will focus on 3 of them, Single base, Double base and Triple base. All of these propellants can be modified to achieve specific effects or exhibit differing properties. Rocket propellants, whilst similar in function will not be considered. Whilst base propellant chemistry defines energetic output, additive selection ultimately governs whether performance gains are achievable within safety, environmental, and lifecycle constraints.

Background

Gun propellants have been in use for hundreds of years with the earliest of which black powder described in Chinese texts in AD 1044 [1]. Since then, it has developed significantly, especially since the invention of guncotton in the 1840s [2], and the expansion of military industries in the first and second world wars. In order to achieve ideal performance for each task, propellants can be modified; in some cases, this is simply by adding more or less energetic to each munition; whilst in others it requires a complex mixture of additives, to achieve maximum muzzle velocity.

Performance considerations

An ideal gun propellant is one that generates a broad pressure time curve with low temperatures and minimal production of erosive gasses. Unfortunately, reality often means that this ideal cannot be met, such that engineers and chemists are required to make compromises. Within large-calibre systems, maximum pressure and combustion temperature typically dominate additive selection, as exceeding thermal limits accelerates barrel erosion more rapidly than marginal gains in muzzle velocity justify, however this is not the case for all systems, such as high-pressure tank guns, ultimately it is the design teams role to compare the following:

- Desired muzzle velocity
The core requirement for any propelling charge is to accelerate the projectile to a specific, repeatable velocity.
- Maximum pressure
All gun systems have pressure limits which should not be exceeded, as to prevent excessive wear or a potential explosion of the system.
- Bore wear
projectiles cause buildup of deposits and propellant gasses can erode the metal of the barrels, minimising this is essential.
- Temperature of combustion
At the temperatures seen in gun barrels the material properties of the gun barrels can change, with impurities being flash-melted into the structure of the barrels themselves – reducing temperatures can reduce this significantly and increase barrel life.
- Mechanical properties
Propellants have to survive harsh conditions in use including temperature cycling and vibration.
- Grain geometry
Through varying the surface area of a propellant differing burn rates can be achieved, the higher the surface area the greater the burn rate.
- Stealth
Light flashes produced by burning propellant should be minimised, especially for night operations where muzzle flash can identify targets from many miles away.

Additive types

Propellant additives are used to vary the performance of propellant around all the above characteristics. They can drastically change the way in which propellant functions and extend service life significantly for the systems they are used in. The following lists the common categories of propellant additives:

- **Stabilisers**
Enhance thermal stability by absorbing decomposition products which would otherwise autocatalyze additional decomposition
- **Burn rate modifiers**
Can be used to increase or decrease burn rates through variation in reaction pathways or modifying surface area on the surface of grains.
- **Deterrent coatings**
Similar to burn rate modifiers, but slow down ignition of each grain by physically blocking the flame front; this erodes and allows the grain underneath to burn after a slight delay, flattening the pressure/time curve.
- **Decoppering agents**
The Driving band of a projectile in rifled guns deposits copper 'smears' into the barrel, decoppering agents remove this buildup by creating brittle copper alloys after firing, allowing subsequent shots to remove the copper deposits.
- **Binders**
Physically binds propellants and additives together, allowing grains to retain their shape even when exposed to extreme service conditions.
- **Flash suppressants**
2 main ways of functioning – active, passive. Active suppressants react with combustion gasses, lowering temperature and reducing fuels or oxidiser available for secondary combustion. Passive reduces temperatures through acting as heat sinks or physically blocking the light emitted from the combustion process.
- **Coolants**
Act as heat sinks, reducing peak temperatures. Some can decompose endothermically, further lowering flame temperature. Additionally, some deposit in the bore of the gun working as an insulator for future firings, reducing heat build-up in the system.

Stabilizers are found in every propellant system in use by the UK armed forces and are especially critical; all other additives can be used as and when required; enabling the creation of bespoke propellants without major changes to production lines.

Environmental impact

Many additives have overlapping properties; allowing one additive to provide multiple benefits. Historically lead based additives have provided the solutions to ballisticians problems. Unfortunately lead has a multitude of environment and health implications, and many additives containing it such as Lead Stearate are gradually being phased out. Whilst there is currently an exemption in UK REACH (registration, evaluation authorisation of chemicals) regulations [3] for propellants, its use will be reduced over time to reduce the risk to personnel and civilians. However whilst reducing heavy metal contamination, many non-lead-based additives such as

ethyl centralite can also have negative health implications with high toxicity and significant effects to marine life [4]. As such engineers must strike a delicate balance

The future

There are many avenues of progression for both propellants and their additives which engineers constantly exploring to improve performance and reduce environmental effects. Current attempts include manufacturing 'green propellants' either through creating 'green additives' [5] or through modifying the entire propellant structure, replacing traditional propellants with 'LOVA' types. [6] Others look to 3d printing; allowing more complex geometry and burn profiles to be developed [7]

Some suggest that the way forward may be non-energetic – with multiple countries developing railgun type systems [8] [9].

As can be seen there are many potential avenues for exploitation and opportunities for development.

Presentation Reflection

This presentation highlights the importance of propellant additive chemistry in OME system design. Ballistic performance must be balanced against chemical stability, service life, environmental impact, and operational safety. The range of available additives demonstrates how chemists and engineers tailor propellant behaviour to meet specific performance requirements while remaining within pressure, temperature, and compatibility limits and respecting environmental concerns. Maintaining a detailed understanding of propellant function throughout manufacture, storage, and use is critical for OME practitioners, as inappropriate selection or misuse of energetic materials can compromise system reliability and pose significant safety risks.

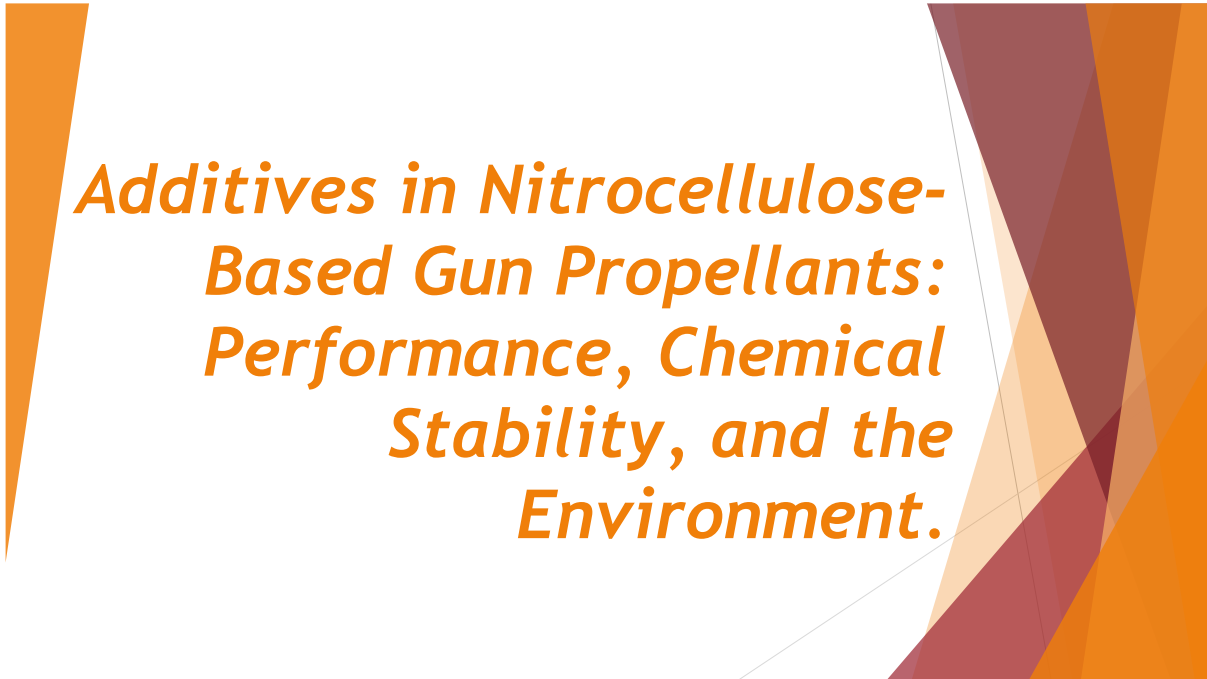
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Annex:

A1- Presentation



Additives in Nitrocellulose-Based Gun Propellants: Performance, Chemical Stability, and the Environment.

Introduction to Gun Propellants

► What are propellants?

Materials which convert chemical energy into kinetic energy.

► What are guns?

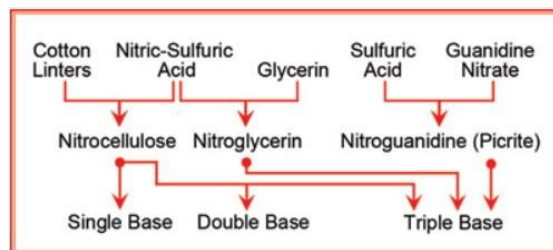
A weapon which fires bullets/shells out of a barrel.



Introduction to Gun Propellants

Main types of propellant:

- Single base (SBP)
- Double base (DBP)
- Triple base (TBP)



- All contain various additives.

[1]

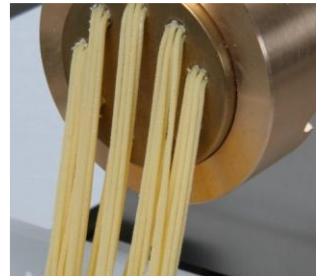
Introduction to Gun Propellants

► Gun vs rocket propellants

- Much faster burn rate.
- Physically smaller grains.

► Production

- Mainly extruded through dies (imagine spaghetti).



Introduction to Gun Propellants

► Gun vs small arms:

- Different geometries will have different effects on the pressures and volume of gas produced.
- Different compositions.

► All propellant burn is a surface effect

► More on this later!



[2]



[3]

Performance Overview - Mechanical Considerations

- ▶ What we want to avoid --->
- ▶ Must avoid massive pressure spikes
 - Keep pressure-time curve as flat as possible
 - Remember that burn rate is dependent on pressure!
 - Problems can compound very quickly
- ▶ Prevent too much pressure, too soon
 - Both chemical & physical modifications to the propellant can help ensure this



Performance-Influencing Characteristics (Physical)

- ▶ Neutral Burning:
 - No net change in surface area as grain burns
- ▶ Progressive Burning
 - Surface area increases as grain burns
- ▶ Regressive Burning
 - Surface area decreases as grain burns



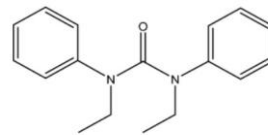
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Service Considerations of Propellants

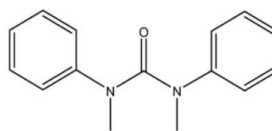
- ▶ Propellant life
 - Stabiliser
- ▶ Bore wear (and wider service implications)
 - Burn rate modifiers
 - Deterrent coatings
 - Decoppering agents
 - Coolants
- ▶ Mechanical properties
 - Binders
- ▶ Stealth
 - Flash suppressants

Stabilisers

- ▶ What they do?
 - Enhance thermal stability, prolonging safe shelf life of propellants.
- ▶ Examples:
 - Diphenylamine (DPA) $C_6H_5NHC_6H_5$
 - ACARDITE II $C_{14}H_{14}N_2O$
 - Ethyl Centralite $C_{17}H_{20}N_2O$ (a)
 - Methyl Centralite $C_{15}H_{16}N_2O$ (b)



(a) Centralite I



(b) Centralite II

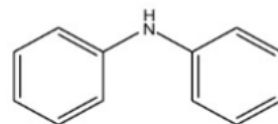
[5]

Stabiliser - Selection

- ▶ Stabiliser selection is determined by
 - Propellant composition
 - Desired performance
 - Expected storage and operation conditions
 - Environmental considerations

Chemistry: Stabilisers

- ▶ Diphenylamine (DPA)
 - NC decomposition is auto catalytic.
 - Produces NO_x and free radicals.
 - DPA neutralises degradation products in SBPs.
- ▶ **Performance benefits:**
 - Prevents autocatalytic degradation and some loss of available energy BUT...
- ▶ ...decomposition of DPA produces carcinogenic products - N-nitrosamine derivatives.



Diphenylamine (DPA)

[5]

Burn Rate Modifiers

► What they do?

- Modify the natural burn rate of the propellant grain...
- which controls pressure within the chamber and barrel.

► Why do we use them?

- Desired performance within safe pressure limits.
- Supply change simplicity - propellants matches the need, reducing costs and increasing supply.

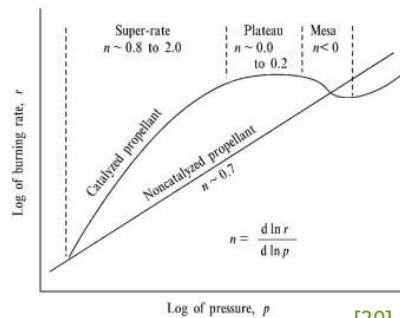
Chemistry: Burn Rate Modifier

► Lead stearate:

- Ballistic modifier in propellants - controls burn rate and reduce sensitivity to pressure changes.

► Environmental Considerations

- Toxic.
- Banned under REACH (Registration, Evaluation, Authorisation of Chemicals (REACH)). Being phased out!

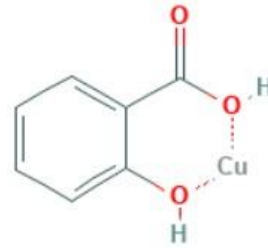


[20]

Examples of Burn Rate Modifiers

Examples include:

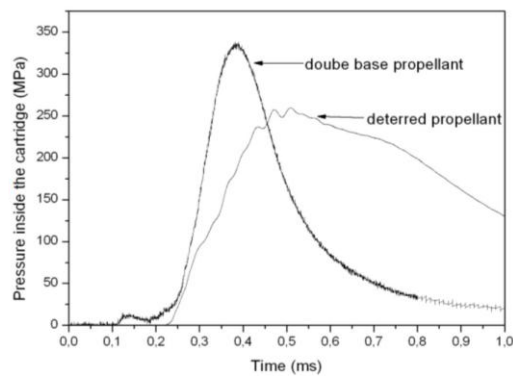
- ▶ Copper salicylate
- ▶ Lead 2,4-dihydroxybenzoate
- ▶ Lead salicylate
- ▶ Lead stearate
- ▶ RDX
- ▶ Oxamide
- ▶ Nanoparticles (e.g. iron oxide)



Copper salicylate [6]

Deterrent Coatings

- ▶ What are they?
 - Thin layer on the outside of the propellant used to control the surface burn rate
 - Physical blockers of the flamefront - slow down ignition of individual grains.
- ▶ Why do we use them?
 - Used to control temperature and gas production - it flattens the curve
 - Important subset of burn rate modifiers - reducing burn rate.



Examples of Deterrent Coatings

Examples include:

- ▶ Ethyl centralite $C_{17}H_{20}N_2O$ - used in SBP, DBP, and TBP.
- ▶ Methyl Centralite -
- ▶ Dinitrotoluene - banned since in EU since 2015.



Waste propellant burn
(unused charges)

Chemistry of Deterrent Coatings

▶ Ethyl centralite

- Ethyl centralite has a multitude of uses, but in this case it is used as a deterrent coating.
- This process does not rely on changing the reactions between the propellant, but rather as a physical barrier to the flame front.
- As the burn continues the deterrent layer is degraded, allowing the grain material beneath to ignite, once this is achieved, the grain will burn at the normal rate as this is a surface only effect.
- This provides a controlled and consistent burn, reducing the likelihood of pressure spikes and flattening the pressure time curve.

▶ Environmental considerations:

- Harmful to aquatic life with long-lasting effects.
- May form carcinogenic degradation products.

Decoppering Agents

- ▶ Why use them?
 - In rifled guns copper from the driving band is deposited after each firing; this can lead to significant buildup which can increase pressures and restrict the projectile.
- ▶ How do they work (top level)
 - Additives form alloys with the copper which are brittle, allowing a follow-up shell to clear the copper deposited by its predecessor.
 - Barrels still need to be cleaned but a lot less regularly.



Examples of Decoppering Agents

- ▶ Tin dioxide SnO_2
- ▶ bismuth trioxide Bi_2O_3
- ▶ bismuth subcarbonate
- ▶ bismuth nitrate
- ▶ bismuth antimonide
- ▶ Lead (foils)
- ▶ Lead oxide
- ▶ Lead carbonate
- ▶ Lead stearate - also acts as a lubricant.



Chemistry: Decoppering Agents

► Chemistry - Bismuth Nitrate

- Initial reduction: Bismuth Nitrate $\text{Bi}(\text{NO}_3)_3 \rightarrow \text{Bismuth Oxide } \text{Bi}_2\text{O}_3 + \text{NO}_2 \text{ and } \text{O}_2$ [7]
- 2nd reduction: bismuth oxide + fuel $\rightarrow \text{Bi} + \text{CO}_2$
- The copper left in rifling alloys with the bismuth forming a more brittle material which is cleared by the next projectile. [8]

► Lifecycle & Environmental Considerations

- Bismuth and Tin Better than lead
- Still can be toxic to plant life.
- Lead difficult to replace - multitude of different jobs

Binders

► What do they do?

- ...what it says on the tin!

► How do they work

- Encapsulating & holding together chemical components...hence why most are polymers
- Preventing break up of grains, not allowing formation of dust

Examples of Binders

- ▶ Ethyl acetate
- ▶ Poly(glycidyl nitrate) (PGN)
- ▶ Poly(3-nitratomethyl-3-methyloxetane) (Poly-NIMMO)
- ▶ Polyvinyl acetate
- ▶ Polyurethane
- ▶ Polyethelene
- ▶ Polybutadiene

Chemistry: Binders

- ▶ Ethyl Acetate [\[9\]](#):
 - Dissolves energetic polymers (due to its nature as a polar aprotic solvent)
 - Allows the mixture to be cast or extruded in a uniform slurry, aiding consistency
 - Evaporates once shaping is complete
 - Does not contribute any energy to the propellant
- ▶ Poly-Nimmo [\[10\]](#):
 - Long-chain energetic polymer
 - Polymer “backbone” contains repeating oxetane units with nitrate ester groups
 - When cured, forms a 3D network that physically encapsulates other particles
 - Strong and crack-resistant when cured (good resistance to mechanical stresses)
- ▶ Lifecycle & Environmental Considerations
 - Ethyl Acetate is a VOC, yet requires proper drying for performance
 - Poly-NIMMO must be given the same consideration as other energetics

Flash Suppressants

- ▶ What's the problem with muzzle flash?
 - Gives away your position
 - Contributes significantly to blast overpressure
- ▶ Active & Passive Chemical Mechanisms:
 - Active: endothermic oxidation, producing inert/cooling gas
 - Passive: absorbing heat
- ▶ Overall flash not governed by additives alone
 - Barrel length still plays a significant part



Examples of Flash Suppressants

- ▶ Potassium Nitrate
- ▶ Potassium Sulphate
- ▶ Potassium Carbonate / Bicarbonate
- ▶ Carbon black



Chemistry: Flash Suppressant

- ▶ Most propellants have a negative Ω , resulting in the formation of CO and H₂. Hot products react with atmospheric oxygen at the muzzle. Both reactions are highly exothermic, contributing to the flash.
 - $2\text{CO} + \text{O}_2 = 2\text{CO}_2$
 - $\text{H}_2 + \text{O}_2 = \text{H}_2\text{O}$
- ▶ Three principal methods of reducing flash:
 - Reduce oxidisers
 - Remove CO and H₂ from combustion products
 - Lower gas temperature

Chemistry: Flash Suppressant

- ▶ Passive: Potassium Sulphate [11]:
 - Sulphate ions are fully oxidized - they do not burn
 - Particles melt and partially condense in the bore
 - Particles absorb heat & lower flame temperature
- ▶ Active: Potassium Carbonate [11]:
 - $\text{K}_2\text{CO}_3 \xrightarrow{\text{heat}} \text{K}_2\text{O} + \text{CO}_2$
 - This decomposition is endothermic, consumes energy, lowers flame temperature
 - CO₂ is non-combustible
- ▶ Environmental and Service Life Considerations
 - Potassium Sulphate: minimal toxicity
 - Potassium Nitrate: can cause eutrophication of water bodies
 - Salts have no effect on chemical stability, but potassium carbonate decomposition products can harm barrels long term

Coolants

- ▶ Why use them?
 - Reducing the temperature of the flame front protects the metal of the barrel from the instantaneous thermal effects.
 - Reduces barrel wear and can enable higher rates of fire.
- ▶ How do they work (top level)
 - Additives can work as thermal heat-sinks reducing the amount of energy available to transfer to the barrel,
 - they can also decompose endothermically, reducing the energy.
 - Some coolants deposit on the bore of the gun, acting as barriers on the next firing.

Examples of Coolants

- ▶ Talc
- ▶ TiO_2
- ▶ Graphite
- ▶ Oxamides



Chemistry: Coolants

► Chemistry

- Talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) acts as a insulating material; reducing heat transfer
- At high temperatures (<800°C) talc can decompose, breaking several O-H bonds [12]
- this reaction is endothermic, cooling temps

► Lifecycle & Environmental Considerations

- Talc is mostly considered environmentally safe
- and is used in a variety of products for use in domestic settings.
- The dusts generated can sometimes be problematic
- Some of the decomposition products can be abrasive

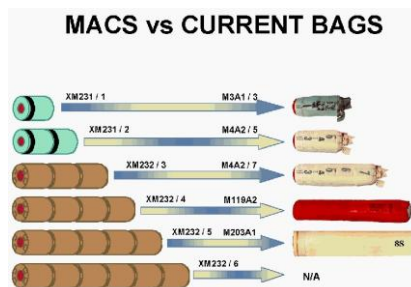
Future of Propellants

► Green propellants and 'better' additives

- Constantly looking for ways to improve environmental effect without compromising performance
- alternatives like 'green coatings' to improve burn rate consistency [13]
- Removal of lead products and derivatives
- Replacement of traditional propellants with LOVA type - reducing lifecycle emissions [14]

► Development of true modular charge system

- Current UK systems use bag or bi-modular charges
- Still can lead to wastage or suboptimal charge stowage which a true MCS would fix.



US Bi-modular charge system

Future of Propellants

► Electro-magnetic gun

- Some nations look to reduce/ remove propellants from certain areas of service
- Japan actively testing their own version of the so called 'railgun' [\[15\]](#)
- US spent millions developing; paused at the start of the pandemic but recently restarted [\[16\]](#)



Future of Propellants

► Variety of Novel approaches:

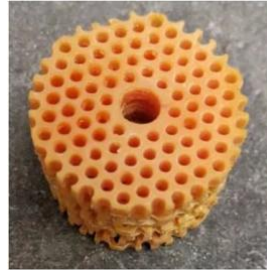
- Electro-thermo-chemical gun [\[17\]](#) - previously too expensive and lacked maturity, will development restart?
- Cellulose free alternatives? - global supply lines getting less reliable - do western nations still want to rely on Chinese imports? [\[18\]](#)
- Propellant flow synthesis - large scale manufacture on UK soil [\[19\]](#)



Future of Propellants

► Novel Geometries

- 3D printing complex geometries - previously couldn't be manufactured [17]
- Different ways of achieving ideal pressure time curves both for rocket and gun propellants [18]



[18]

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Thank you for listening!

► Any questions?