Nano-Structured Propellants and Launch Systems

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Abstract - *A new class of nanostructured composite solid rocket propellants, enabled through the unique materials processing capabilities with supercritical fluids is introduced. The processing technology is green, scalable, flexible, and cost effective, allowing manufacture of energetic particle system designs with optimum physical and chemical compositional specifications. The proposed solid propellant technology is expected to provide significant cost savings through standardization and streamlining of launch operations, faster launch response times, improved, flexible and tailored propulsion systems for design to mission specific requirements, and improved safety in all propellant related manufacturing and launch operations.*

Keywords: NSEP, NanoStructured Energetic Particle, Burn Rates, Specific Impulse, Supercritical Fluids

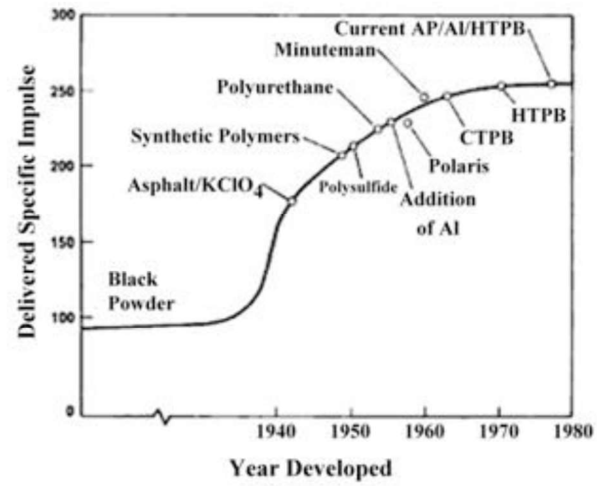

Figure 1. Historical development trend in modern solid propellants.

1 Introduction

The aerospace industry has seen no significant enhancements in performance, safety, or costs of operations of solid propellants since the 1970s. Figure 1 illustrates the development path taken which has culminated in the "modern" solid propellant formulations which are based on Ammonium Perchlorate as the Oxidizer. In these propellants, powdered pyrophoric aluminum powder is used as the fuel. These ingredients are combined and mixed with Hydroxyterminated Polybutadiene polymer which acts as a binder to form the solid propellant. These formulations are designated AP/AL/HTPB or APAL. APAL propellants with the best combination of burn rates and Specific Impulse (I_{sp}) are generally comprised of key ingredients in the approximate ratio of AP (65%)/Al (15%)/HTPB (20%). currently used both commercially and by the government (both NASA and the Military) [1].

It is interesting that numerous other oxidizers have been identified that would provide better performance in propellant burn rates, Specific Impulse (I_{sp}) and energy density, than AP since 1970, however none have found use in commercially available propellants. This is true in spite of the fact that there are numerous problems with APAL propellants, a few of which are: 1) both manufacture and use of these propellants generate significant environmental problems; 2) the need to use excessive quantities of Al to increase burn rates and I_{sp} create problems in combustion performance and motor operation; and 3) the manufacturing process is dangerous, and the properties of the solid propellant limit launch vehicle designs.

2 Stability and Performance of Oxidizers in Solid Propellants

As depicted in Figure 2, there are better oxygen sources available than what we use today. Ammonium Perchlorate (AP) is used as the oxidizer in our most powerful (highest Specific Impulse) commercially available rocket engines (Space Shuttle). In this figure, we see that there are better oxidizers which can be used to make more powerful rocket propellants, among them are ADN (Ammonium Dinitramide) and CL-20 (developed at the Naval Air Warfare Center, China Lake). They are not used commercially due to combustion instability issues and/or difficulty in manufacturing the solid propellants made from them. Not shown on this plot are HNF (Hydrazinium Nitroformate) and NP (Nitronium Perchlorate) that are also more powerful than AP. To allow comparison between oxidizers, the same hydrocarbon polymer was used as both the fuel and binder for all propellants made from the oxidizers shown in the figure. Note also in this figure the high weight fraction of oxidizer which is required to achieve maximum I_{sp}. For AP propellants, for instance, 90% of the propellant blend must be salt-like oxidizer for best performance to be achieved. No propellant manufacturing technique known can produce mechanically stable solid propellants with that high a weight fraction of solid salt-like material.

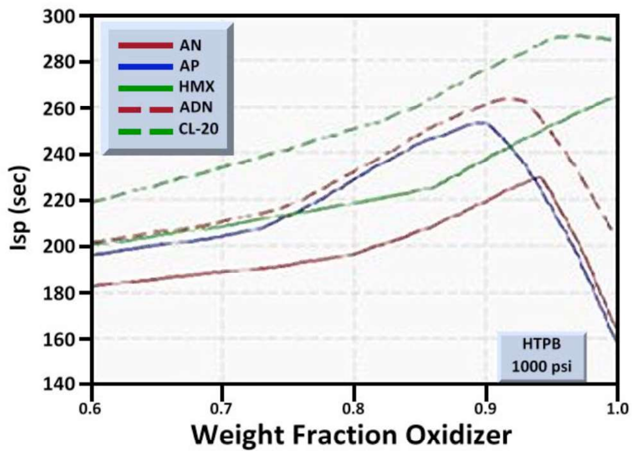

Figure 2. Specific Impulse (I_{sp}) as a function of weight fraction of various oxidizers.

3 Burn Rates of Solid Propellants

Generally, the Burn Rate of a solid propellant is directly related to how hot the oxidizer burns [2, 3]. Again, in Figure 3, we see that AP has a low flame temperature, and therefore a low burn rate. Many oxidizers, as shown in the figure, have much higher Burn Rates. The Burn Rate of propellant significantly affects the design of the engine to achieve maximum performance, and can change with time as the propellant grain is consumed during flight. Currently available commercial propellants are composed of an essentially uniform composition propellant grain. As the rocket burns, since the burn rate remains essentially constant while the amount of propellant undergoing combustion increases as a function of time, the performance of the rocket engine also changes as a function of time.

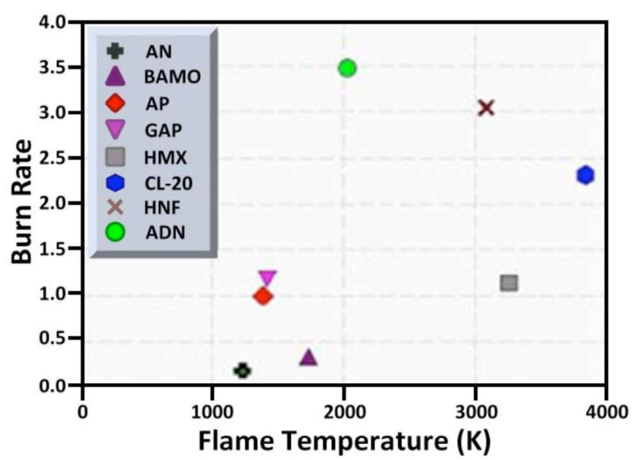

Figure 3. Relative Burn Rates of various potential and current oxidative solid propellant ingredients.

The grain composition is therefore designed for the best average performance for the launch vehicle, which is well below the theoretical optimal performance the rocket can achieve. *The ideal situation would be to modify burning rate characteristics of the propellant as a function of changing chamber geometry to achieve maximum performance of the rocket at all times during the powered flight. The ability to adjust the Burn Rate as a function of time during the flight would better achieve maximum theoretical performance of the engine.*

4 The Affect of Energetic Fuels on the Performance of Solid Rocket Propellants

Many energetic fuels that will improve *both* the Specific Impulse and Burning Rate performance of a solid propellant cannot be used in commercial propellants due to both the current manufacturing technology limitations and the final structural form of the solid propellant [2]. The process for making today's solid propellants is to simply mix all the ingredients together in a big pot, just as if you are making bread dough. A very large amount (about 80%) of salt-like solid oxidizer and powdered Aluminum fuel is used, so the consistency of a rocket propellant after mixing is like bread dough made with too much flour [4]. Casting that stiff dough into the large propellant shapes for a rocket engine (called a propellant grain) without forming holes in the grain (voids) or generating cracks, is very difficult. If voids or cracks are present in the grain, the rocket engine performs below design specification or will even explode. *The large amount of high energy oxidizer used precludes the use of very good fuels because when the oxidizer touches the fuel there could well be an immediate reaction which is extremely dangerous and/or, at best, would lead to reduced propellant shelf life.*

4.1 Affect of High Energy Fuels on Composite Solid Propellant Performance – Propellant Specific Impulse and Weight Fraction of Oxidizer

The most powerful commercially available propellants are composite solid propellants. They consist of separate fuels and oxidizers. The best oxidizer available to date is Nitronium Perchlorate (NP, 6 oxygen atoms), which can be used in formulating solid propellants with performance capabilities approaching that of liquid propellants. However, primarily due to its sensitivity to atmospheric moisture, it cannot be used in current commercially available solid propellant formulations. The worst performing commercially available oxidizer used in solid propellant formulations is Ammonium Nitrate (AN). Although inexpensive, it has poor performance, as measured by I_{sp} (Specific Impulse), and there are difficulties in making stable solid propellant grains.

In Figure 4, model calculations [5,6] show both enhancements in Specific Impulse, and favorable shifts in the ratio of fuel to oxidizer to lower levels of the salt-like oxidizer that is required to achieve maximum performance of a solid propellant blend. In this figure, TGD (a metal containing "fuel" (boron)) and HCO (a hydrocarbon "fuel") are *low molecular weight* fuels (compared to polymeric fuels). Both TGD and HCO show Specific Impulse improvements when they replace the pure high molecular weight polymer "fuels". Interestingly the performance of even the poor oxidizer AN shows performance improvements with the metal containing fuels to above that for the current AP/Al/HTPB propellants. Because poor fuels such as polymers are used in today's commercial solid propellants, it is essentially impossible to achieve either the best ratios of fuels and oxidizers to achieve maximum performance, or use a fuel that would enhance the Specific Impulse and/or Burn Rate of a solid propellant formulation.

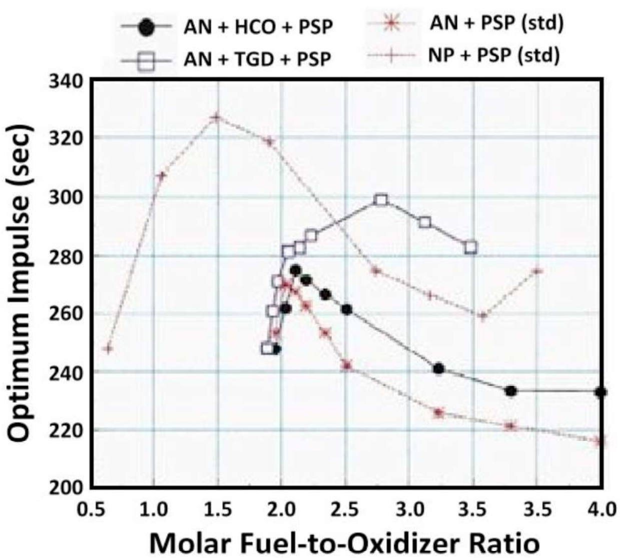

Figure 4. Standard vs. NSEP Formulation.

The current use of Aluminum as fuel in AP propellants increases I_{sp} by increasing chamber temperature and forming higher molecular weight exhaust products, but leads to numerous problems, some of which are: 1) except at large concentrations, conventional pyrophoric aluminum does little to enhance the burn rate of propellants; 2) liquid aluminum melt can pool on the burning surface of the propellant, inhibiting combustion; 3) the rocket exhaust through the nozzle contains large quantities of erosive particulate Aluminum Oxide, a particulate pollutant, which increases nozzle diameter through abrasion, thereby reducing Specific Impulse [2, 7, 8]. The work done with low molecular weight, high energy fuels and alternate high energy oxidizers, discussed in this and the preceding sections, indicates that equivalent or greater enhancement in Specific Impulse can be obtained without the problems associated with use of Aluminum.

4.2 Affects of High Energy Fuels on Solid Propellant Performance – Heats of Reaction and Propellant Burn Rates

The ability to use good, comparatively low molecular weight, fuels would also enhance burn rates of composite propellants, as demonstrated in Figures 5. Chamber total heat of reaction is a measure of how much heat energy is produced upon reaction of the oxidizer and the fuel. This can be related to a value called the Reaction Q-value, or Heat of Reaction. Higher heats of reaction are associated with higher Q-values. From this figure we see that better fuels (stronger reducing agents), such as the Boron containing TGD, produce higher Heats of Reaction than the pure hydrocarbon fuel, HCO.

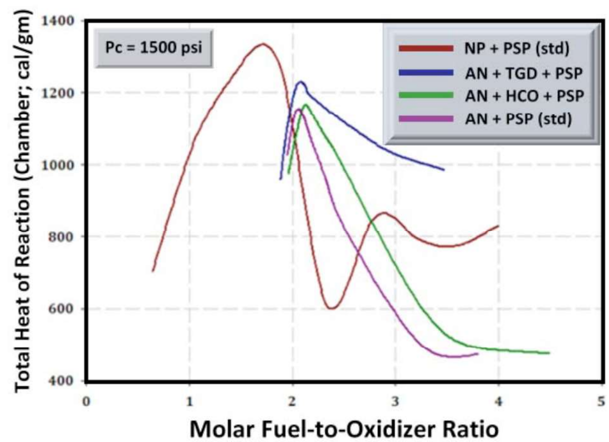

Figure 5. NSEP formulations vs. Standard composition. Pc is chamber pressure in this figure.

In Figure 6, propellant reaction (burn) rate predictions were made as a function of both combustion Reaction Q-Values and chamber pressure using the well-accepted, thermodynamics-based, Hermance Model [9]. This model agrees with several other predictive models [3] that are alternatively based on geometric and/or statistical mechanics-based considerations that propellant burn rates are determined almost exclusively by surface and sub-surface reactions.

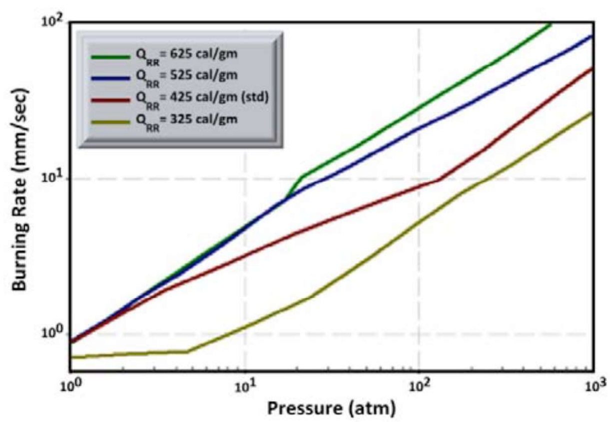

Figure 6. Hermance Model Predicted NSEP Burn Rates based on reaction Q value (Q_{RR}) of formulation.

Therefore, unlike AP/Al/HTPB and other conventional composite propellants, design of appropriate fast reactions between light high energy fuels and energetic oxidizers should significantly affect the determination and therefore tailoring of both burn rates and specific impulse (properties of the whole propellant grain), via design and control of reactions at the microscopic level in the propellant, which is specifically what the NSEP (NanoStructured Energetic Particle) *is designed to do.*

5 The NSEP Propellant

How do you stabilize the use of nearly ANY combination of propellant ingredients, containing even the most powerful oxidizers, and fuels, into a stable solid propellant? If you can stabilize these combinations, how do you then make it ignitable at reasonably achievable ignition temperatures comparable to current propellants, yet be at least as stable as current commercial solid propellants? And how would you then manufacture them on a commercial scale?

5.1 Design of NSEPs

The NSEP, Figure 7, is a spherical composite propellant particle. In general, it is slightly larger than three grains of salt arranged side by side, yet contains all the ingredients necessary for a solid propellant. Internally, a core of oxidizer is completely surrounded and encapsulated in a sub-micron to micron thin, nearly perfect, layer of defect-free (no pinholes) polymer. This protective polymer layer is in itself a low-energy fuel, and it therefore not only protects the central oxidizer core from contact with high-energy fuels, but also controls the ignition temperature of the propellant grain inside the rocket engine. Immediately external to this protective polymer layer is a high-energy fuel. The protective layer of polymer prevents contact and mixing of the high-energy fuel and oxidizer. An outer "thick", by comparison, polymer "rind" encapsulates and completes the NSEP. This outer rind is used to strongly chemically bind the fuel cell to other fuel cells in the propellant grain (cross-linking), and to any binder polymer, if present.

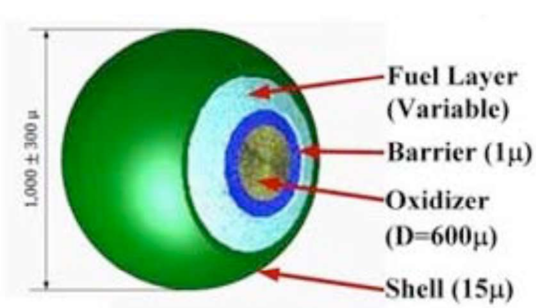

Figure 7. The NSEP (NanoStructured Energetic Particle).

The outer polymeric encapsulating shell of the NSEP can be the same polymer on all possible propellant formulations, regardless of internal composition of the fuel cell, thus allowing standardization of propellant grain casting into the rocket engine. This outer polymer "rind" also will allow for strong engine case to grain bonding, since it is only polymer/polymer bonding and no salt-like oxidizer or powdered metal comes in contact with the engine casing lining, which reduces adhesion strength.

5.2 Design of Solid Propellants Using NSEPs

As shown in Figure 8, NSEP-based solid propellants are cast into the engine casing to create the propellant grain by first "pouring" the NSEPs into the engine casing and using a mandrel to define the open axial cylindrical port. The NSEPs are like marbles poured into a jar, and can be tightly packed, with no large void spaces. A bi-modal size distribution of NSEPs is used to maximize packing efficiency and therefore total mass of the highest energy propellant ingredients. The micro-porous structure which is formed by the packed spherical NSEPs can be formed into a monolithic grain structure using several techniques, including supercritical routes that allow enhanced mass transfer rates due to lower polymer dense gas solution viscosities, followed by curing [10]. The principle of this technique is already demonstrated in the manufacture of what are called double or triple-base homogeneous solid propellant engines [11]. Curing can be done thermally at moderate temperature or, alternatively, by UV initiated free-radical polymer curing processes. The engine loading process is safe, since it is merely bonding the pre-made NSEPs into a final grain structure. *It is therefore conceivable to load engines on demand at the launch site using NSEPs shipped safely as loose "propellants" to the site, like liquid propellants. Further, if casting is done at the site, large engines can be cast without segmentation, and engines with diameters, not restricted by shipping limitations, can be cast in place*. These techniques allow mass energy densities of final cast propellants to exceed the mass densities of current propellants that use less energetic components.

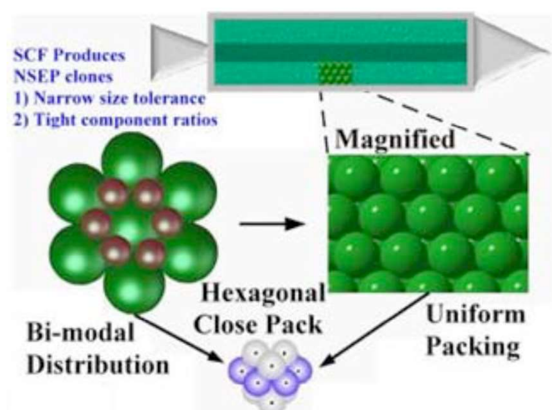

Figure 8. Packing of bi-modal NSEP particle distribution in solid propellant grain prior to binder infusion and casting.

Figure 9 demonstrates another unique aspect of this NSEP grain casting technique - the ability to configure multi-layer grains with NSEP's of different chemical composition, and hence different Burn Rates and Specific Impulses. This allows the chemistry of the propellants to determine thrust-profiles of the propellant grain, rather than grain port geometries – the port for NSEP propellants need only be cylindrical [12]. This multi-layering technique can further be applied axially to reduce non-linear combustion instabilities [13,14].

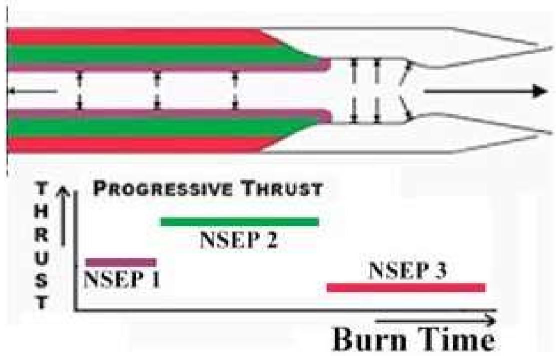

Figure 9. NSEP based thrust profiling in propellant grain through multi-layering of NSEPs with different performance properties (I_{sp} and Burn Rate).

5.3 Safety and Stability of NSEP Propellants

The University of South Florida Chemical Engineering Department performed a detailed safety and hazards analysis of NSEPs in bulk storage and after casting in solid rocket engines [15]. The conclusion of this report is that although the structure of the NSEP allows for inclusion of highly energetic materials, the NSEPs are safe to store and use providing conventional industrial safety procedures are followed. *The propellants themselves are essentially insensitive.* The report further notes that, although closed form solutions are not possible for predictive modeling of kinetic performance properties (such as burn rates) of current propellants in use today, *accurate predictive closed form solutions for kinetic properties for prediction of propellant burn rates are possible for NSEP propellants due to the cellular nature and uniformity inherent in the NSEP based propellants.* Closed form solutions would be of inestimable value to the industry in allowing for pre-screening and design of solid propellant formulations.

5.4 NSEP Manufacture Using Supercritical Fluids

The manufacture of these multi-layer NanoStructured Energetic Particles using a cost effective, flexible, controllable, scalable and green technology led to development of a novel micro-encapsulation technique that involved a circulating supercritical fluidized bed [15]. The technique was demonstrated by microencapsulation of AN by HTPB [16]. Supercritical fluids provide a unique processing medium for high volume micron and nano-scale manufacture due to tunable solvation and favorable transport properties, resulting in defect-free nano-scale thin-film formation with minimal surface roughness. Supercritical Fluids have been used in energetic materials development, comminution, and re-processing for over three decades [17]. A judicious use of supercritical fluid aided materials processing techniques [18] allow tailored manufacture of particles with desired particle size, particle size distributions, layer-by-layer particle structuring, efficient compounding of formulations, and precise component ratios. Compounding of the various layers in an NSEP can be performed, allowing the intimate mixtures of components such as single or mixed oxidizers, with burn rate modifiers, and ingredients for reduction and elimination of combustion instabilities.

6 Conclusions

The development of commercially scalable SCF based NSEP manufacturing technology circumvents the inherent limitations of conventional solid propellant manufacturing technology. This is accomplished by providing a method for standardized manufacture of essentially identically cloned multi-layer propellant particles (NSEPs). These NSEPs can be assembled and compounded on a layer-by-layer basis using an extremely wide portfolio of propellant ingredients comprised of oxidizers, low molecular weight high energy fuels, combustion modifiers, polymers, and nano-particulate materials such as aluminum. This compounding capability allows for either uniform mixtures of ingredients within a core or layer, or even for formation of nano-scale concentration gradients within the central core and/or outer layers of the NSEP.

This manufacturing process can create internal structures (barrier layers) within the NSEP that both isolate reactive components of the NSEP and allow design of predefined triggering conditions for onset of the chemical reactions, such as the conventional ignition temperature of a solid propellant. The NSEP particle design further provides a means to specifically design (formulate) energetic reactions with micro-scale accuracy, assuring macroscopic optimization of propellant grain performance properties (burn rates and Specific Impulse), thus providing a means to control, on a highly uniform structured basis, of the surface and sub-surface reactions of the solid propellant grain on the micro-scale of the NSEP.

Further, since NSEPs are liquid-like and pour like liquids, nested mandrels can be used to produce layered macroscopic propellant grain structures before binder infusion and final casting. Such layering, comprised of externally identical NSEPs with different internal chemical compositions, can produce grains with different thrust profiles. Performance of engines can be enhanced since simple cylindrical perforations could be used, thus potentially eliminating the current need to use different grain perforation geometries for thrust profiling.

NSEPs have been shown to be essentially insensitive propellants. Thus, once manufactured, they can be shipped and stored using industry standard techniques for hazardous, highly flammable, materials (like gasoline). Both standardization of the polymeric outer shells of compositionally different NSEPs, and the non-standard, infusion based, method for grain casting of NSEPs, would permit "fast casting" of both segmented and non-segmented rocket stages. These features would apply to launch site processing of even the largest expendable or re-usable boosters which can be imagined, and not just small, single-stage engines. Further, since casting of engines would occur at the launch site, there would also be no shipping size limitations on engine diameters. "Fast casting" at the launch site from a variety of stored NSEP formulations will further allow tailoring of motor performance on a per stage, per mission, basis.

Using these manufacturing techniques, the aerospace industry will finally be able to produce the next generation of solid rocket propellants which will allow development of more effective solid rocket motors, and significantly decrease life-cycle costs, including environmental costs, while substantially improving both the safety and the tailorability of propellant performance to meet a wide variety of mission specific needs.

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