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Environmentally Compatible Solid Rocket Propellants

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Abstract

Hercules' clean propellant development research is exploring three major types of clean propellant: (1) chloride-free formulations (no chlorine containing ingredients), being developed on the Clean Propellant Development and Demonstration (CPDD) contract sponsored by Phillips Laboratory, Edwards Air Force Base, CA; (2) low HCl scavenged formulations (HCl-scavenger added to propellant oxidized with ammonium perchlorate [AP]); and (3) low HCl formulations oxidized with a combination of AN and AP (with or without an HCl scavenger) to provide a significant reduction (relative to current solid rocket boosters) in exhaust HCl. These propellants provide performance approaching that of current systems, with less than 2% HCl in the exhaust, a significant reduction (≥70%) in exhaust HCl levels. Excellent processing, safety, and mechanical properties were achieved using only readily available, low cost ingredients.

Two formulations, a sodium nitrate ($NaNO_3$) scavenged HTPB and a chloride-free hydroxy terminated polyether (HTPE) propellant, were characterized for ballistic, mechanical, and rheological properties. In addition, the hazards properties were demonstrated to provide two families of class 1.3, "zero-card" propellants. Further characterization is planned which includes demonstration of ballistic tailorability in subscale (one to 70 pound) motors over the range of burn rates required for retrofit into current Hercules space booster designs (Titan IV SRMU and Delta II GEM).

Introduction

The national initiatives to reduce the amount of hazardous substances released into the environment have expanded to include solid rocket propellants. The environmentally more compatible propellants are known in the industry as "clean propellants" and feature HCl levels at least an order of magnitude lower than conventional propellants. These propellants are typically formulated with either chlorine scavengers such as sodium nitrate or chlorine-free oxidizers such as ammonium nitrate[1,2,5].

Hercules initiated development on chloride-free propellants formulated with ammonium nitrate as early as 1986. Shortly thereafter, work was also initiated to develop low-HCl using a combination of oxidizers such as ammonium nitrate, ammonium perchlorate and sodium nitrate (an HCl scavenger). The Air Force/Phillips Laboratory Clean Propellant Development and Demonstration Contract[4] was awarded in 1989 to provide a chloride-free propellant for the Advanced Launch System. Promising candidate formulations were identified and a baseline propellant was selected. Funding for further propellant development, scaleup, and characterization work was discontinued in 1991 and then partially restored in the fourth quarter of 1993. Plans for scaleup and demonstration of an improved version of the baseline propellant are on hold pending additional funding.

Discussion

Formulation

Hercules' chloride-free propellants are formulated with low energy HTPE (hydroxy terminated poly ether) binders, ammonium nitrate oxidizer, and magnesium-aluminum metal alloy fuels. Low energy binders utilize an energetic plasticizer such as BuNENA (n-butyl 2-nitratoethyl nitramine) or TEGDN (triethylene glycol dinitrate) in order to increase burning rates, improve combustion efficiency, and increase performance. These improvements are needed to compensate for the use of ammonium nitrate as the primary solid oxidizer. The amount of energetic plasticizer is limited, however, to maintain a hazard classification of 1.3 and a critical diameter of greater than six inches. Magnesium-aluminum metal alloy fuels are utilized for the same reasons that low energy binders are used. It is necessary to use an alloy rather pure magnesium in order to avoid compatibility problems. Ammonium nitrate was selected for use, even though it adversely affects ballistics, because of its availability, low cost, and lack of chlorine.

Hercules has done work to develop two types of low HCl propellants. The first type is an HTPB/AP/$NaNO_3$/Al-based propellant specifically formulated for retrofit of the Titan IV SRMU booster. The second type of low HCl propellant being developed is similar to the chloride-free propellant already described except it utilizes a low level of ammonium perchlorate in combination with aluminum powder as the primary metal fuel. Up to 20% ammonium perchlorate can be utilized, without an HCl scavenger, before exceeding an HCl level of ~6% in the exhaust.

Propellant Trade Studies

Trades studies comparing the performance, HCl levels, ballistics, and ingredient costs of these clean propellants, along with selected alternative clean propellants, are summarized in Tables I through III. Titan SRMU and Delta GEM booster propellants (QDT and QDL respectively) are included as references. Performance trade-off analyses were conducted using payload partials derived for Hercules expendable launch vehicles.

Only two propellants currently offer the potential of a completely chloride-free exhaust. These propellants include our (Hercules) HTPE chloride-free propellant and the HAN/AN/Al emulsion propellant currently being developed by Aerojet. Aerojet's propellant is formulated with an eutectic of hydroxy ammonium nitrate (HAN) and ammonium nitrate. Both chloride-free propellants offer roughly the same theoretical payload capabilities in the Titan IV SRMU and Delta II GEM boosters (i.e., 86-93% and 93-97% respectively). However, both propellants currently only deliver Isp efficiencies of about 90%.

The burning rate of the emulsion propellants can be tailored over a fairly broad range; however, these propellants reportedly also have a very high pressure exponent (~0.82)[3]. Pressure exponents of less 0.50 are needed for any type of space booster retrofit application. The emulsion propellants reportedly have a shock sensitivity of greater than zero cards and, therefore, a critical diameter of less than three inches[3]. A demonstrated critical diameter of greater than six inches is required to verify that the clean propellants hazards characteristics are similar to those of current large space booster propellants. In addition, the HAN/AN/Al emulsion propellants soften over time, presumably due use of highly hygroscopic oxidizers[3].

Hercules' HTPE chloride-free propellant currently can only be tailored over a fairly limited burn rate range (0.20 to 0.30 in/sec); however, the pressure exponent for these propellants has been measured to be less than 0.50. In addition, HTPE chloride-free propelants have been shown to have a card gap sensitivity of 0 cards and are estimated to have critical diameter of greater than six inches.

Based on this assessment, the Air-Force's Phillips Laboratory has designated Hercules' HTPE propellant as a near term development chloride-free propellant. A summary of the properties measured for the Hercules HTPE chloride-free propellant, WFS, are shown in Table IV.

Assuming a limited amount of HCl will be acceptable in the exhaust from future space boosters, a number of propellant options exist. Of these options, the scavenged (HTPB/$NaNO_3$/AP/Al) propellants appear to offer the best overall trade-offs. HCl levels as low as 2% can be achieved while still providing 91% to 96% of the current payload capability of Titan IV SRMU and Delta II GEM boosters. These propellants also offer a broad range of ballistic tailorability and ingredient costs which are comparable to those of existing low cost space booster propellants. Hercules's HTPB/$NaNO_3$/AP/Al scavenged clean propellant, QEH-1, has also been shown to have mechanical and rheological properties which would allow it to be retrofit into Titan SRMU boosters (Table IV).

Summary and Conclusions

Hercules' HTPB/$NaNO_3$/AP/Al scavenged clean propellant is currently available for a retrofit of the Titan IV SRMU and Delta II GEM boosters. This propellant is readily tailorability to provide the optimum burn rate for both motors, and is only a minor refinement of the current formulations. The scavenged propellant reduces the exhaust HCl level from ~21% to ~2%.

Hercules' HTPE propellants offer the potential for completely chloride-free exhaust without drastically reducing payload capabilities. They are also estimated to have critical diameters of greater than 6 inches and rheological/mechanical properties which would allow for the retrofit of existing space boosters. Additional development is still needed to resolve the following key issues: (1) Isp efficiency needs to be improved by reducing two-phase flow losses and increasing the flame temperature, and (2) burn rate tailorability is limited and higher rates are necessary for a Titan retrofit.

Future Work

During the remainder of the 1994 calendar year, we will select, scale up and demonstrate in subscale (~15 lb.) motors an improved HTPE chloride-free propellant. This formulation will be tailored to provide a burn rate approaching that required for a Titan IV SRMU retrofit. Next year, if funding is available, we will scale up this or a similar formulation for characterization and demonstration in an 800-lb. or larger scale motor. At the completion of these projects, we anticipate that a viable chloride-free propellant will be ready for additional characterization and demonstration in larger scale (1,700 to 33,000-lb.) demonstration motors. Parameters of potential demonstration motors are given in Table V.

TABLE I
Preliminary Performance/HCl Level Trade-Off Used to Select the Most Viable Clean Propellant Candidate

PROPELLANT APPROACH	PAYLOAD (lbm)		HCl (%)
	DELTA II (TO GTO)	TITAN IV (TO LEO)	
TITAN - QDT DELTA - QDL	--- 4,000	40,000 ---	21.3 21.1
HTPE CHLORIDE-FREE (AN/MgAl) LOW HCl (AN/AP/Al)	 3,722 3,855	 34,304 36,981	 0 6.0
SCAVENGED $HTPB/NaNO_3/AP/Al$	3,845	37,032	2.0
HTPB/AP/Mg-NEUTRALIZED	3,675	33,388	15.2
HAN/AN/Al EMULSION	3,867	37,250	0

TABLE II
The Ballistic Properties of Current Clean Propellant Formulations are Nearly Equivalent to Those of the Titan IV SRMU and Delta GEM Propellants

APPROACH	BALLISTICS		COMMENTS
	r_{1000} (in/sec)	n	
TITAN IV SRMU - QDT DELTA GEM - QDL	0.32 0.26	0.30 0.34	88% solids HTPB/AP/Al baseline propellants.
HTPE CHLORIDE-FREE (AN/MgAl) LOW HCl (AN/AP/Al)	 0.20-O.30 0.25-0.50	 0.45 0.60	Limited burn rate range with chloride-free option, lower pressure exponent needed for low HCl option.
SCAVENGED $HTPB/NaNO_3/AP/Al$	0.20-0.60	0.40	Already demonstrated to have acceptable ballistics and combustion efficiency (800-lb. demonstration).
HTPB/AP/Mg-NEUTRALIZED[4]	0.30-0.50	0.40	2,000-lb. demonstration motor tested.
HAN/AN/Al EMULSION[3]	0.30-0.60	0.82	Significantly lower pressure exponent needed.

TABLE III The Cost of Clean Propellant Ingredients is Similar to That of Conventional Propellants		
APPROACH	INGREDIENT COST ($/lb.)	COMMENTS
TITAN IV SRMU - QDT DELTA GEM - QDL	1.80 2.60	QDT utilizes low cost R45AS, atomized Al, and E/A bonding agent.
HTPE CHLORIDE-FREE (AN/MgAl) LOW HCl (AN/AP/Al)	5.74 [3.08]* 5.23 [3.15]*	Higher costs related to use of liquid nitramine plasticizer (currently $18/lb.) partially compensated for by low cost AN.
SCAVENGED HTPB/$NaNO_3$/AP/Al	1.90	Cost reduced by use of $NaNO_3$ - higher cost R45M used.
HTPB/AP/Mg NEUTRALIZED(4)	3.20	Higher cost related to use of R45M and HX-752.
HAN/AN/Al EMULSION(3)	5.12	High cost associated with HAN - potentially lower processing costs.
* Values in brackets based on estimated future ingredient costs for large quantities.		

TABLE IV Clean Propellants Currently Being Tailored to Meet Estimated Titan IV SRMU Retrofit Requirements			
		HERCULES PROPELLANTS	
PROPERTIES	SRMU RETROFIT REQUIREMENTS	QEH-1	WFS
HCl (%) PAYLOAD (lbm)	--- *	2 36,314	0 34,247
BALLISTICS r_{1000} (in/sec) n	 0.33 - 0.35** < 0.50	 0.26 - 0.36 0.39	 0.24 - 0.29 0.46
MECHANICAL PROPERTIES TENSILE STRENGTH (psi) ELONGATION (%)	 100 35	 134 52	 114 39
PROCESSABILITY EOM VISCOSITY (kP) POT LIFE (hr)	 <10 >15	 5 16	 1 25
* Current maximum payload to LEO is 40,000 lbm. ** Estimated burn rates needed to achieve equivalent thrust.			

TABLE V Hercules Has Several Options for Large Scale Demonstration of Chloride-Free Propellants				
	PARAMETERS			
MOTOR OPTIONS	ACTION TIME (sec)	DIAMETER (in.)	PROPELLANT WEIGHT (lb.)	COMMENTS
GEM BOOSTER	63	40.0	29,950	High L/D ratio, comparable to larger booster. Vectorable nozzle demonstrated April 1994.
ORION 50S-XLG	69	50.2	33,229	High L/D ratio, larger diameter, ground launched, vectorable nozzle.
ORION 50	74.5	50.2	6,665	Larger diameter, vectorable nozzle.
ORION 38	64.4	38.0	1,700	Can accommodate higher burn rate by adjusting throat diameter, vectorable nozzle, lowest cost motor.

References

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