[2] Penner, S. S., *Introduction to the Study of Chemical Reactions in Flow Systems* (Butterworth Scientific Publications, London, 1955), Chap. 3.

[3] Bray, K. N. C. and Appleton, J. P., "Atomic recombination in nozzles: Methods of analysis for flows with complicated chemistry," Dept. of Aeronautics and Astronautics, Univ. of Southampton, Rept. 166 (1961).

[4] Penner, S. S., Porter, J., and Kushida, R., "Rate and radiative transfer processes during flow in de Laval nozzles," *9th Symposium (International) on Combustion* (Academic Press Inc., New York and London, 1963), pp. 748–758.

[5] Westenberg, A. A. and Favin, S., "Complex chemical kinetics in supersonic nozzle flow," *9th Symposium (International) on Combustion* (Academic Press Inc., New York and London, 1963), pp. 785–789.

[6] Bray, K. N. C. and Appleton, J. P., "Atomic recombination in nozzles: Methods of analysis for flows with complicated chemistry. Part II," Dept. of Aeronautics and Astronautics, Univ. of Southampton, Rept. 178 (1961).

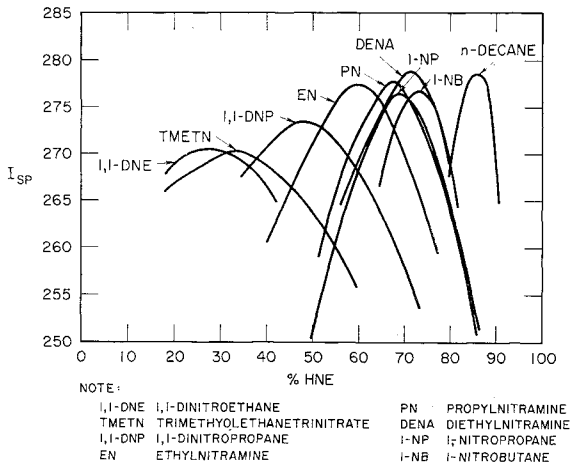

Fig. 1 Performance calculations of HNE propellant slurries.

Hexanitroethane Propellant Slurries

MILTON B. FRANKEL,* LELAND D. CHRISTENSEN,† AND EDGAR R. WILSON‡
Stanford Research Institute, Menlo Park, Calif.

Introduction

RECENT developments in the synthesis of hexanitroethane (HNE) have renewed interest in its use as a possible high energy oxidizer. The chemical reactivity and the physical properties of HNE have recently been reported.[1] As might be expected for such an energetic compound, HNE is chemically reactive with many compounds, particularly curable organic binders. HNE does not lend itself well to a castable, curable propellant system because 1) it requires low-temperature mixing and casting, 2) it is incompatible with standard binders and curing agents, and 3) it may undergo phase transition. The problems associated with using HNE in a conventional composite type of propellant could possibly be circumvented by utilizing noncurable slurries of HNE. This paper describes the preparation and evaluation of noncurable HNE propellant slurries.

Performance Calculations

Performance calculations§ were made of propellant systems composed of HNE with the following fuels: polyethylene, decane, 1-nitropropane, 1-nitrobutane, 1,1-dinitroethane, 1,1-dinitropropane, 1,1,1-trinitropropane, ethyl nitramine, propyl nitramine, diethyl nitramine, and trimethyolethane trinitrate. The propellant systems containing the saturated hydrocarbons, mononitroalkanes, and the primary and secondary nitramines gave calculated specific impulses of 275–278; the main difference is that 84% HNE was required for the hydrocarbon systems, whereas 70–72% HNE was needed for the mononitroalkanes and only 55–65% was required for the nitramines. The hydrocarbon system has too high a solids loading for a castable slurry, but the mononitroalkanes and nitramines with the lower solids loading would qualify as castable systems. 1,1-dinitroethane has an optimum specific impulse of 270 at 24% HNE, whereas 1,1-dinitropropane peaks at 273 with 46% HNE. The higher homologs of the 1,1-dinitroalkanes, such as 1,1-dinitrobutane and 1,1-dinitropentane, will undoubtedly give a specific impulse of 275–277 at a practical oxidizer loading. Nitrate esters such as trimethyolethane trinitrate do not give specific impulses in excess of 270 and are not of interest. The results are summarized in Fig. 1. The heats of formation of the liquid fuels that were used in the performance calculations are compiled in Table 1.

Compatibility Studies

Compatibility studies were run on HNE and the following compounds: decane, oronite polybutene #6, 1-nitroethane, 1-nitropropane, 2-nitropropane, 1-nitrobutane, 1,1-dinitropropane, 1,1-dinitrobutane, butyl nitramine, methyl ethyl nitramine, and diethyl nitramine. The mononitroalkanes were samples from Commercial Solvents Company and were used as received with the exception of 1-nitrobutane that was purified by fractional distillation. The 1,1-dinitroalkanes were prepared by the Lockheed Missiles and Space Company, and the nitramines were synthesized at Stanford Research Institute. Both the 1,1-dinitroalkanes and the nitramines had purities greater than 99% as indicated by vapor phase chromatography.

Stoichiometric mixtures of HNE and the liquids were placed in manometric tubes and the gas evolution was measured as a function of time at ambient temperature. HNE showed excellent compatibility with decane and the 1,1-di-

Table 1 Heat of formation data on HNE propellant components

Compound	Heat of formation, kcal/100 g
Hexanitroethane	9.53
Polyethylene	−42.99
Decane	−50.56
1-nitropropane	−45.32
1-nitrobutane	−44.69
1,1-dinitroethane	−28.87
1,1-dinitropropane	−29.85
1,1,1-trinitropropane	−15.66
Ethyl nitramine	−22.85
Propyl nitramine	−25.79
Diethyl nitramine	−21.57
Trimethyolethane trinitrate	−39.70

Received September 3, 1964. The authors are indebted to Lockheed Missiles and Space Company for the financial support of this work and for permission to publish this paper. We are also indebted to P. Noble Jr. of Lockheed for his assistance in carrying out this work and for supplying the samples of hexanitroethane and 1,1-dinitroalkanes.

* Senior Chemist, Propulsion Sciences Div.
† Senior Engineer, Propulsion Sciences Div.
‡ Senior Propellant Technician, Propulsion Sciences Div.

§ Performance calculations are based on mobile equilibrium, isentropic expansion between 1000 psia chamber pressure and an exhaust pressure of 14.7 psia.

Table 2 Manometric stability studies of HNE propellant slurries[a]: ΔP (mm) with time at ambient temperature

Time, hr	Decane	PB#6[b]	1-NE[b]	1-NP[b]	1-NB[b]	MENA[b]	DENA[b]	1,1-DNP[b]	1,1-DNB[b]
17	0	101	0	0	0	0	0	0	0
24	0	152	0	0	0	112	27	0	0
93	0	...	0	56	1	...	29	0	0
164	0	...	96	105	42	...	29	0	0
260	0	...	145	140	87	...	...	0	0
329	0	...	225	170	...	...	...	0	0

[a] Measurements were made on stoichiometric mixtures of HNE and liquid.
[b] PB #6 = oronite polybutene, mol. wt. 330; 1-NE = 1-nitroethane; 1-NP = 1-nitropropane; 1-NB = 1-nitrobutane; MENA = methyl ethyl nitramine; DENA = diethyl nitramine; 1, 1-DNP = 1, 1-dinitropropane; 1, 1-DNB = 1, 1-dinitrobutane.

nitroalkanes at ambient temperatures. A slurry of HNE and 1,1-dinitrobutane gave no gas evolution after 329 hr at ambient temperature. The mononitroalkanes and nitramines showed poor compatibility with HNE. The results are summarized in Table 2.

Formulation and Casting Studies

The formulation studies were carried out on a small scale. Up to 50 g of propellant were manually mixed in a plastic beaker and the slurry was cast at atmospheric pressure with vibration into Lucite tubes. To eliminate the possibility of settling at the lower oxidizer concentrations, the slurries were thickened by the addition of a small amount of poly(methyl methacrylate) (PMMA). The PMMA was dissolved by warming it with the nitroalkanes and then the solution was allowed to cool to ambient temperature. A stock solution of the PMMA in the nitroalkane was blended in the required amounts with HNE.¶ The mixture was allowed to warm to room temperature before casting. Unlike HNE itself, there was no agglomeration of the HNE crystals when the slurry warmed to ambient temperature. It was found that this slurry had high viscosity and settling did not occur; furthermore, the slurry appeared to be thixotropic since it underwent shear thinning and flowed well under vibration.

Burning Rate Studies

Burning rates of the slurry propellants were determined using both a Crawford strand-burning bomb (where strands up to $\frac{1}{4}$ in. in diameter could be burned) and a large window bomb (in which strands up to 1 in. in diameter could be accommodated). In order to test out the slurry concept, model studies were first made with ammonium perchlorate as the oxidizer in the following propellant composition: 70% ammonium perchlorate (APC)/24% 1-nitropropane (1-NP)/6% poly(methyl methacrylate). This propellant slurry was then cast into 4-in. lengths of Tygon tubing having approximately a $\frac{1}{4}$-in. i.d.. These slurries burned smoothly in the strand burning bomb over a pressure range of 200–1000 psi. The burning rates ranged from 0.17 to 0.20 in./sec, with a pressure exponent of 0.10. The results are shown in Fig. 2. Similar efforts to obtain burning rates of HNE slurries in Tygon tubing were unsuccessful. Above 200 psi, flashing occurred down the side of the grain. To overcome this difficulty, burning rate measurements were then attempted on larger propellant samples in Lucite tubes in the window bomb. The HNE slurries were cast into 3-in.-long Lucite tubes with $\frac{1}{2}$-in. i.d. and were tested over a pressure range of 200–1400 psi. The propellant compositions studied were 50% HNE/45% 1,1-dinitropropane/5% poly(methyl methacrylate) and 70% HNE/28% 1-nitrobutane/2% poly(methyl methacrylate). The slurries burned smoothly in each case. The burning rates ranged from 0.2 to 0.4 in./sec. with a pressure exponent of about 0.8 (Fig. 2).

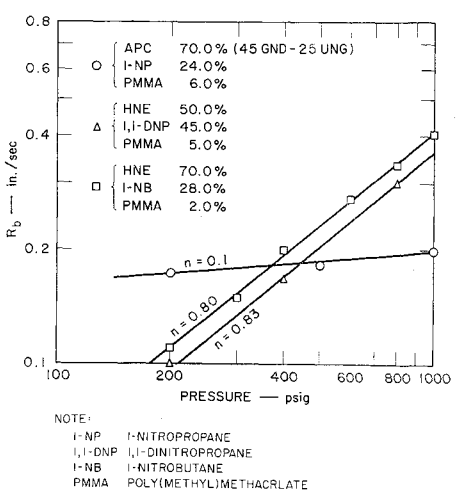

Fig. 2 Burning rates of ammonium perchlorate and hexanitroethane propellant slurries.

Normally a framing camera was used to record the burning, and burning rates were calculated from the time required for the propellant to burn between two gage marks. Because the slurry was translucent, it was somewhat difficult to determine accurately the burning surface of the propellant from some of the film records. A collimator-photoelectric detector was employed in an effort to circumvent this problem. The collimator was used in conjunction with a pair of photoelectric cells and the output from the cells was fed into a Sanborn strip-chart recorder. The burning of the propellant strand produced two blips on the recorder chart. From the data, the time of burning between the parallel slits of the collimator was measured. This technique was faster than the photographic method and, under the circumstances, appeared to be somewhat more accurate.

Conclusions

Performance calculations have shown that the high specific impulse (275–278 sec) of the nonmetallized HNE-hydrocarbon propellant system can be retained, whereas the solids loading can be reduced to a practical castable level by the replacement of the hydrocarbon with nitroalkanes or nitramines. Stability studies have indicated that HNE has the best compatibility with 1,1-dinitroalkanes. Propellant slurries of HNE-nitroalkanes burned smoothly over the pressure range tested which varied from 200 to 1400 psi. The burning rates are moderate but the pressure exponents (0.8) are excessive.

¶ The HNE had been recrystallized from methylene chloride, dried under vacuum, and stored in a refrigerator at 0°.

References

[1] Noble, P., Jr., Reed, W. L., Hoffman, C. J., Gallaghan, J. A., and Borgardt, F. G., "Properties of hexanitroethane," AIAA J. 1, 395–397(1963).