Technical Comments

Comments on "Preignition Phenomena in Small A-50/NTO Pulsed Rocket Engines"

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A RECENT paper by Perlee et al.[1] on the vacuum ignition of hypergolic propellants (hard start) has led to some interesting thoughts which may lead to a possible solution of this problem. The results of Perlee et al. indicate that hydrazine, A-50, and monomethyl hydrazine yield nitrates characteristic of their own basic compounds. Their paper also shows that another derivative of hydrazine (UDMH) yields ammonium nitrate (AN). The reasons for AN formation have not been determined. The explosive potential of AN has been found to be the lowest of the four nitrates investigated. Friedman et al.[2] found that dried ammonium nitrate did not decompose under hard vacuum when heated to 300°C, but was relatively stable when dried under vacuum conditions; only after water vapor had been added and heated gradually to 180°C did decomposition commence.

Having taken a preliminary look at this problem, I find a trend that indicates that there is a correlation between the concentration of the alkali impurities in the propellants and the formation of ammonium nitrates, which are the least potentially hazardous of the nitrates. Perlee's infrared data show that AN is formed only in the UDMH system. In repeated testing of production samples of the above fuels, UDMH exhibited significantly larger quantities of alkali-metal impurities than any of the other fuels. Table 1 shows the findings of the various investigators who have published data on these systems.

It is interesting, therefore, to speculate that these impurities may act as catalysts in the oxidation processes which ultimately produce the ammonium nitrates. Alternatively, if certain of these impurities (e.g., Na and Li) are added in sufficient quantities, they may decompose the nitrate without detonation and may reduce or eliminate the pressure spike associated with hard starts.

To my knowledge, no experimental program has been designed to evaluate the hard start problem with the objective of determining the effects of adding alkali metals to the various hydrazines. Since several laboratories are already involved in research on these fuels and their effects on hard-starts, it might be profitable for them to undertake such a program.

Table 1 Alkali metal impurities, ppm

Fuel	Na	K	Li
UDMH[a]	2.7–3.9	0.5–2.0	0.5–2.0
N_2H_4[a]	1.0	0.2	0.2
N_2H_4[b]	0.2 ± 0.1	0.2 ± 0.1	0.01 ± 0.01
A-50[a]	0.71–0.94	0.27–0.42	0.27–0.42
A-50[b]	0.6	0.3	0.5
MMH[b]	0.13	0.013	0.5

[a] See Ref. 3.
[b] See Ref. 4.

References

[1] Perlee, H. E. et al., "Preignition Phenomena in Small A-50/NTO Pulsed Rocket Engines," *Journal of Spacecraft and Rockets*, Vol. 5, No. 2, Feb. 1968, pp. 233–235.

[2] Friedman, L. and Bigeleisen, J., "Oxygen and Nitrogen Isotope Effects in the Decomposition of Ammonium Nitrate," *Journal of Chemical Physics*, Vol. 18, No. 10, Oct. 1950, pp. 1325–1331.

[3] Miller, W. J., Pergament, H. S., and Calcote, H. F., "Radar Interference Effects in the LEM Descent Engine Exhaust Plume," TP-118, July 1965, AeroChem Research Labs. Inc., Princeton, N.J.

[4] Jensen, A. V., private communication, April 4, 1968, Chemical Propulsion Information Agency, Johns Hopkins University. Applied Physics Lab., Silver Spring, Md.

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DR. Baulknight's observations and comments concerning the contribution of the alkali metal impurities to the preignition formation of ammonium nitrate rather than the fuel nitrates in the reactions between various hydrazine fuels and nitrogen tetroxide are certainly worthy of future consideration. However, experiments conducted both by us and by other investigators,[1] concerning the reactions between these hydrazine fuels and nitrogen tetroxide in the vapor phase, indicate that the product spectrum described in our paper is the result of a vapor-phase reaction rather than a condensed-phase reaction. This fact, it seems, casts some doubt on the contribution of such small quantities of nonvolatile alkali metal impurities contained in the liquid phase to the gas-phase reaction mechanism.

Reference

[1] Zung, L. B. et al., "Analysis of Reaction Products and Ignition Threshold Study for the System N_2O_4/N_2H_4," Quarterly Rept. NAS7-438-Mod. #3, March 1, 1968, NASA, pp. 1–38.

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