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## Modification of the Hydrazine-Nitrogen Tetroxide Ignition Delay

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**I**GNITION delay measurements were made on the system hydrazine-nitrogen tetroxide, and the effect of additives on the ignition delay time was determined. The apparatus used was of the type developed by Kilpatrick and Baker,<sup>1</sup> but was modified as described below. Delay times were both shortened and lengthened by additives, but the majority of the compounds tested tended to shorten the ignition time.

Vapor-phase studies of the hydrazine-nitrogen tetroxide system have been reported in the literature,<sup>2</sup> and a thermal rather than free radical reaction mechanism has been proposed for the reaction. Studies of liquid phase interactions of hydrazine and nitrogen tetroxide have been concerned primarily with explosion hazards,<sup>3</sup> hence, ignition delay times were not reported. The purpose of the experiments reported here was to determine the effect of additives on the ignition delay time for liquid nitrogen tetroxide and hydrazine. Additives were selected with the hope that a clue to the reaction mechanism could be obtained from the delay data. For example, thermal moderators, free radical traps, free radical sources, and surface active agents were used. The latter agents were used because of suspected immiscibility of the two reactants. The fact that nitrogen tetroxide and hydrazine are immiscible was subsequently proved by photographing<sup>4</sup> the dropwise addition of  $N_2O_4$  to  $N_2H_4$ .

### Apparatus and Experimental Procedures

The apparatus for the measurement of ignition delay times consisted of a reaction chamber of approximately 450-cm<sup>3</sup> volume, two injection pistons of 0.515- and 0.466-in. diam and

0.375-in. stroke, and a driving piston that, when acted upon by compressed gas, drove the two small pistons simultaneously. The drive gas was contained in an accumulator bottle of about 1-ft<sup>3</sup> volume at 1500 psig and was released by a quick acting solenoid valve (90% open in 2 msec).

Hydrazine was contained behind the larger of the two injection pistons; thus, all measurements were made at a volume ratio  $N_2H_4/N_2O_4 = 1.22$ . Valves located in the casing surrounding the small pistons facilitated refilling between runs. An overflow was incorporated into the fill system to insure the absence of gas bubbles. The propellant storage spaces were sealed from the reaction chamber by 5-mil teflon disks, which were held in place by washers and lock bolts. Each of the lock bolts was drilled with a 0.060-in hole that constituted the injection orifice. The two streams were injected at 90° to each other in a swirl chamber, resulting in tangential mixing. The reaction chamber was cleaned after each run and was flushed with nitrogen for 20 min prior to each measurement.

Delay time was measured by photographing an oscilloscope trace that recorded both light emission and pressure. The photocell pickup was located in the end of the reactor to insure the maximum view of the reaction chamber. The photocell amplifier was operated at maximum gain to insure the detection of the initial light release. The pressure sensor was mounted flush with the inner wall of the reactor and was located 3 in. from the injection ports.

In initial runs, a 1-mil teflon seal was used between propellants and reaction chamber. It was observed in these runs that light was emitted coincident with a small pressure rise and that the more rapid pressure rise conventionally associated with ignition occurred later. It was also difficult to obtain reproducible results in these experiments. This initial small pressure rise was identified as ignition by  $N_2O_4$  vapor, which had prematurely leaked by the teflon disk and

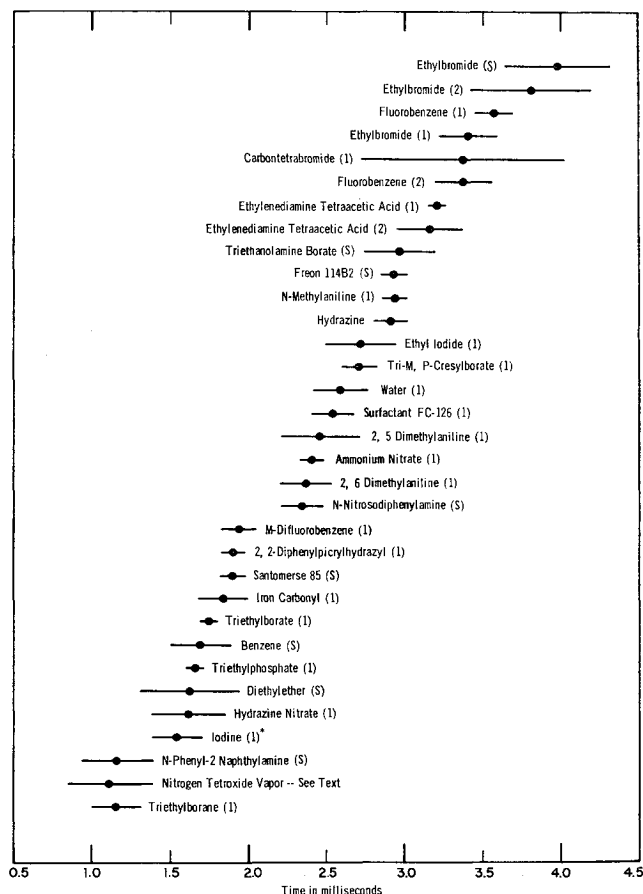


Fig. 1 Ignition delay data where an asterisk indicates that the substance is added to  $N_2O_4$ .

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was eliminated by substitution of the 5-mil teflon. In succeeding experiments, the light emission and sharp pressure rise occurred nearly simultaneously, the light preceding the pressure rise on the average of 0.1 msec. Since the light deflection values can be read more accurately from the phototrace, it is these values that are reported here.

Olin Mathieson technical grade anhydrous hydrazine density 1.004, which was certified by the manufacturer to contain 1.4% water and 0.005% insoluble matter, was used without further purification. Nitrogen tetroxide, having a reported minimum purity of 99.5%, was obtained from the Mathieson Company and was also used directly as supplied.

### Results

A summary of the ignition delay data for the hydrazine-nitrogen tetroxide system, both with and without additives, is shown graphically in Fig. 1. The values given in Fig. 1 were obtained by normalizing on an average delay time value for hydrazine. This was necessary because slight differences in delay times were observed for pure hydrazine during the course of the experimental program when it became necessary to change to a new lot. In the graph, the dots represent the average delay times and the horizontal lines the average errors for each set of determinations. In most cases, the delay time was obtained as the average of three separate measurements. The error limits are small enough to establish that the additives are effecting real changes in the delay times. The large spread of values obtained in the runs with carbon-tetrabromide is attributed to chemical reaction with the hydrazine, since a pressure build-up in the hydrazine storage indicated a slow reaction with carbontetrabromide.

With the exception of iodine, which was added to the nitrogen tetroxide, all additives were dissolved in the hydrazine. The numbers in parenthesis in Fig. 1 indicate the concentration of additive in weight percent. In a few cases, indicated by (s) in Fig. 1, the additive was only partially soluble in the hydrazine. In these cases, 1% of additive was placed in the hydrazine, the liquid was agitated until no more additive appeared to be dissolving, and the resulting saturated hydrazine solution was then decanted from the remaining undissolved additive.

The fact that delay times were shortened with surfactant FC-126 and Santomerse 85, two surface active agents, indicates that solubility of the two reactants is a factor in the delay times. Two possible intermediates in the reaction, hydrazine nitrate and ammonium nitrate, also reduced the ignition time.

In one set of experiments the reactor was flushed with  $N_2O_4$  instead of nitrogen, and the delay time for  $N_2H_4-N_2O_4$  without additives was measured. As expected, a significant decrease in the ignition delay time was observed. These results are in agreement with those observed for the triethylamine-nitric acid reaction,<sup>5</sup> where the delay times became shorter when the initial gas-phase oxidant concentration ( $O_2$  or  $N_2O_4$ ) was increased. It is reported,<sup>5</sup> in fact, that shortest delay times were obtained when nitrogen tetroxide was substituted for air in the bomb reactor. Acceleration by gas-phase oxidant, coupled with the fact that most gas-phase reactions involve free radical mechanisms, makes us believe that the hydrazine-nitrogen tetroxide reaction proceeds by a free radical mechanism, although the delay reported here does not conclusively support this view.

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## Payload Scaling Laws for Boost Rockets

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### Explanatory

FOR a given change in payload weight, we wish to determine what compensatory changes (i.e., scaling) must be made in other rocket parameters (such as thrust and initial stage weights) in order that the final burnout position, velocity, and time be unaffected. This is a problem of interest in preliminary design studies when numerical data generated for one payload are to be applied to other payloads. In this article, we determine the scaling laws that leave a boost rocket trajectory invariant to payload weight changes. These laws are different from the usual "payload exchange ratios" used in mission design where only the characteristic velocity is held invariant.

### Derivation of Scaling Laws

The rocket parameters appearing explicitly in the differential equations of motion must be invariant to changes in payload weight if the trajectory is to be unaltered. The invariant parameters can be found by examining the equations of motion:

$$\mathbf{a} = (F/m)\mathbf{r} - (D/m)\mathbf{r} - \mathbf{g}$$

where  $\mathbf{a}$  is the acceleration,  $\mathbf{r}$  a unit vector parallel to the rocket's longitudinal axis,  $\mathbf{g}$  the acceleration of gravity,  $m$  the mass,  $F$  the thrust, and  $D$  the drag force. We assume thrust and drag act parallel to the longitudinal axis. We neglect lift for the present discussion, since angles of attack are small during the gravity turn. This will not affect the generality of the scaling laws. Boldface characters denote vector quantities.

The thrust<sup>1</sup> consists of a momentum thrust  $F_m$  and a pressure thrust  $F_p$ :

$$F_m = p_e r^{-1} a f(\gamma, r)$$

$$F_p = a(p_e - p)$$

where  $p_e$  is the design chamber pressure of the rocket motor,  $p_e$  the pressure at the exit of the nozzle,  $p$  the ambient pressure (a function of altitude),  $\gamma$  the ratio of the specific heats of the exhaust gases,  $r$  the ratio of the nozzle area at the exit to the area at the throat,  $a$  the cross-sectional area of the nozzle exit, and  $f(\ )$  denotes "function of." For scaling, we shall assume that the parameters  $\gamma$ ,  $p_e$ ,  $p$ ,  $r$  are invariant. It turns out that vacuum specific impulse (a property of the propellant) must be an invariant, so that it is reasonable to assume  $\gamma$  to be invariant. The only thrust parameter to be scaled is  $a$ .

The drag force is given by

$$D = \frac{1}{2} \rho V^2 A C_D$$

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