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RESEARCH MEMORANDUM

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SUMMARY OF NACA RESEARCH ON IGNITION LAG OF SELF-IGNITING FUEL - NITRIC ACID PROPELLANTS

By Gerald Morrell

Lewis Flight Propulsion Laboratory
Cleveland, Ohio

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RESEARCH MEMORANDUM

SUMMARY OF NACA RESEARCH ON IGNITION LAG OF SELF-IGNITING FUEL - NITRIC ACID PROPELLANTS

By Gerald Morrell

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SUMMARY

Ignition-lag data obtained during the period 1949 to 1956 are summarized in terms of dependence on temperature, pressure, reactor geometry, mixing method, and propellant composition. The data were obtained largely in a small-scale rocket engine and an open-tube bench apparatus; some data were obtained from a rapid-mixing closed-bomb device. Analysis of the results and comparisons with data from other sources indicate agreement with a chemical kinetics model provided that mixing is reasonably energetic.

The effect of temperature on ignition lag follows an Arrhenius relation with temperature coefficients of 0 to 10,000 Btu per mole. A few exceptions to this behavior are shown to be due to poor mixing. The effect of initial ambient pressure is shown to be roughly a function of percent open area in the reactor and temperature, or ignition lag, at sea-level reference pressure. Reactor geometry is important insofar as it influences the effective charge concentration and the loss of reacting material by quenching or by flow from the reactor. Water in the acid increases ignition lag, but this effect can be compensated for by addition of nitrogen dioxide or sulfuric acid. With respect to fuel composition, there appears to be little difference among aromatic and unsaturated aliphatic amines. The most reactive fuels are ethylenimine, hydrazine and its derivatives, and the organic phosphites and thiophosphites.

The relation between ignition lag and rocket-engine starting is discussed briefly.

INTRODUCTION

The NACA Lewis research program on ignition characteristics of self-igniting (hypergolic) rocket propellants was initiated in June 1949 when scattered field reports began to indicate that altitude starting could be a serious problem. The first project (ref. 1) was a short, qualitative

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study at simulated altitude conditions with a 200-pound-thrust rocket engine with jet fuel - nitric acid - sulfuric acid systems. Temperature rather than pressure appeared to be the primary variable affecting ignition.

As a part of the research that followed this first study, ignition lag was evaluated as a function of propellant composition, temperature, pressure, and reactor configuration both in open-tube and small-scale rocket-engine apparatus. It was reasoned that pressure surges and explosions during engine starts were caused by ignition of accumulated liquid propellants in the rocket combustor. A short ignition lag would minimize this accumulation and permit rapid, full-flow starts to satisfy operational requirements. Hence, the practical object of these studies was to learn how to obtain short ignition lags at the low temperatures and pressures that could be encountered at altitudes where rocket-thrust augmentation was required.

Concurrently, rocket-engine studies were conducted to evaluate chemical methods of starting the jet fuel - nitric acid system, which does not ignite spontaneously, since this system has many tactical applications both in missiles and in piloted aircraft. In these engine studies, emphasis was placed on learning how to stage the flow of self-igniting and main-stage propellants so as to achieve reliable starts at -76° F, the specification freezing point of jet fuel.

More recently, studies have been conducted in a closed bomb with minimal mixing times in order to establish the mechanisms of spontaneous ignition with nitric acid.

The results of this research on ignition lag and engine starting with self-igniting propellants are summarized in the present report. Ignition-lag theory is discussed in terms of the effects of propellant composition, temperature, pressure, and reactor size.

MEASUREMENT TECHNIQUES AND APPARATUS

Many methods have been used to measure the ignition lag of liquid rocket propellants. These techniques vary principally in the way of detecting ignition, in the speed and efficiency of mixing, and in the reactor configuration selected. The method of detecting ignition should be of minor consequence in most propellant systems, since experience has shown that light emission, pressure, and conductance measurements give nearly the same results.

Generally, the reactor configuration has been chosen rather arbitrarily in regard to geometry and degree of enclosure. As will be shown, this factor has a considerable influence on ignition lag; and many of the discrepancies reported in the literature may have their origin in the reactor configuration.

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The speed and efficiency of mixing should greatly influence the measured lag if it is assumed that every propellant system has an intrinsic ignition lag imposed by the chemical kinetics of the ignition process and that this intrinsic lag is small compared with the over-all lag usually measured. The observed decrease of ignition lag with increase in mixing energy supports this assumption, as does the observed similarity of ignition-lag - temperature and viscosity - temperature relations for small mixing energies.

Examples of extremes in mixing energy are the high-pressure, piston-driven injector of references 2 and 3 and the drop-test apparatus of reference 4. In the intermediate range of mixing energies are found apparatus that employ impinging-jet mixing (with and without splash plates), jet-pool mixing, and sheet-pool mixing (refs. 5 to 7).

In order to simulate mixing processes that might occur in a rocket engine, two types of apparatus giving intermediate mixing energies were used in the NACA studies. One type (shown in fig. 1) was a modified open-tube apparatus in which an ampoule of fuel was crushed beneath the surface of the acid. Light emission picked up by a photocell was used to detect ignition. The apparatus is described in detail in reference 8.

The second apparatus used in the NACA studies is shown in figure 2. This was a nominal 50-pound-thrust impinging-jet rocket motor with transparent walls and a convergent nozzle. Provisions were made for varying the reactor volume and aspect ratio as well as the nozzle-throat diameter. The temperature of the propellants and injector head could be maintained at any value in the range from -90° to 160° F, and initial pressure altitudes up to 95,000 feet were obtained by evacuating the large plenum chamber into which the rocket was fired. Light emission, recorded by a high-speed camera, was again used to detect ignition. Reference 8 gives the details of this apparatus.

More recently, experiments aimed at studying the mechanism of ignition have been conducted in an apparatus modeled after that of references 2 and 3 and described in reference 9.

Studies on the use of self-igniting propellants to start the jet fuel - nitric acid system were conducted in a 200-pound-thrust rocket engine. The rocket fired into a 1500-cubic-foot plenum chamber that could be evacuated to a pressure altitude of about 95,000 feet. A refrigeration system cooled the propellants, flow system, and rocket to -80° F. A similar test unit without a plenum chamber was also used for low-temperature tests. The complete system is described in references 10 and 11.

RESULTS OF IGNITION-LAG STUDIES

The NACA data obtained from the small-scale engine and open-tube experiments are summarized in this section. The effects on ignition lag

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of the following variables are presented: initial propellant temperature, initial reactor pressure, reactor configuration, method of mixing, acid composition, and fuel composition. A detailed discussion of the results and comparisons with other data are given in the section entitled DISCUSSION.

Effect of Initial Propellant Temperature

With several exceptions, a decrease in temperature produced an increase in ignition lag. If the major portion of the ignition-lag period is characterized by a constant pressure and a presumably constant temperature condition, as shown in references 2, 3, and 9, an Arrhenius-type relation between ignition lag τ and temperature should correlate the data:

$$\tau = Ae^{E/RT}$$

where the temperature coefficient E has the dimensions of an activation energy, and the proportionality constant A may be considered as the extrapolated value of ignition lag for infinite temperature. The variations of ignition lag with temperature reported in references 12 to 19 are plotted on this basis in figures 3 to 12. The corresponding temperature coefficients and proportionality constants are shown in table I. For the most part, the data give reasonable straight-line relations and thus lend support to the original assumptions about the characteristics of the delay period. The break encountered near -70° F with the open-tube apparatus does not appear to be characteristic of the propellant systems, since similar breaks did not occur in the engine experiments for the same propellants. This behavior might be due to the inability of the apparatus to mix adequately propellants with high viscosities.

Effect of Initial Reactor Pressure

The effect of initial pressure altitude on ignition lag was studied only in the small-scale engine equipment (refs. 12, 14, 18, 19, and 20). Data for the usual reactor configuration (2-in. diam., 4-in. length, 0.4-in.-diam. nozzle) are summarized in table II. No particular trend with temperature is apparent from these experiments. With one exception, the absolute variation in ignition lag from sea-level to pressure altitudes of 60,000 to 90,000 feet did not exceed 4 milliseconds and averaged 1.3 milliseconds for a variety of propellant compositions. Because of the nearly constant difference between sea-level and altitude ignition lag, the percentage change in ignition lag increased as the sea-level lag decreased.

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The data of reference 19 indicate that the effect of initial pressure on ignition lag is a function of the ratio of nozzle area to reactor cross-sectional area as well as a function of the sea-level ignition lag. The first function should affect the rate of material loss from the reactor, and the second factor should determine the rate of pressure rise. A rough correlation is shown in figure 13. It is immediately apparent that the usual engine configuration failed to show a large altitude effect because of the low ratio of nozzle area to combustor area. It is also apparent that partial or complete blockage of the nozzle throat could eliminate high-altitude ignition difficulties caused by low ambient pressure. Application of this principle to the second stage of the Bumper-WAC sounding rocket eliminated such a difficulty.

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Effect of Reactor Configuration

In closed, clyindrical bomb experiments with rapid mixing (ref. 9) the ignition lag for the triethylamine - white fuming nitric acid system was directly proportional to the ratio of reactor volume to charge volume (reciprocal of concentration). These data are plotted in figure 14.

Similar results were obtained with other propellant systems in the small-scale engine studies of reference 19. It was found that ignition lag is a function of reactor volume, reactor surface area, and nozzle-throat area. For the diallylaniline-triethylamine - red fuming nitric acid system, ignition lag is given by

$$\log \tau = \log A_t^* - 0.001608T - 0.211$$

where τ is the ignition lag in milliseconds, A_t^* is an effective surface area in square inches, and T is the temperature in degrees Fahrenheit. The effective surface area is the sum of the reactor surface area A_t and an effective nozzle area A_n^*. An empirical expression for the effective nozzle area is

$$A_n^* = A_n[(0.1307L - 1.051)T - 28.83L + 253.65] + (0.00143T - 0.271)(D - 1)$$

where L and D are, respectively, the combustor length and diameter in inches and A_n is the nozzle throat area. Since, in these experiments, a variation in surface area was accompanied by a similar change in volume, A_t includes both surface area and volumetric effects.

The independent effect of reactor surface area was measured by experiments in which reactor volume was kept nearly constant. These data on the effect of combustor surface area on ignition lag are summarized in the following table:

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Reactor surface area, A_t, sq in.		Effective nozzle area, A_n^*, sq in.	Effective surface area A_t^*, sq in.	Volume, V, cu in.	Ignition lag, τ, millisec	
Actual	Relative				Experimental	Calculated
30.5	1.0	9.3	39.8	11.8	15.1	15.7
39.6	1.3	↓	48.9	11.8	14.8	19.3
49.0	1.6		58.3	11.8	16.2	23.0
68.4	2.2		77.7	11.5	19.4	30.7

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Apparently, in the empirical correlation, the actual effect of surface area is small compared with the effect of reactor volume, and the A_t^* correlation thus results from the way in which the experiments were conducted.

Several experiments with another fuel, triethyl trithiophosphite, showed that its behavior was similar to that of diallylaniline. Data for the two fuels at 120° F are plotted in figure 15; the only difference is in the slope of the τ - A_t^* line. To construct this figure, the A_n^* correlation was assumed to be the same for both fuels.

Effect of Mixing Method

All comparable ignition-lag data from the open-tube and small-scale engine equipment from references 12, 13, 14, 15, 17, 18, and 20 are listed in table III. For the most part, no great difference exists between the results from the two apparatus when the viscosity of one or both propellants is less than 20 centistokes. In the region of 20 to 40 centistokes, the open-tube lags become appreciably longer than the engine lags, and the deviation becomes greater as viscosity increases beyond these values. The data also indicate that, the greater the reactivity of the propellants, the higher the viscosity at which the results from the two apparatus begin to deviate.

The effect of stream impingement on the walls appears to be negligible. The data of reference 19 show no difference in ignition lag between conditions where the resultant mixed stream impinged on the reactor walls and where the resultant stream was axially directed.

Effect of Acid Composition

In general, for acids containing only small percentages of nitrogen dioxide, ignition lag increased rapidly as the water content was increased.

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This effect could be largely offset by the addition of 8 to 15 percent (or more) of nitrogen dioxide. Table IV summarizes the observed effects of acid composition on ignition lag in the open-tube apparatus from references 13, 16, and 21. Data for ortho-toluidine from table IV are plotted in figure 16 in order to illustrate the above observations. Reference 12 reports a similar effect of water on ignition lags of xylidine - triethylamine fuel in the small-scale engine, and reference 17 shows that the ignition lag of furfuryl alcohol is affected in the same way (illustrated in fig. 10).

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Two practical points are brought out by the data of reference 12 and table IV: (1) White fuming nitric acid containing up to 2 percent water, and low-freezing-point red fuming nitric acid containing 2 to 4 percent water and 16 to 19 percent nitrogen dioxide give essentially equivalent ignition lags at the same temperature; (2) as long as the water content of white fuming nitric acid is not much greater than 2 percent, variations in water content do not appreciably affect ignition lag. Reference 18 further supports point (1), as shown in figure 17. With propylene - N,N-dimethyl amidophosphite, no great difference exists between the two acids; with mixed alkyl thiophosphites, the difference is small and constant (although the percent difference is large).

Effect of Fuel Composition

The fuels included in the ignition-lag studies were selected from the following classes: aromatic and aliphatic amines, alcohols and mercaptans, phosphites and thiophosphites, and miscellaneous classes including terpenes, hydrocarbons, and aliphatic imines. In many of the studies, -40° F was selected arbitrarily as a suitable temperature for screening fuels for possible low-temperature application. Therefore, data obtained at this temperature permit comparisons among the greatest number of fuels. Table V contains a summary of ignition-lag data at -40° F for fuels arranged by classes for three acids (refs. 12 to 18, 20 to 22). The compositions noted for the oxidants are only approximate (e.g., FNA-2-0 represents water concentrations of 0 to 2 percent and NO_2 concentrations of 0 to 1 percent).

Many of the fuels that were chemically interesting were much too viscous at -40° F to be used neat, and therefore were blended with varying percentages of triethylamine to reduce viscosity. In some cases a synergistic effect on ignition lag was observed; that is, the lag of the mixture was less than the lag of either pure component. In other cases, the blending agent acted merely as a diluent; that is, ignition lag increased with increasing concentration of blending agent. This behavior is illustrated in figure 18.

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With respect to ignition lag (table V), little difference occurs among the aromatic amines and the unsaturated aliphatic amines; the alcohols and mercaptans are somewhat less reactive; and the organophosphorus fuels are considerably more reactive than any of the fuels studied, with the exception of ethylenimine.

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DISCUSSION

The ignition lag, or induction period, may be considered as the time required to generate the threshold concentration of active particles necessary for flame initiation or at least for high-temperature reaction. If, as observed in reference 9, the ignition-lag period is characterized by constant pressure and presumably constant temperature, this ignition-lag time should depend on the rate of production of active particles and the rate of their removal by any mechanism such as wall-quenching, flow from the reaction zone, or side reactions.

For a closed reactor with fixed charge and with dimensions much larger than the mean free path of the reactant molecules, ignition lag should vary mostly with concentration, that is, with reactor volume. For an open tube, on the other hand, concentration should vary with exit pressure, and therefore ignition lag should be a function of ambient pressure. Two important factors in this case are flow turbulence, which should increase the importance of wall-quenching by promoting diffusion, and removal of material at the tube exit, which also should retard ignition. The effectiveness of the exit as a quenching device should decrease as the tube length is increased.

The rocket engine is a partially closed flow reactor, and ignition-lag behavior should lie between the extremes discussed in the preceding paragraph. Accordingly, for a given flow rate, the reactor volume could be expected to control ignition lag for a given propellant and temperature. As the nozzle opening is increased, the lag should increase because of the removal of reacting material, and the pressure dependence also should increase. The fixed-charge open-tube apparatus, at first glance, should behave something like a rocket engine with respect to ignition lag. Although the "open nozzle area" is large, the absence of a through-put velocity should decrease the loss rate of material through the tube axis. In comparison with the small-scale engine apparatus, the thermostatically controlled walls of the open tube should have a greater quenching effect at low initial temperatures.

In the following sections, the results previously presented are discussed in terms of this qualitative model, and comparisons are made with other ignition-lag data.

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Temperature Coefficient of Ignition Lag

The data of references 2, 3, and 9 indicate that during a major portion of the ignition-lag period pressure is nearly constant. If it is assumed that the temperature is also constant, the rate of production of active particles should have an Arrhenius-type behavior with respect to temperature; that is, rate = $f(e^{-E/RT})$, where E is an activation energy for ignition. Reference 23 makes a similar assumption based on empirical plots of ignition lag against temperature.

The rate of reaction during the ignition-lag period can be represented by

$$-\frac{dC}{dt} = AC^n e^{-E/RT} = \frac{dC_a}{dt}$$

where T is the initial propellant temperature, A is a constant that depends on the nature of the reactants, C is the concentration of reactants (assumed equal for all species), and C_a is the concentration of active particles. For a second-order reaction ($n = 2$), assuming that the concentration C_τ at time τ is small compared with the initial concentration, the integral is $\tau = e^{E/RT}/C_\tau A$. For a fixed-charge or steady-flow system the concentration should be inversely proportional to reactor volume V_c. With this relation substituted in the above equation, the expression for ignition lag becomes

$$\tau = KV_c e^{E/RT}$$

The value of the constant K probably depends on the reacting species, reactor geometry, pressure, mixing energy and efficiency, and perhaps other factors. For a given reactor and propellant system, then, the logarithm of ignition lag should be proportional to $1/T$:

$$\tau = K' e^{E/RT}$$

The data of table I (plotted in figs. 3 to 12) generally follow this expression with activation energies of 0 to 10,000 Btu per mole (0 - 5600 cal/mole). The significance of these temperature coefficients is uncertain; they may be consistent with a neutralization reaction or with the primary step in a nitration reaction (refs. 23 to 25). On the other hand, since activation energies of solution and viscosity also lie in this region (ref. 23), the ignition lag could be controlled by the rate of mixing. Comparable data on triethylamine - nitric acid (refs. 9, 23, and 25) indicate, however, that the ratios of ignition lags are not inversely proportional to the ratios of mixing energies when it is assumed that all potential energy in the apparatus is available for mixing. It then appears likely that, for any reasonable rate of mixing, the temperature dependence of ignition lag is associated with a change in specific reaction rate.

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In terms of the model, a decrease in propellant temperature should decrease the rate of reaction as well as the rate at which material leaves the reactor. Since the former process is an exponential function of temperature and the latter depends on the square root of temperature, the net effect should be an increase in ignition lag with a decrease in temperature. Indeed, it might be argued that for systems with appreciable loss rates, an increase in delay should follow increase in temperature if the chemical activation energy is zero; this behavior is observed occasionally (e.g., refs. 16, 23, and 26). 4578

The large activation energies measured in the open-tube apparatus at temperatures below -76° F (table I) cannot be attributed to a change in reaction mechanism, since the same propellants did not behave similarly in the small-scale engine apparatus. It is more likely that the combination of low mixing energy and high viscosity produced little mixing and, hence, extremely fuel-rich or acid-rich regions. Reference 9 shows that ignition lag increases quite rapidly in these mixture ranges.

Ignition-Lag - Pressure Dependence

It would be expected from the model that the effects of ambient pressure on ignition lag would depend on several factors: the ratio of exit area to reactor volume, the aspect ratio of the reactor, the charge rate or charge per unit volume, and, to some extent, the temperature or ignition lag at a reference condition such as sea-level ambient pressure. These factors all could affect the net rate of production of active particles and their concentration.

Altitude ignition data from the usual small-scale engine configuration (2-in. diam., 4-in. length, 0.4-in. nozzle diam.) shown in table II show no particular trend with temperature. The absolute difference between sea-level and altitude ignition lags is quite small, with the one exception noted in table II. Therefore, the percentage changes in ignition lag can become quite large as ignition lag is decreased. Apparently this reactor behaves as a nearly closed volume. The other extreme in behavior, a definite pressure limitation on ignition, is described in reference 27. These experiments were conducted with a ratio of very low charge volume to reactor volume.

Two factors appear to be responsible for the variable effects of ambient pressure on ignition lag: poor mixing and loss of material from the reaction zone by flow or diffusion. These effects, taken singly or together, would decrease the net rate of production of active particles and hence would increase the ignition lag. Reference 28 reports that fluid jets injected into a region where the ambient pressure is less than the vapor pressure of the fluid quickly atomize and become diffuse. This effect is there assumed to account for the observed effects of ambient

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pressure on ignition lag. It would be valid, however, only for cases where either the charge per unit volume of reactor is quite small or the exit area per unit volume is large. The phenomenon was observed as a transient in the experiments presented in table II but, because the ambient pressure quickly exceeded the vapor pressure in this nearly closed reactor, the jets rapidly solidified, and normal reaction conditions were obtained after a few milliseconds. This accounts for the rather small effect of ambient pressure on ignition lag.

Figure 13 illustrates the combined effects of increased material loss and decreased reactivity (temperature effect) on ignition lag at altitude. The percentage change in ignition lag at altitude is shown to be roughly a function of the sea-level lag and the ratio of nozzle-exit area to chamber area. This behavior could explain many of the contradictory effects of ambient pressure on ignition lag reported in the literature. Thus, the data of reference 29 for a different propellant system at the same altitude (90,000 ft) agree rather well with the plot of NACA data in figure 13, whereas a comparison that did not include geometric effects showed a large deviation in ignition-lag behavior at altitude.

Ignition-Lag - Reactor-Volume Dependence

The discussion of temperature effects showed that, for a fixed-charge or constant-flow system, ignition lag could be related to reactor volume as well as to temperature:

$$\tau = f(V_c e^{E/RT})$$

where V_c is the volume per unit charge (reciprocal of concentration). The nature of the functional relation between τ and V_c depends on the order of the rate expression. For a second-order reaction, ignition lag should vary linearly with reactor volume. Both the closed-reactor studies of reference 9 and the flow-system studies of reference 19 seem to follow a nearly linear relation. The data of reference 9 (fig. 14) depart positively from the linear relation at high values of reactor volume and thus indicate a quenching effect of the walls that increases as the surface area per unit charge increases. The data of reference 19 (fig. 15) actually correlate best with an effective surface area which accounts for material loss as well as concentration effects. It appears, then, that for reasonably well-mixed reactors the ignition-lag period is determined by the rate of the second-order reaction between fuel and acid.

If it is assumed that the effective nozzle area is independent of the fuel used, the τ - A_t^* correlation can be extended to other fuel - acid systems. A single ignition-lag measurement at a given temperature should establish the slope of the τ - A_t^* line. Figure 15 shows such a linear relation for a second propellant system, triethyl trithiophosphite - nitric acid. Thus, a single ignition-lag measurement in a continuous-flow

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reactor similar to the rocket combustor used in reference 19 should be sufficient to predict the effects of changes in reactor geometry on ignition lag. Therefore, laboratory-measured ignition lags can be extrapolated to those lags that might be expected in the igniter of a full-scale rocket engine.

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If, optimistically, the correlations of reference 19 are assumed applicable to fixed-charge as well as to continuous-flow systems, it should be possible to relate the ignition-lag data obtained from a variety of apparatus. The data for diallylaniline-triethylamine - nitric acid reported in reference 13 provide a basis for testing this assumption. The measured ignition lags varied from 14 to 35 milliseconds, with an average of 26 milliseconds at -40° F. The calculated lag for this configuration is 17 milliseconds, which falls within the range but misses the average by a wide margin. The charge per unit volume for the open tube, 2.29×10^{-3} pounds per cubic inch, is greater than the maximum equivalent charge for the engine, 0.99×10^{-3} pounds per cubic inch, so that the deviation may be attributed to a greater effect of material loss for a fixed-charge device and possibly to the greater quenching from the thermostatically controlled walls of the tube. The assumption may also be checked by comparing the results of references 18 and 26 for the triethyl trithiophosphite - nitric acid system at 75° F. This comparison is shown in figure 19 together with the line predicted from figure 15 by taking the ratio of slopes. The agreement between the engine data and with the calculated relation is quite good. Agreement with the open-tube data improves as the available mixing energy increases. It is reasonable to suppose, therefore, that the empirical correlation can be applied either to fixed-charge or constant-flow systems provided that the mixing energy is reasonably high, say of the order of 100 to 1000 foot-pounds per pound mass of propellant at normal temperatures. The lower limit probably should be raised as temperature is decreased.

At any rate, the concept of an ignition-lag - volume or effective-surface-area relation has many possibilities for extending the usefulness of individual ignition-lag measurements by extrapolation to other geometry and temperature conditions. From an engineering standpoint, the producing of an arbitrary ignition lag to match any desired engine-starting sequence might now be possible with a priori design.

Mixing as a Factor in Ignition-Lag Measurements

For most propellant systems, the rate and efficiency of mixing definitely have an important influence on ignition lag. The NACA open-tube and engine apparatus have available mixing energies of 17 and 800 foot-pounds per pound mass of propellant, respectively. The data of table III show that this difference in energy becomes increasingly important as the propellant viscosity or reactivity increases.

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In the former case, mixing efficiency presumably decreases as viscosity increases until a point is reached where only extremes in mixture ratio are produced for a particular apparatus. As shown in reference 9, ignition lag can become quite large at these extreme ratios. Reference 23 reports that ignition-lag and viscosity behaviors with temperature are quite similar in some cases. A possible explanation for this behavior might be the fact that, at extreme mixture ratios, the extent of reaction must be quite small; hence, the total production and average concentration of active particles must be low. In terms of the model presented, this condition would either prevent ignition or at least make the ignition lag dependent on the rate of additional mixing that is produced as a result of the limited initial reaction.

For propellants of high reactivity, mixing time can be important even when viscosity is low. The data and discussion of references 2 and 3 support the observations from table III in this respect. In fact, for materials that react instantaneously on contact, the actual mixing time would be the ignition lag.

A threshold mixing energy above which an increase produces no effect on ignition lag is apparent in many cases; the data of figure 19 illustrate this point. For similar effective areas an increase from 28 to 810 foot-pounds per pound mass of propellant produces little variation in ignition lag, whereas an increase from 17 to 810 foot-pounds per pound mass produces a relatively large change in ignition lag. References 19 and 30 report similar phenomena, and a comparison of the hydrazine data from table III with those of references 2 and 3 shows the phenomenon to a lesser extent. Therefore, it appears that even moderate mixing energies (several hundred ft-lb/lb mass of propellant) should be sufficient to eliminate mixing as an important factor in ignition-lag measurements.

An interesting suggestion for further decreasing the influence of mixing energy on ignition lag is found in reference 31. The addition of 2 to 3 percent of a surfactant to the propellants decreased ignition lag as much as 60 percent without a change in mixing energy; the effect was greater for surfactants with lower molecular weight.

Effect of Acid Composition on Ignition Lag

If the proposition is accepted that the important preignition reaction is either a neutralization or the first step in a nitration (the reactions are quite similar), the concentration of nitronium ions NO_2^+ or nitrosonium ions NO^+ should have a considerable influence on ignition lag. The appropriate equilibriums, as discussed in reference 24, are

$$2\ HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O$$

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and

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$

Thus, the addition of water to nitric acid should increase ignition lag by decreasing the concentration of NO_2^+, and this effect in turn should be offset by the addition of N_2O_4. This behavior is indicated in table IV, figures 11, 16, and 17, and in references 9 and 12, and similar effects have been observed in other investigations (e.g., refs. 31 and 32). This evidence lends considerable support to the proposition that a Lewis neutralization reaction is an important step in the preignition period. 4578

A third equilibrium (ref. 24),

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3\overset{+}{O} + 2HSO_4^-$$

may indicate why mixed acid (nitric plus sulfuric) sometimes produces ignition with fuels that do not ignite with fuming nitric acid (see table V). Supporting data obtained with nitric acid - alkane sulfonic acid mixtures are reported in reference 33.

Relation Between Fuel Structure and Ignition Lag

The search for fuels having low ignition lags has preoccupied most of the workers in this field of investigation. A large number of fuels and blends representing many classes of compounds have been studied. Inevitably, disagreements have arisen over ignition lags measured by different investigators and sometimes over the relative order of reactivity. These disagreements led to attempts to correlate results from different experiments and to recommend standard ignition-lag measurement methods (e.g., ref. 26). Undoubtedly, the discrepancies were caused largely by variations in the parameters discussed previously. The discovery of several fuel types having low ignition lags at low temperatures and the gradual shift in emphasis toward high-energy propellant systems have removed most of the impetus for continued research in this area.

Despite the discrepancies previously noted, certain inferences about the relation of fuel structure to ignition lag can be drawn. The relations observed in the NACA program are indicated by the data of table V. Little difference was observed among aromatic amines, unsaturated aliphatic amines, furfuryl alcohol, and butyl mercaptans. A large decrease in ignition lag could be obtained with organophosphorus compounds like the alkyl thiophosphites and the amidophosphites, with ethylenimine, and probably with hydrazine. These observations do not appear to conflict with any published data.

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References 4 and 25 present results obtained with several hundred fuels representing a wide variety of classes; these data were obtained in a drop-test apparatus having a mixing energy of the order of 0.1 foot-pound per pound mass of propellant. This low mixing energy raises the question as to whether the results observed within homologous series possibly are obscured by mixing effects; in many cases, lack of ignition seems to be correlated with increased viscosity. Nevertheless, the trends probably are qualitatively good, especially among the classes of fuels. The results should be useful for guiding syntheses within classes but probably cannot be used to predict new classes of fuels of potential use. Examples of the results obtained in references 4 and 25 are:

(1) For molecular isomers of aliphatic amines, the order of activity for the three fundamental amine structures is

tertiary > secondary > primary

(2) In aromatic amines with no other ring substituents, the order of activation by the amino substituent is

N,N-dialkyl > N-alkyl > NH_2

Reference 32 confirms the supposition that hydrazine is considerably more reactive than the aromatic amines, as well as the observation in table V that the reactivity of hydrazine hydrate is considerably less than that of hydrazine. The effect is shown to be equivalent to adding water to acid, and the countereffects of added N_2O_4 in the acid are quite similar to those discussed in the previous section on acid composition. Reference 5 reports the following order of reactivity with red fuming nitric acid:

hydrazine > furfuryl alcohol > aniline

which, again, agrees reasonably well with other observations. Data for a variety of fuels with red fuming nitric acid reported in reference 34 also agree with the data of references 4 and 25 and table V.

Currently, the fuels that seem to be the most promising (low ignition lags and wide temperature range) include hydrazine derivatives, such as unsymmetrical dimethyl hydrazine and allyl hydrazines (ref. 35); organophosphorus compounds, such as amidophosphites and alkyl thiophosphites (table V and refs. 30, 32, and 36); and imines, such as ethylenimine (table V and ref. 4). In regard to the mechanism of ignition, the fuel-structure - ignition-lag studies can give only qualitative answers. The possibility of a Lewis-type neutralization being an important and perhaps rate-controlling step (in the absence of mixing effects) is certainly not ruled out and, in fact, receives support from the kinetic studies of reference 9 as well as the studies of acid-composition effects.

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ROCKET-ENGINE STARTING WITH SELF-IGNITING PROPELLANTS

Early engine experiments (ref. 1) indicated the desirability of short ignition lags to prevent large pressure transients during the starting period. Elementary analyses of the situation (e.g., ref. 5) show that, for a given propellant - engine system, the product of flow rate ω and ignition lag τ determines the maximum pressure that can be realized:

$$P_{max} \leq K\omega\tau$$

where K is a constant that depends on the geometry and the propellant system. It follows, then, that short ignition lags are very important for cases where high initial flow rates are required. It also is apparent that fuels with long ignition lags can be used successfully to ignite rockets if the initial flow is properly programmed. Thus, short ignition lags are desirable to improve the margin of safety during engine starts but are not necessary to achieve satisfactory ignition, that is, ignition free from pressure surges. This conclusion is amply supported by the engine experiments of references 10 and 11, which show that smooth ignition can be obtained when the valve opening times are decreased with decreasing temperature. This amounted to decreasing the initial flow rate as the ignition lag increased. It is thus possible to obtain low temperature starts with propellants having poor ignition characteristics (55-percent hydrazine, ref. 11).

A possible safety factor was observed at low temperatures (ref. 10): as the propellant valve opening time was decreased below the value producing maximum pressure rise, the pressure continually decreased until no ignition was obtained. This behavior, however, might be expected to depend strongly on the exact engine and flow-system configuration and therefore cannot be considered typical.

Another factor that should be considered in extrapolating laboratory data to engine conditions is the effect of mixture ratio on ignition lag. References 9 and 31 show large increases in ignition lag at extreme fuel-rich and oxidant-rich ratios, and reference 10 shows that a lead of one propellant can cause extreme variations in mixture ratio during the pre-ignition period. Accordingly, unless care is taken to prevent wide variations in mixture ratio during engine starts, laboratory ignition-lag data for normal operating mixture ratios may have little or no value in predicting engine transients. On the other hand, the laboratory data are significant to the engine designer since excess flow of one propellant may be a prime cause for starting malfunction.

CONCLUDING REMARKS

The data and analysis presented emphasize the point that ignition lag cannot be considered as a property of a propellant system. At best,

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under well-defined experimental conditions, ignition lag is a measure of reaction rate that can be extrapolated with some confidence to other conditions or to full-scale engines. At worst, under ill-defined experimental conditions, ignition lag may be meaningless. Even comparative studies may have little validity under these conditions if the results are confused by such factors as poor mixing or excessive material loss.

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Reliable and well-defined ignition-lag data can be of considerable importance either in a priori rocket-engine design or in engine-starting problems either in development or in field use.

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In the former case, the designer can select initial flows that will ensure freedom from excessive pressure transients, or he can assume that the possible propellant accumulation is within the safety requirements for a particular application. In this respect, recent NACA experiments in small-scale engines with axial-flow igniters have shown that adherence to the design factors discussed previously has permitted smooth reproducible starts at temperatures approaching the freezing point of one or both propellants.

In the latter case, a knowledge of the factors affecting ignition behavior can simplify the experimental approach for solving engine-starting problems that arise during engine development or in unforeseen applications in the field.

SUMMARY OF FINDINGS

Analysis of NACA ignition-lag data for self-igniting fuel - nitric acid rocket propellants and comparisons with data from other sources have indicated the following trends:

1. Ignition lag follows an Arrhenius relation with respect to temperature provided that mixing is reasonably energetic. The activation energies observed, 0 to 10,000 Btu per mole, are best explained by assuming that a Lewis-type neutralization is the rate-controlling step.

2. The effect of ambient initial pressure on ignition lag is related to the percent open area of the reactor and to the initial temperature or ignition lag at sea-level reference pressure.

3. The effect of reactor geometry is important. Ignition lag is minimized by maximizing the effective charge per unit volume.

4. An increase in mixing energy causes a decrease in ignition lag; however, there appears to be a threshold energy above which further increase has little effect on ignition lag.

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5. Water in the acid causes an increase in ignition lag. This effect can be largely compensated for by the addition of nitrogen dioxide or sulfuric acid.

6. With respect to fuel composition, aromatic and unsaturated aliphatic amines as well as heterocyclic alcohols appear to have nearly the same ignition lags. The most reactive fuels at present are hydrazine and its derivatives, organo-phosphites and thiophosphites, and ethylenimine.

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Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, July 22, 1957.

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TABLE I. - TEMPERATURE COEFFICIENT OF IGNITION LAG[a] IN NACA EXPERIMENTS

Fuel (b)	Acid (c)	Temperature coefficient, E, Btu/mole×10^{-3}	Proportionality constant, A, millisec	Temperature range, °F	Reference	Type of apparatus (d)
Hydrazine hydrate	FNA - 2 - 1	2.1	2.53	80 to 120	12	E
Hydrazine hydrate	FNA - 2 - 1	7.95	.01	-40 to 70		
50% Diallylaniline - 50% triethylamine	FNA - 2 - 1	1.88	1.77	-40 to 100	12	E
	FNA - 3 - 16	2.74	2.2	-90 to 100		
	FNA - 3 - 19	3.03	.98	-90 to 100	19	E
		1.7	4.0			
		1.96	5.76			
		.87	9.15	-40 to 80	13	T
		69.5	3.16×10^{-38}	-105 to -76		
Aromatic amine - triethylamine[e]		.98	9.48	-40 to 80	13	T
		25.2	1.11×10^{-13}	-105 to -76		
o-Toluidine - triethylamine[f]		1.98	2.11	-80 to 120	14	E
Allylamine		2.45	4.61	-105 to -40	15	T
50% Allylamine - 50% triethylamine		3.97	.16	-105 to -40		
30% Allylamine - 70% triethylamine		5.63	.027	-80 to -40		
Mixed alkyl thiophosphites		0	9	-80 to -40	15	T
50% Mixed alkyl thiophosphites - 50% triethylamine		4.26	.09			
30% Mixed alkyl thiophosphites - 70% triethylamine		3.12	.71			
Mixed alkyl thiophosphites	FNA - 4 - 20	1.42	2.92	-70 to 70	16	E
Triethyl trithiophosphite	FNA - 2 - 0.5	-5.24	1100	-40 to 70	16	T
Furfuryl alcohol	FNA - 2 - 0.5	0	26.5	40 to 70	17	T
	FNA - 2 - 0.5	0	17	0 to 120	17	E
	FNA - 5 - 0.5	6.23	.048	-40 to 80		
	FNA - 16 - 0.5	10.3	.0019	0 to 75		
Mixed alkyl thiophosphites	FNA - 2 - 0.5	0	6	-40 to 120	18	E
	FNA - 3 - 20	0	3.5	-70 to 120		
	FNA - 3 - 20	8.82	2.55×10^{-5}	-90 to -76		
Triethyl trithiophosphite	FNA - 2 - 0.5	0	6	-40 to 120	18	E
	FNA - 3 - 20	1.22	.9	-90 to 120		
Propylene - N,N-dimethyl amidophosphite	FNA - 2 - 0.5	1.22	.9	-40 to 120	18	E
	FNA - 3 - 20	2.64	.13	-90 to 120		

[a] $\tau = Ae^{E/RT}$; Arrhenius-type function for ignition lag τ (see text) where E is temperature coefficient, R is universal gas constant, T is absolute temperature, and A is proportionality constant.

[b] Numbers indicate volume percent of each component.

[c] Fuming nitric acid; first number following indicates approximate percent water, and second number is approximate percent nitrogen dioxide.

[d] E = small-scale engine; T = open-tube apparatus.

[e] Average value for a series of similar aromatic amines.

[f] Both 1:1 and 3:7 volume ratios.

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TABLE II. - EFFECTS OF PRESSURE ALTITUDE ON IGNITION LAG (SMALL-SCALE ENGINE)

Fuel (a)	Acid (b)	Pressure altitude, ft x10^{-3}	Temperature, °F	Altitude ignition lag, τ_a, millisec	Sea-level ignition lag, τ_o, millisec	$\tau_a - \tau_o$	$\frac{\tau_a - \tau_o}{\tau_o}$	Reference
50% Diallylaniline - 50% triethylamine	FNA - 2 - 0.5	81±5	110	10.5	9.2	1.3	0.14	12
		82	80	10.8	10.6	.2	.02	
		81	50	11.7	11.2	.5	.04	
		83±3	20	17.4	13.6	3.8	.28	
		81±3	-10	16.8	13.6	3.2	.24	
		82±2	-40	19.7	16.7	3.0	.18	
		86±2	-50	22.9	22.7	.2	.01	
	FNA - 3 - 16	82	110	11.1	13.6	-2.5	-.18	
	FNA - 3 - 16	94	-95	53.4	55.2	-1.8	-.03	
50% o-Toluidine - 50% triethylamine	FNA - 3 - 19	91	120	10.3	12.0	-1.7	-.14	14
30% o-Toluidine - 70% triethylamine	FNA - 3 - 19	89	-95	29.9	27.7	2.2	.08	
Hydrazine	FNA - 2 - 0.5	62	72	6.5	5.6	.9	.16	20
Mixed butyl mercaptans		62	72	83.9	38.2	45.7	1.2	
Mixed alkyl thiophosphites		77	120	5.4	5.6	-.2	-.04	18
Triethyl trithiophosphite		90	120	5.0	6.0	-1.0	-.17	
Triethyl trithiophosphite		90	-40	5.8	5.3	.5	.09	
Propylene - N,N-dimethyl amidophosphite		90	120	2.8	2.7	.1	.04	
Propylene - N,N-dimethyl amidophosphite		90	-40	5.2	4.1	1.1	.27	
Mixed alkyl thiophosphites	FNA - 3 - 20	86±4	120	5.5	3.4	2.1	.62	
Mixed alkyl thiophosphites		90	-90	6.1	5.7	.4	.07	
Triethyl trithiophosphite		90	121	4.1	2.1	2.0	.95	
		90	-70	6.2	5.7	.5	.09	
		90	-95	5.5	4.9	.6	.12	
Propylene - N,N-dimethyl amidophosphite		90	120	2.6	1.3	1.3	1.0	
Propylene - N,N-dimethyl amidophosphite		90	-92	6.4	8.0	-1.6	-.20	

[a]Numbers indicate volume percent of components.

[b]Fuming nitric acid; first number following indicates approximate percent water, and second number is approximate percent nitrogen dioxide.

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TABLE III. - COMPARISON OF IGNITION LAGS IN SMALL-SCALE ENGINE AND OPEN-TUBE APPARATUS.

Fuel (a)	Acid (b)	Approximate fuel viscosity, centistokes	Approximate acid viscosity, centistokes	Temperature, °F	Ignition lag, τ, millisec		Reference
					Open tube	Engine	
Hydrazine	FNA - 2 - 0.5	1	1	70	58	6	20
Mixed butyl mercaptans		1	1	72	55	38	
Mixed butyl mercaptans		1	2	-37	No ignition	>400	
50% Xylidines - 50% triethylamine	FNA - 0 - 0.5	18	2	-40	34	35	
	FNA - 2 - 0.5	18	2	-40	42	42	
	FNA - 7 - 0.5	18	3	-40	114	423	
50% Diallylaniline - 50% triethylamine	FNA - 0 - 0.5	6	2	-40	17	13	
	FNA - 2 - 0.5	6	2	-40	20	17	
	FNA - 3 - 16	6	6	-40	28	30	
50% o-Toluidine - 50% triethylamine	FNA - 3 - 19	20	6	-40	27	25	
30% o-Toluidine - 70% triethylamine		1	1	68	19	15	
30% o-Toluidine - 70% triethylamine		6	6	-40	24	25	
Hydrazine hydrate	FNA - 2 - 0.5	20	2	-40	No ignition	131	
Furfuryl alcohol	FNA - 2 - 0.5	5 - 10	0.6 - 0.7	36 - 72	26.1	15.6	17
Mixed alkyl thiophosphites	FNA - 3 - 19	12	6	-40	9	4	15,18
		42	29	-80	9	4.4	
		60	50	-90	[c]38	5.7	
30% o-Toluidine - 70% triethylamine	FNA - 3 - 19	22	25	-76	38	28	13,14
		36	44	-87	61	29	
		125	150	-105	210	[c]31	
50% Diallylaniline - 50% triethylamine		14	25	-76	62	44	12,13
		22	44	-87	~1000	50	
		50	150	-105	No ignition	[c]68	

[a]Numbers are volume percent of each component.

[b]Fuming nitric acid; first number following is approximate percent water, and second number is approximate percent nitrogen dioxide.

[c]Value from extrapolated curve.

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TABLE IV. - EFFECT OF ACID COMPOSITION ON IGNITION LAG AT -40° F (OPEN-TUBE APPARATUS)

[Fuel composition, percent by volume in triethylamine.]

Acid composition, percent by weight				Ignition lag, τ, millisec						
H_2O	N_2O_4	HNO_3	H_2SO_4	30% o-Toluidine (refs. 13, 21)	50% Allylamine (ref. 21)	50% Ethyleneimine (ref. 21)	100% Mixed alkyl thiophosphites (ref. 16)	30% Aniline (ref. 13)	30% N-Ethyl aniline (ref. 13)	30% Xylidines (ref. 13)
0.4	0.1	99.5		30	38	20				
.4	2.1	97.5		26						
.4	3.7	95.9		21						
.4	7.4	92.2		20						
2	0	98					8			
2.8	.1	97.1		40	35	23				
1.9	8.0	90.1		25	29	18	2			
1.7	16.1	82.2		28	35	18				
1.3	24.6	74.1		28	33	17	3			
1.6	----	81.3	17.1	36				38	48	42
4.4	.1	95.5		69	52	27				
3.9	8.0	88.1		30	34	26				
3.7	16.0	80.3		34	34	23				
3.0	19.0	78.0		24			9	21	36	31
3.3	24.6	72.1		34	34	22				
6.3	.1	93.6		129	69	36	72			
6.8	.2	93.0		102				23	105	78
5.9	8.0	86.1		40	42	32				
5.8	15.8	78.5		34	52	25				
5.3	24.7	70.0		33	42	22				
8.2	.1	91.7		179	97	37				
7.7	8.1	84.2		68	43	21				
7.7	15.9	76.4		42	46	32				
7.2	24.7	68.1		57	42	29				
10.1	.1	89.8		No ignition	135	No ignition	185			
9.7	8.1	82.2		129	69	28	26			
9.8	15.8	74.5		65	55	40				
9.3	24.4	66.3		39	55	40	48			

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TABLE V. - EFFECT OF FUEL COMPOSITION ON IGNITION LAG AT -40° F

Fuel composition (a)	Ignition lag, τ, millisec			Apparatus (f)	Reference
	MA - 2 - 17[b]	FNA - 3 - 19[c] (d)	FNA - 2 - 0[c] (e)		
Aromatic amines					
N-Ethylaniline	50	No ignition		T	13
30% N-Ethylaniline	48	36			
N,N-Diethylaniline	90	No ignition			
30% N,N-Diethylaniline	65	33			
30% Aniline	38	21			
30% o-Toluidine	36	24			
		26.5		E	14
		28	40	T	21
50% o-Toluidine	36	27		T	13
50% o-Toluidine		24		E	14
30% Xylidines	42	31		T	13
50% Xylidines	32	31		T	13
50% Xylidines			42	E	12
50% Diallylaniline	27	26	42	T	13
50% Diallylaniline		30.5	16.7	E	12
Aliphatic amines					
Triethylamine	No ignition	750		T	13
Triethylamine		422			15
Diethylene triamine	110				13
Allylamine		91			15
50% Allylamine		21			
30% Allylamine		22			
15% Allylamine		39			
50% Allylamine - 50% ethylenimine		34	34		21
Diallylamine		47			15
50% Diallylamine		87			
30% Diallylamine		210			
Hydrazine					
Hydrazine hydrate			131	E	12
Hydrazine			[g]58	T	20
Hydrazine			[g]6	E	20
Mercaptans and alcohols					
Furfuryl alcohol	[h]44			T	22
			54	E	12
			49	T	17
			54	E	17
70% Furfuryl alcohol 30% Xylene	31			T	22
70% Furfuryl alcohol 30% Xylene			56		13
Mixed butyl mercaptans	23		33 - no ignition		13,22
			No ignition		20
			> 400	E	20
Furfuryl mercaptan			23	E	12
3-Mercapto 1-propanol	No ignition			T	13

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TABLE V. - Concluded. EFFECT OF FUEL COMPOSITION ON IGNITION LAG AT -40° F

Fuel composition (a)	Ignition lag, τ, millisec			Apparatus (f)	Reference
	MA - 2 - 17[b]	FNA - 3 - 19[c] (d)	FNA - 2 - 0[c] (e)		
Organophosphorus compounds					
Mixed alkyl thiophosphites		9		T	15
			8	T	16
		17		E	16
		4	6	E	18
50% Alkyl thiophosphite		15		T	15
30% Alkyl thiophosphite		29			15
Triethyl trithiophosphite			2		16
Triethyl trithiophosphite		3	5.5	E	18
90% Triethyl trithiophosphite - 10% n-heptane			9	T	16
80% Triethyl trithiophosphite - 20% n-heptane			18		
70% Triethyl trithiophosphite - 30% n-heptane			37		
60% Triethyl trithiophosphite - 40% n-heptane			54		
Phosphorus trichloride			612		
Propylene - N,N-dimethyl amidophosphite (RF 208)		3	4	E	18
Miscellaneous fuels					
Turpentine	77			T	22
		No ignition	No ignition	T	13
			75	E	12
2-Methyl pentadiene	76			T	13
2,2,4,6-Tetramethyl dihydropyridine	470				
1-Vinyl-cyclohexene - 3-tetrahydrofuran	No ignition No ignition		No ignition		
Ethylenimine		12			15
50% Ethylenimine		14			15
50% Ethylenimine		[i]20	22		21
30% Ethylenimine		24			15
15% Ethylenimine		106			15
50% Ethylenimine - 50% n-heptane		60			
30% Ethylenimine - 70% n-heptane		243			
15% Ethylenimine - 85% n-heptane		No ignition			
2-Ethyl ethylenimine		39			

[a]Unless otherwise indicated, numbers indicate percent by volume in triethylamine.

[b]Mixed acid (nitric plus sulfuric); first number indicates approximate percent water, and second number is approximate percent sulfuric acid.

[c]Fuming nitric acid; first number indicates approximate percent water, and second number is approximate nitrogen dioxide content.

[d]Includes acids containing 3 to 4 percent water and 16 to 20 percent nitrogen dioxide.

[e]Includes acids containing up to 2 percent water and up to 1 percent nitrogen dioxide.

[f]T, open-tube apparatus; E, small-scale engine.

[g]70° F.

[h]-33° F.

[i]Interpolated.

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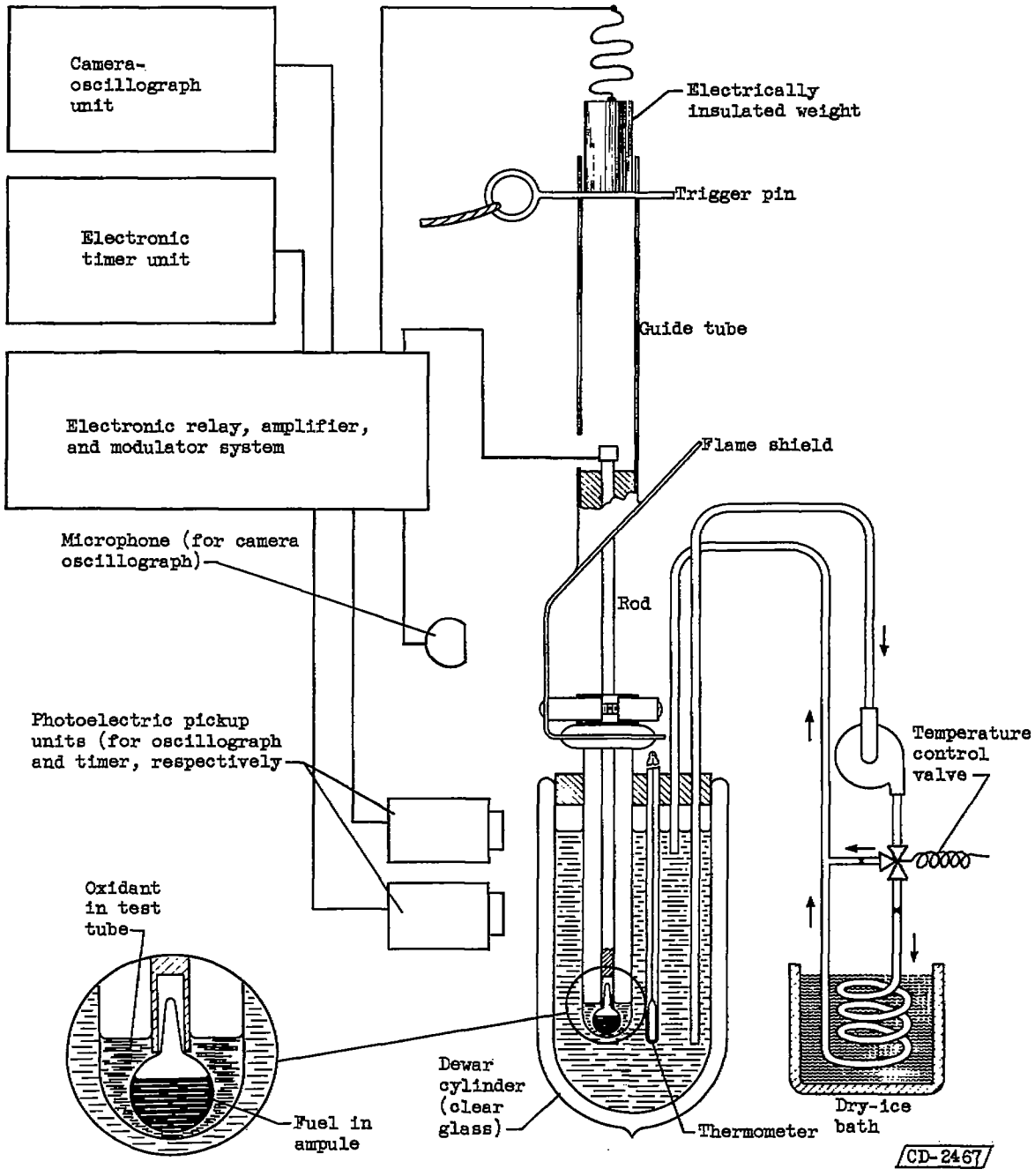

(a) Schematic diagram.

Figure 1. - Modified open-cup ignition-delay apparatus.

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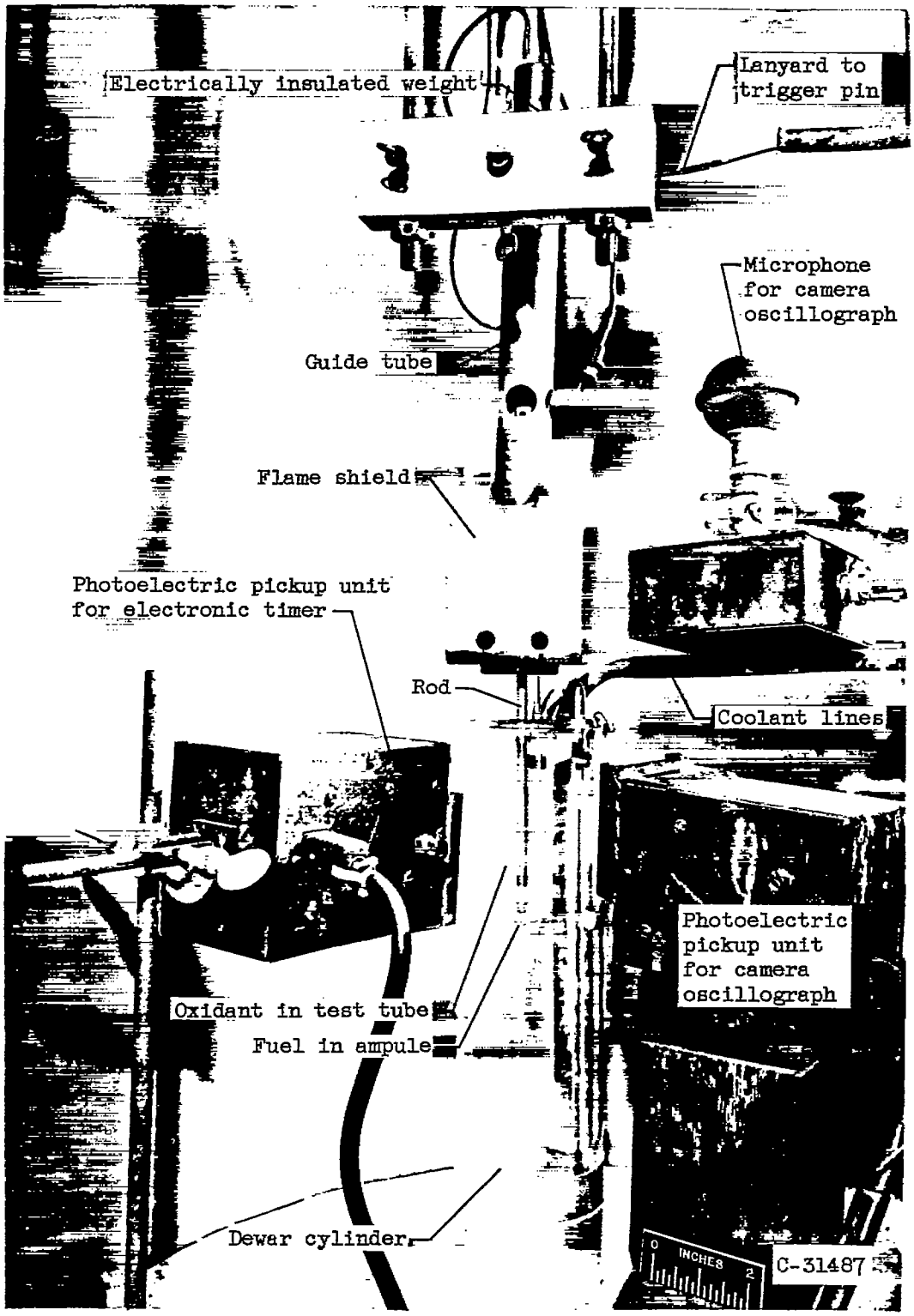

(b) Photograph of assembly.

Figure 1. - Concluded. Modified open-cup ignition-delay apparatus.

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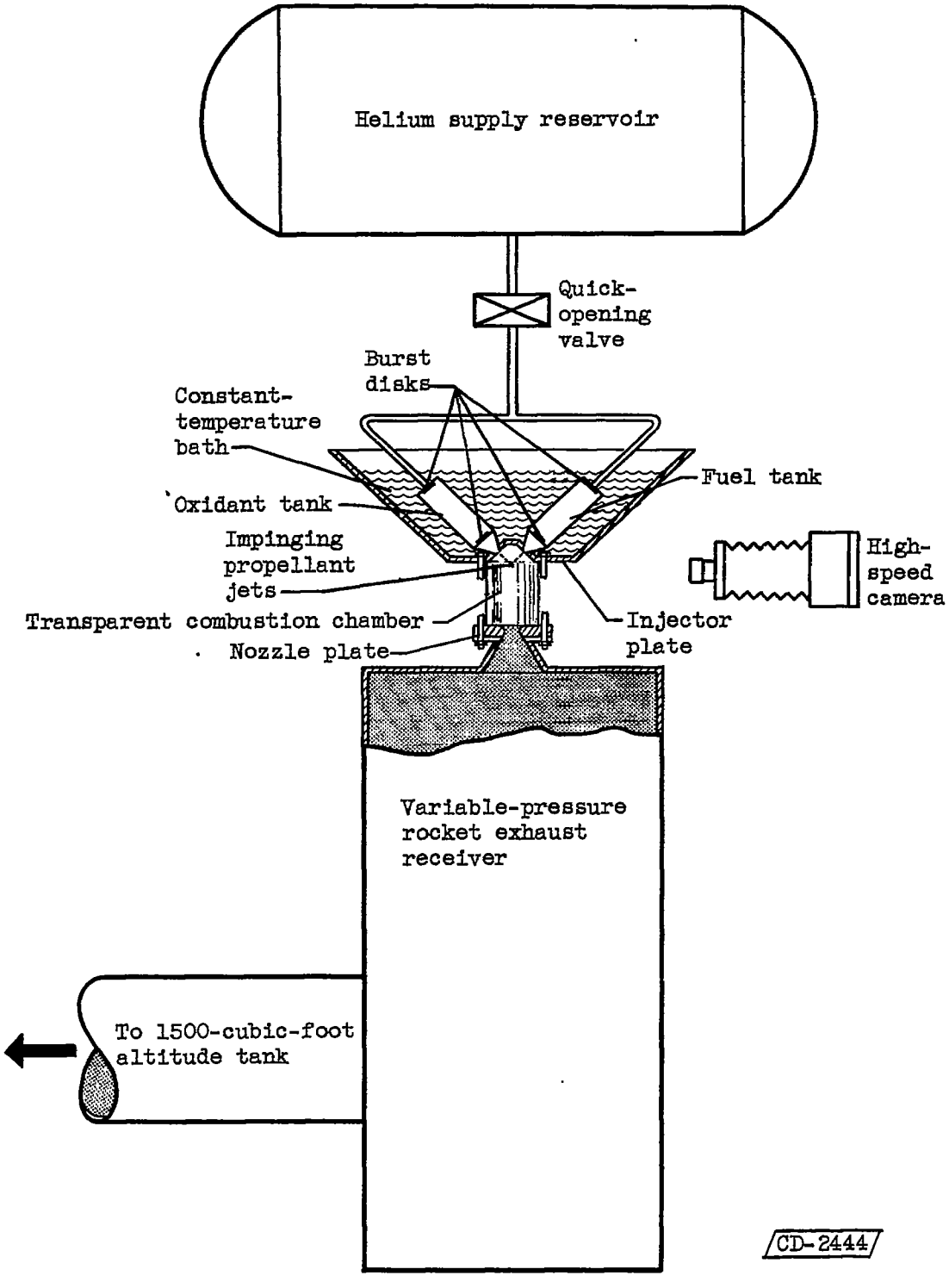

(a) Schematic diagram.

Figure 2. - Small-scale rocket-engine ignition-delay apparatus.

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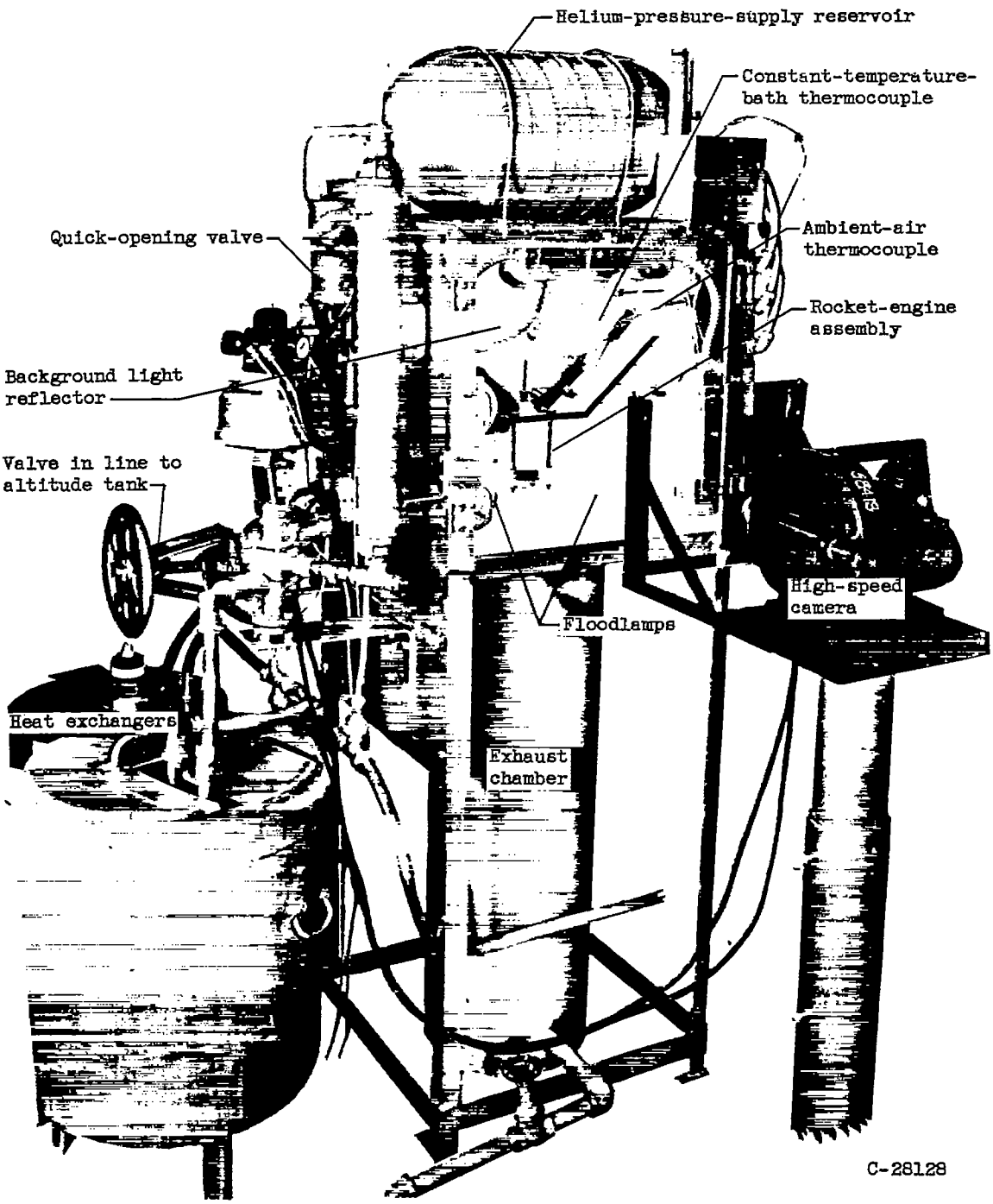

(b) Photograph of assembly.

Figure 2. - Concluded. Small-scale rocket-engine ignition-delay apparatus.

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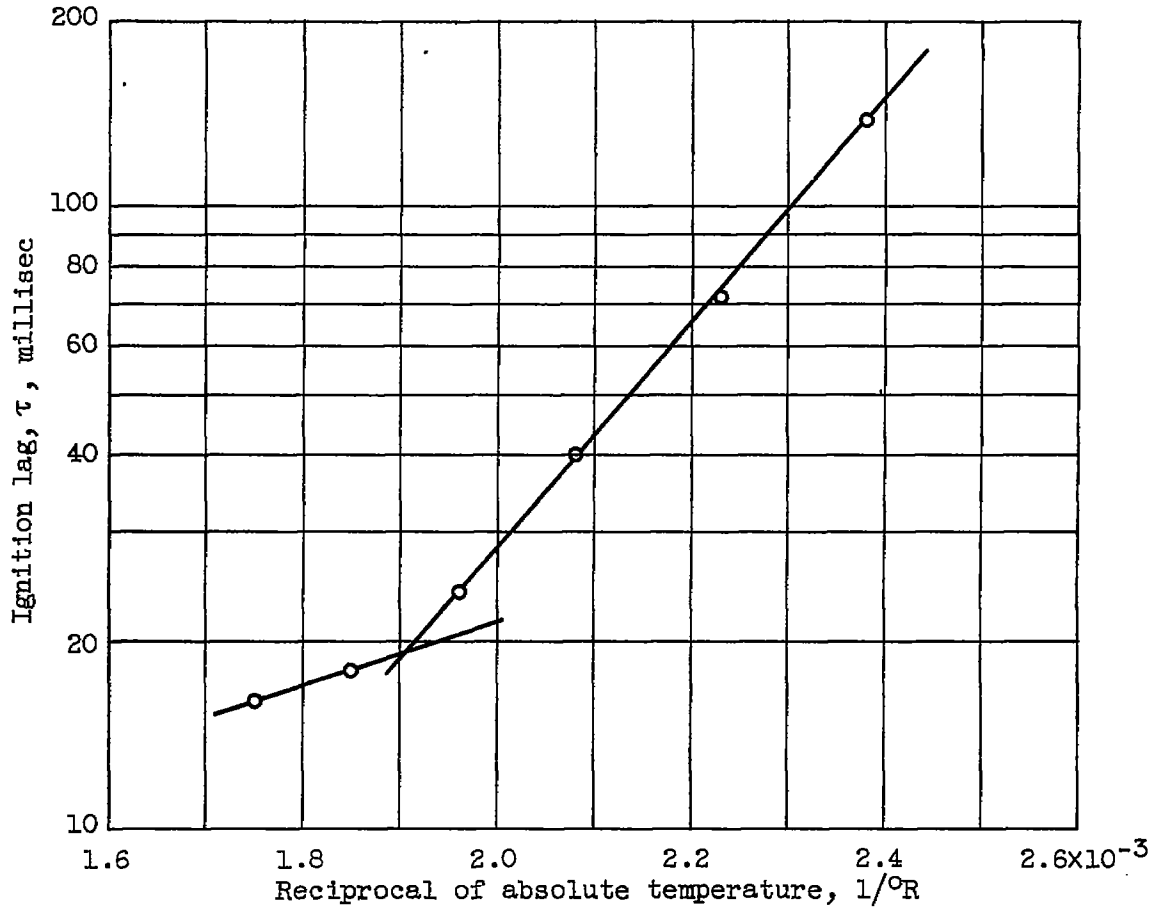

Figure 3. - Ignition-lag - temperature dependence of hydrazine hydrate - fuming nitric acid (2% H_2O, 1% NO_2) (ref. 12, engine).

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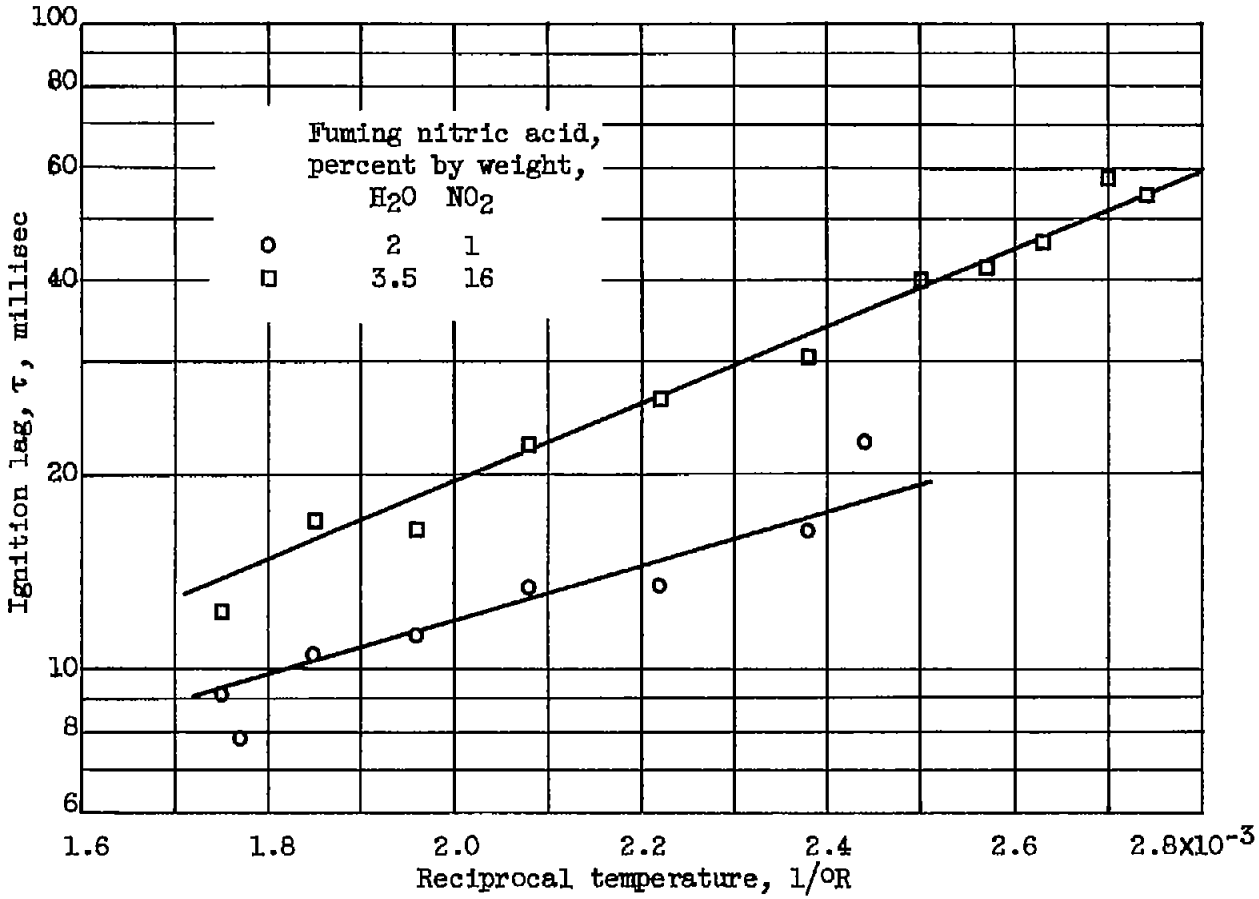

Figure 4. - Ignition-lag - temperature dependence of diallylaniline-triethylamine (50% by vol.) - fuming nitric acid (ref. 12, engine).

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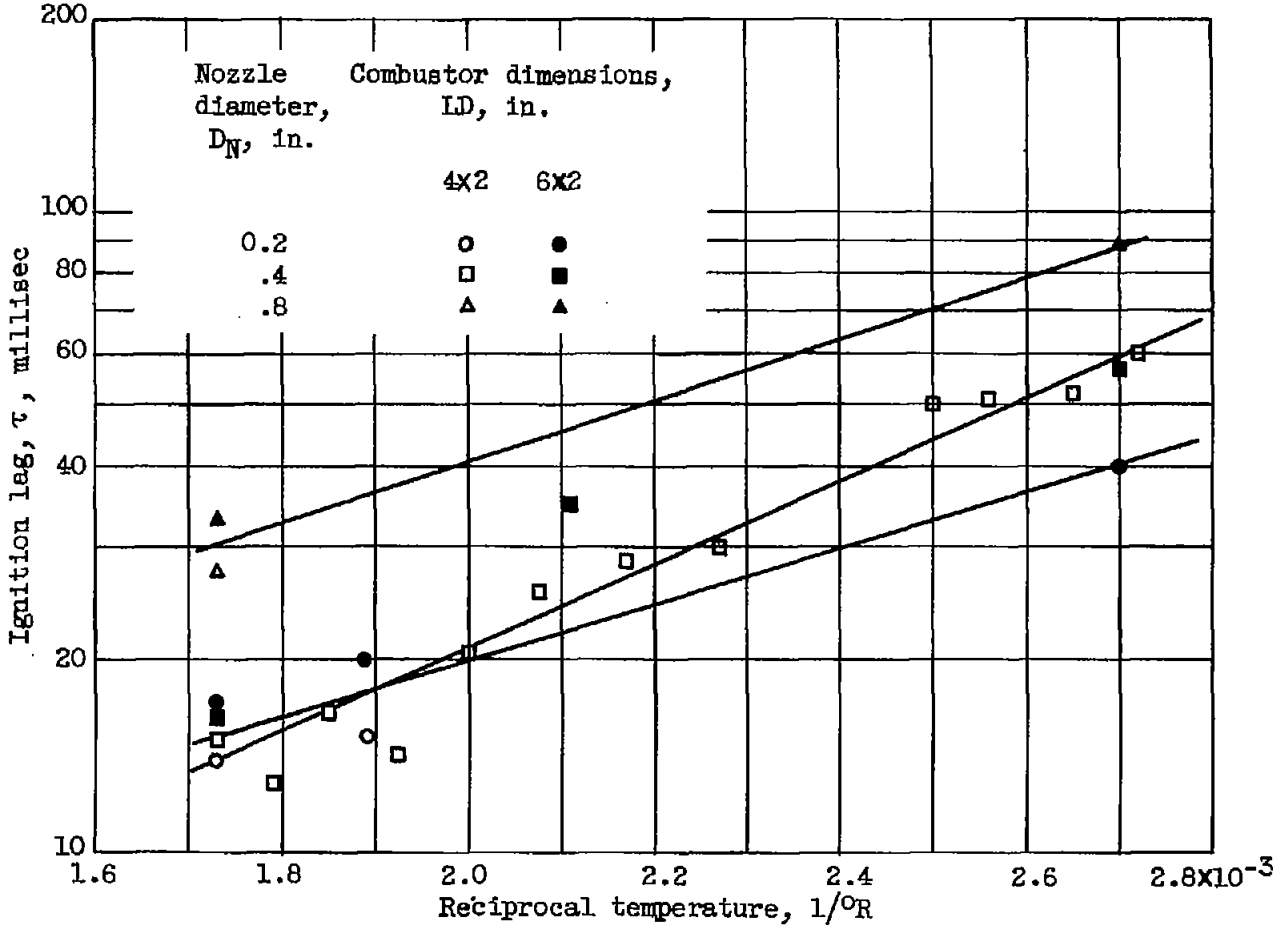

Figure 5. - Ignition-lag - temperature dependence of diallylaniline-triethylamine (50% by vol.) - fuming nitric acid (3% H_2O, 19% NO_2) as function of exit-nozzle diameter (ref. 19, engine).

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CO-5 back

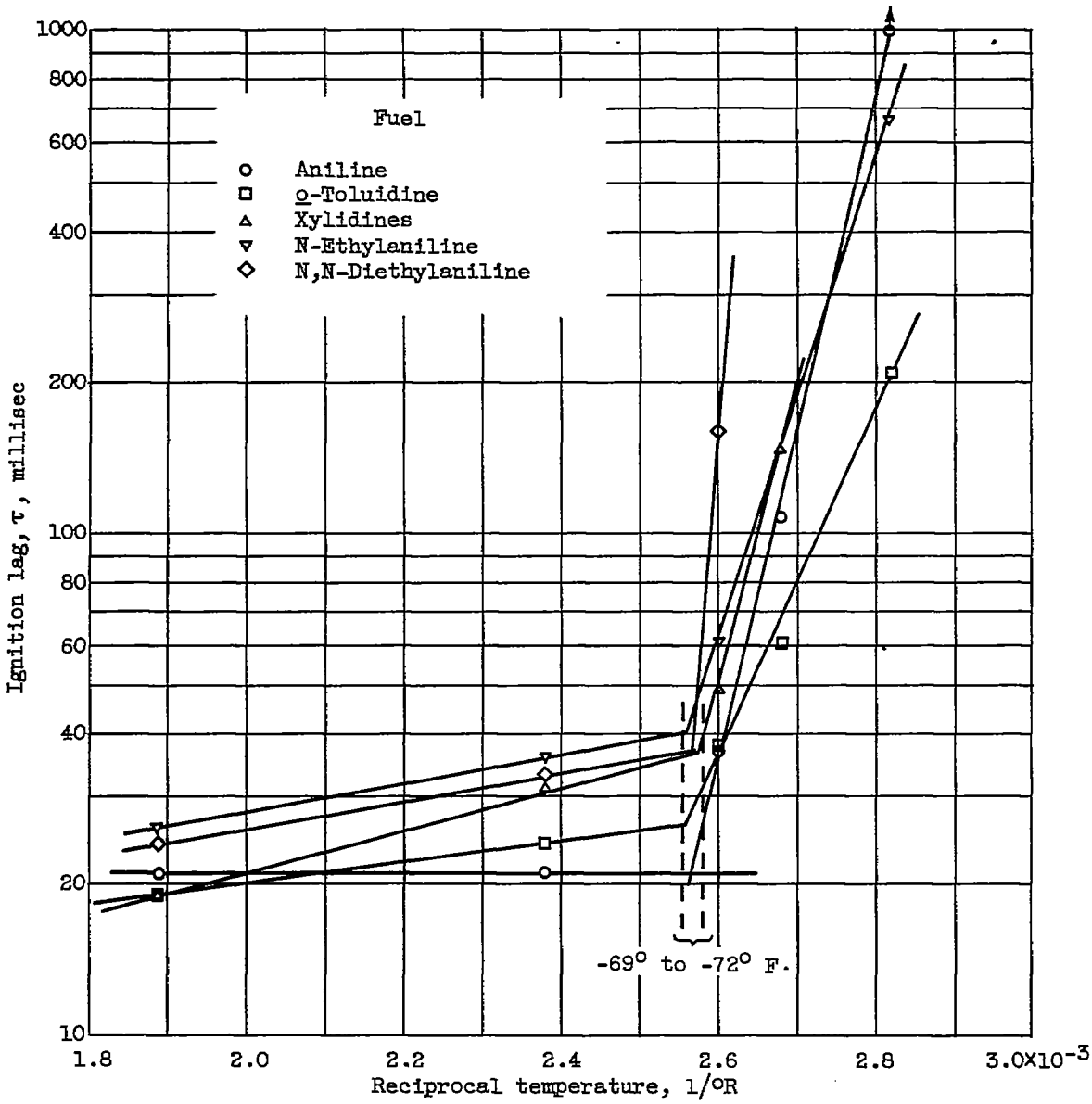

Figure 6. - Ignition-lag - temperature dependence of aromatic amine-triethylamine (3:7 by vol.) - fuming nitric acid (3% H_2O, 19% NO_2) (ref. 13, open tube).

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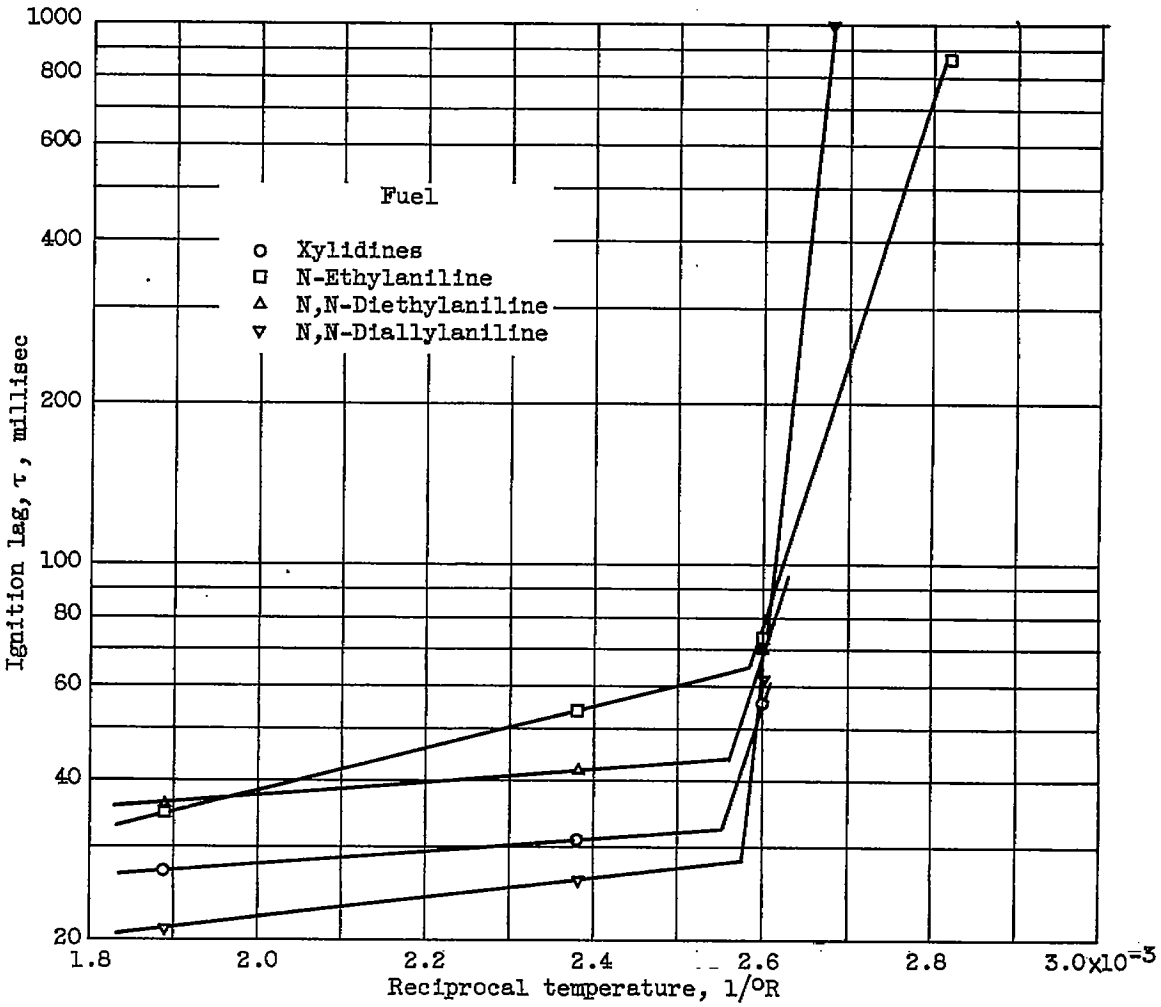

Figure 7. - Ignition-lag - temperature dependence of aromatic amine-triethylamine (50% by vol.) - fuming nitric acid (3% H_2O, 19% NO_2) (ref. 13, open tube).

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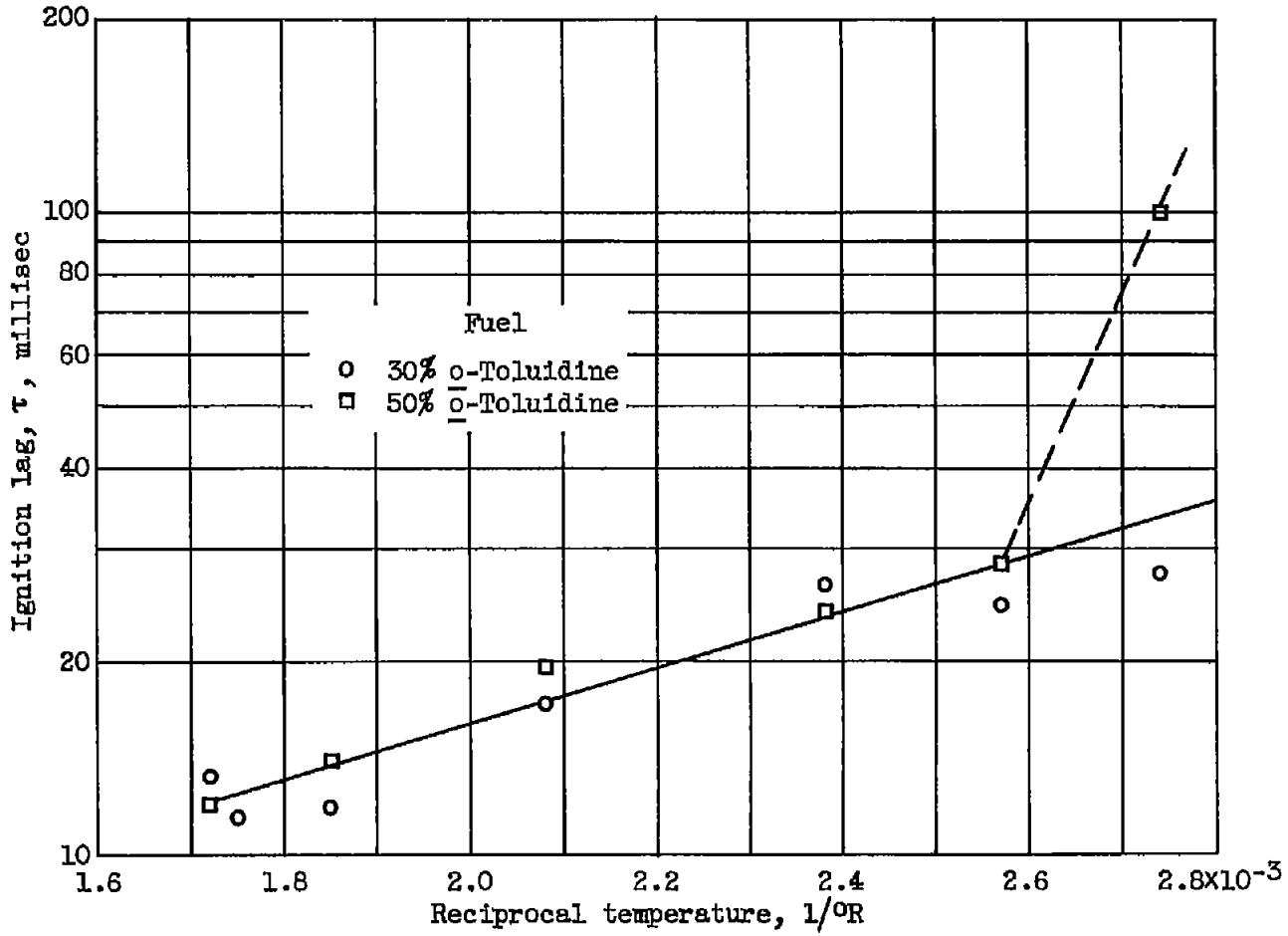

Figure 8. - Ignition-lag - temperature dependence of o-toluidine-triethylamine - fuming nitric acid (3% H_2O, 19% NO_2) (ref. 14, engine).

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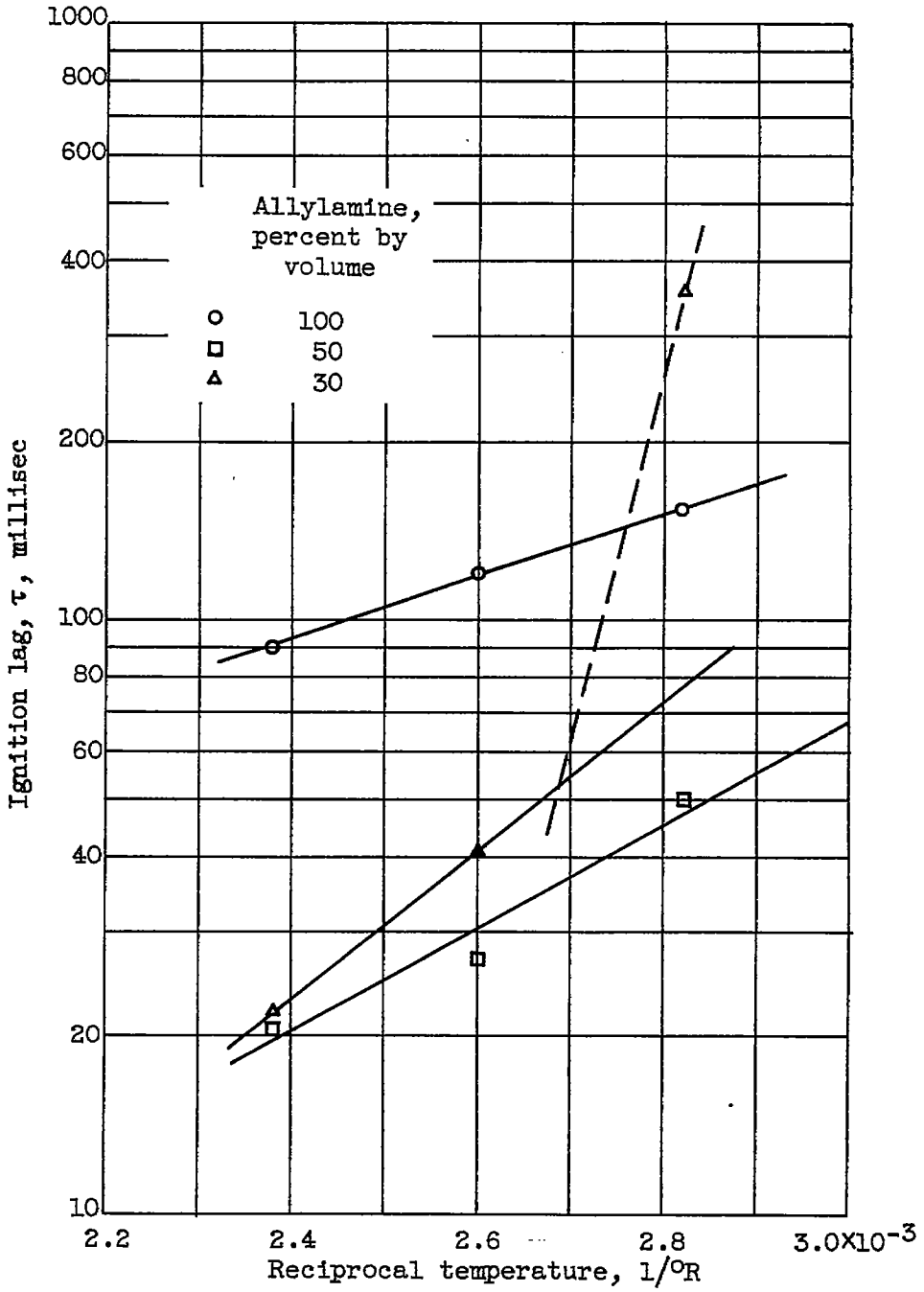

Figure 9. - Ignition-lag - temperature dependence of allylamine-triethylamine - fuming nitric acid (3% H_2O, 19% NO_2) (ref. 15, open tube).

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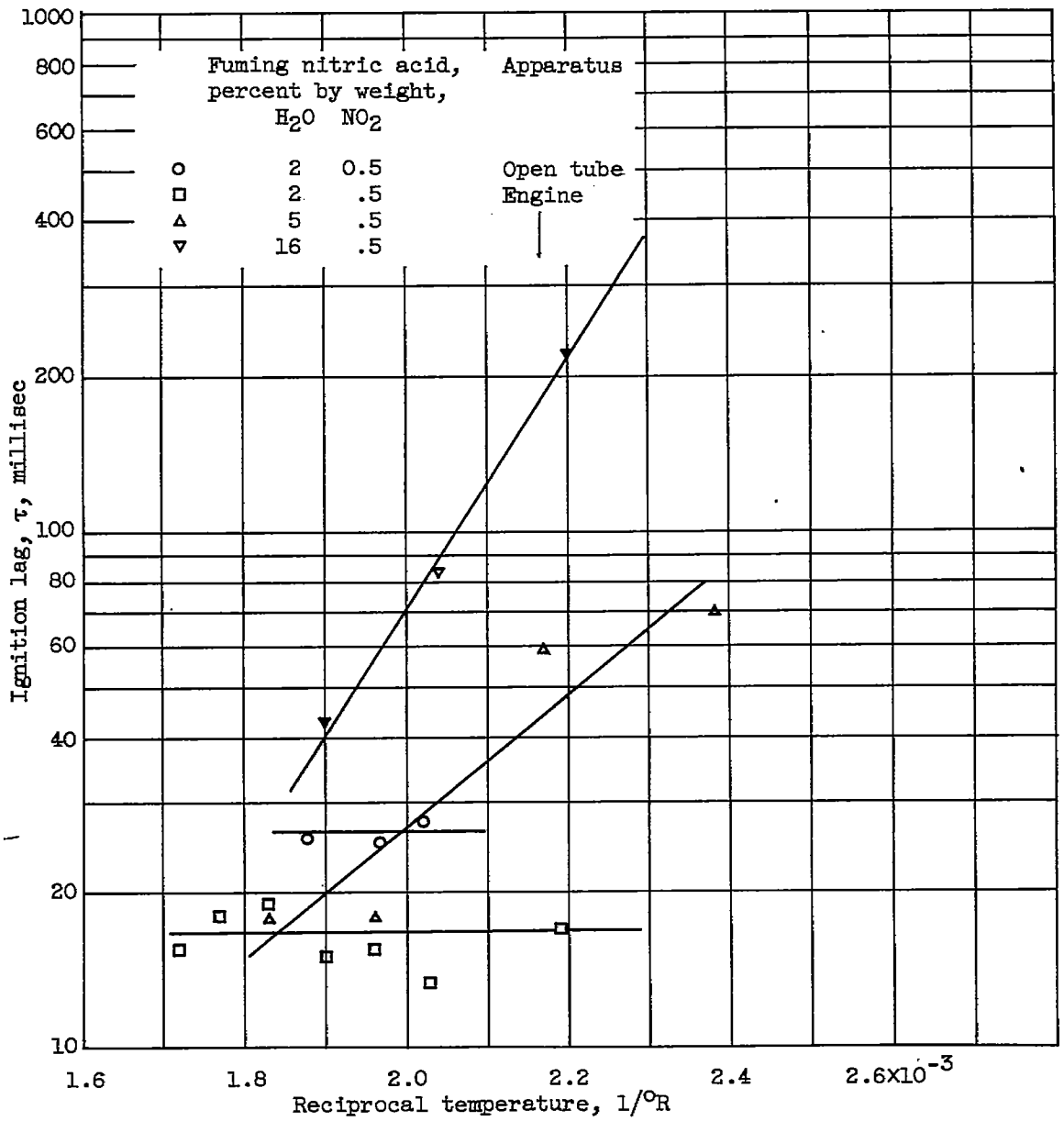

Figure 10. - Ignition-lag - temperature dependence of furfuryl alcohol - fuming nitric acid (ref. 17).

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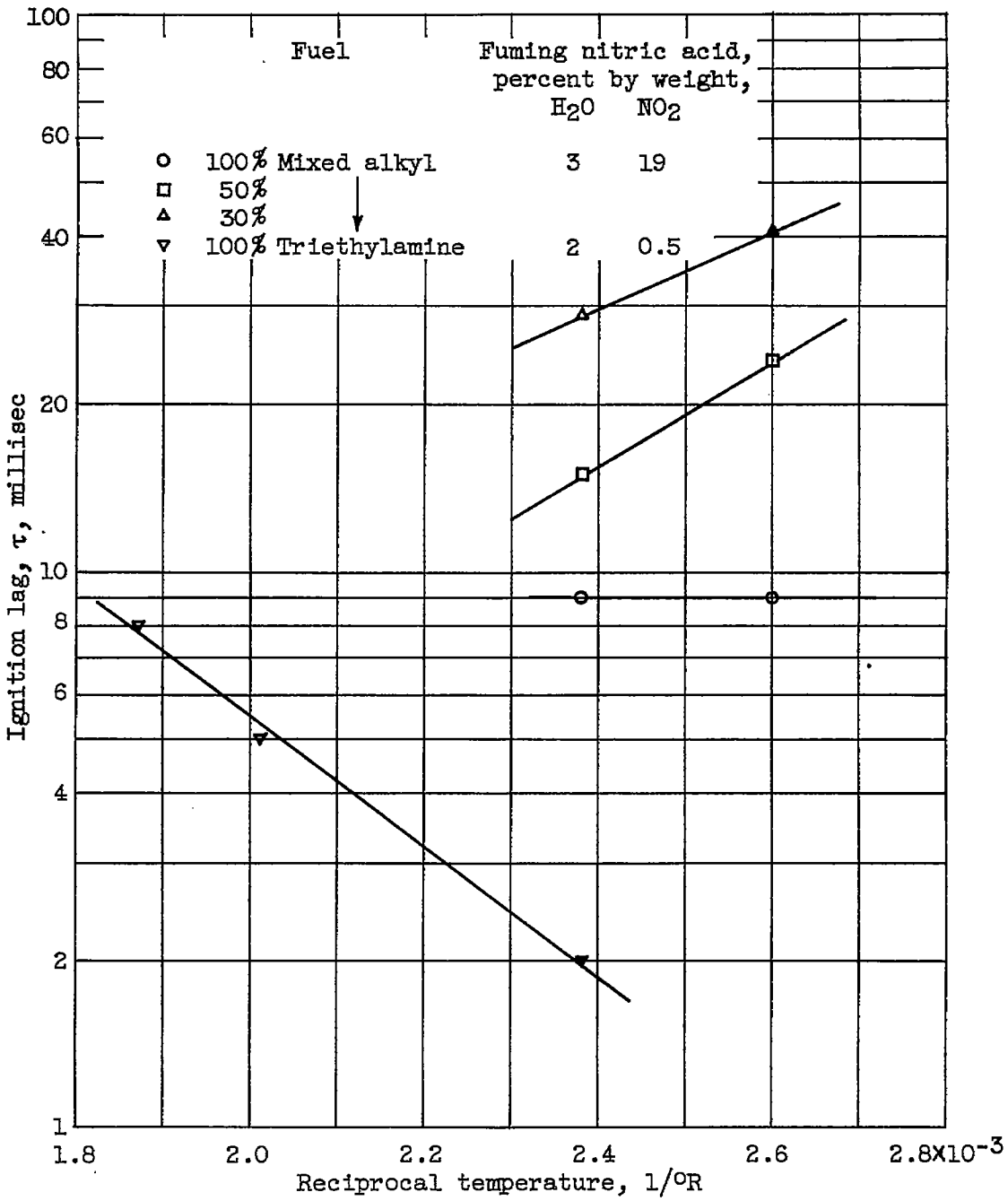

Figure 11. - Ignition-lag - temperature dependence of alkyl trithiophosphites-triethylamine - fuming nitric acid (refs. 15 and 16, open tube).

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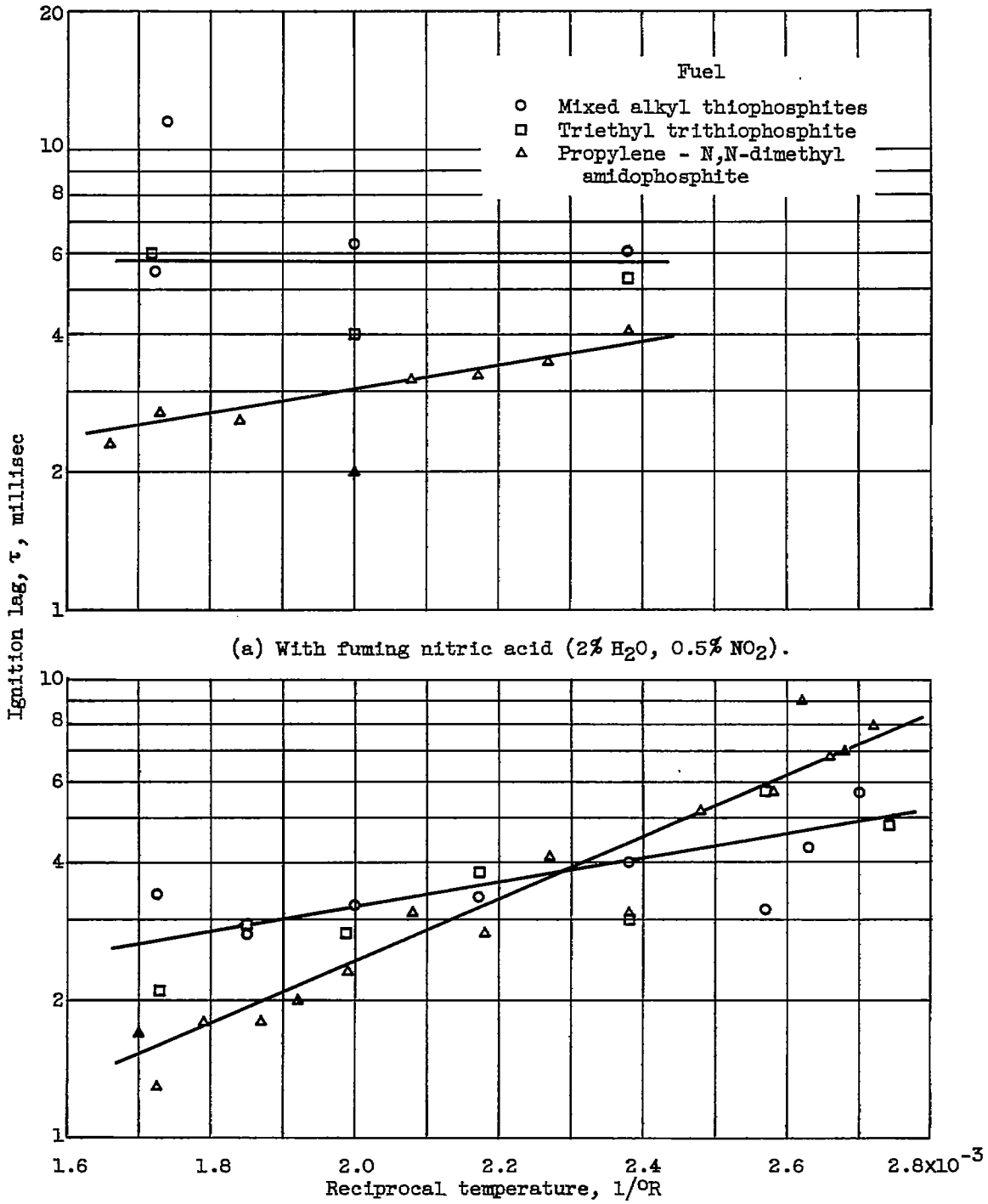

(a) With fuming nitric acid (2% H_2O, 0.5% NO_2).

(b) With fuming nitric acid (3% H_2O, 20% NO_2).

Figure 12. - Ignition-lag - temperature dependence of organophosphorus compounds (ref. 18, engine).

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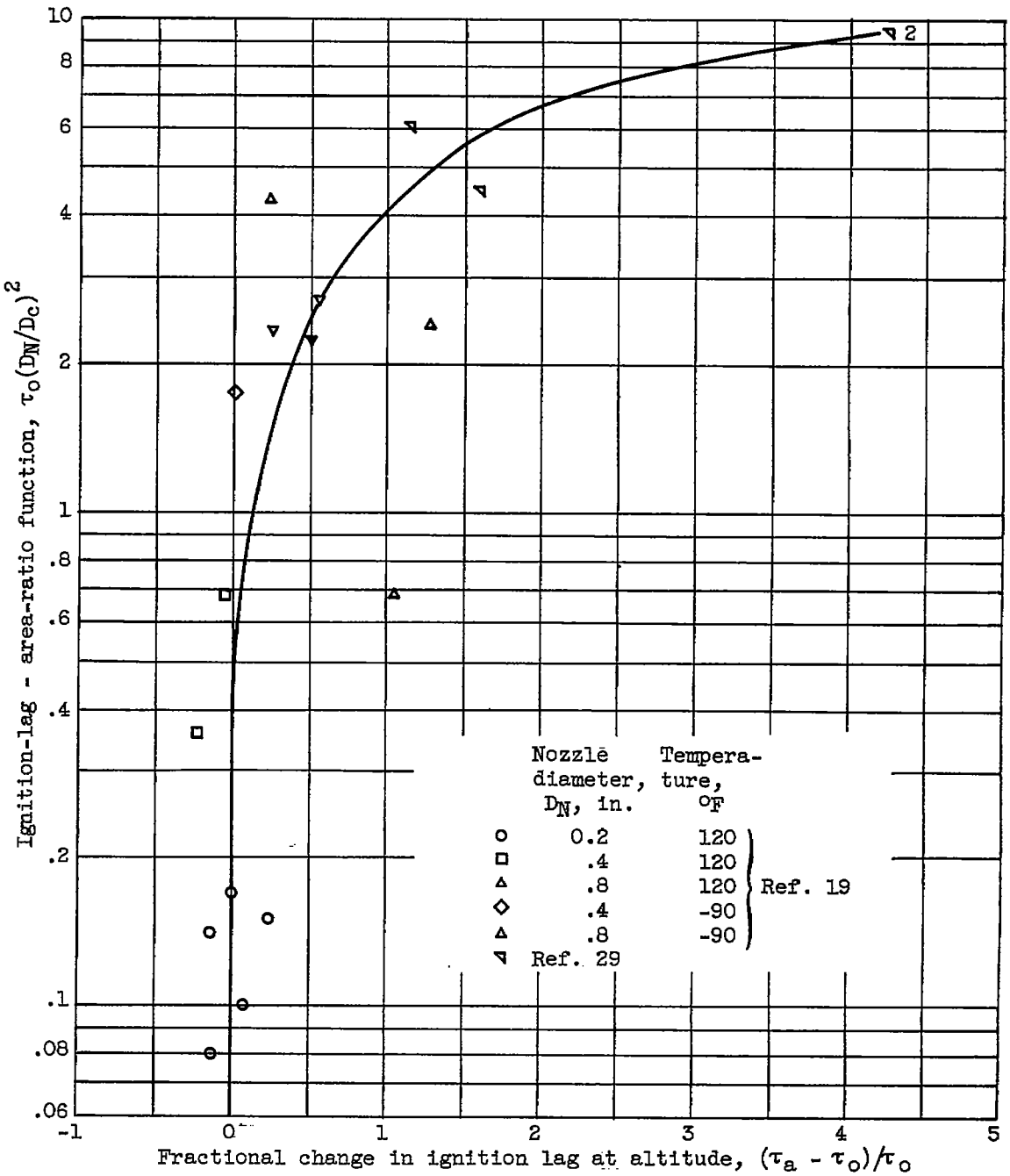

Figure 13. - Ignition lag at 90,000-foot pressure altitude as function of reactor geometry and sea-level lag. D_c, combustor diameter; τ_o, ignition lag at sea-level; τ_a, ignition lag at 90,000-foot pressure altitude.

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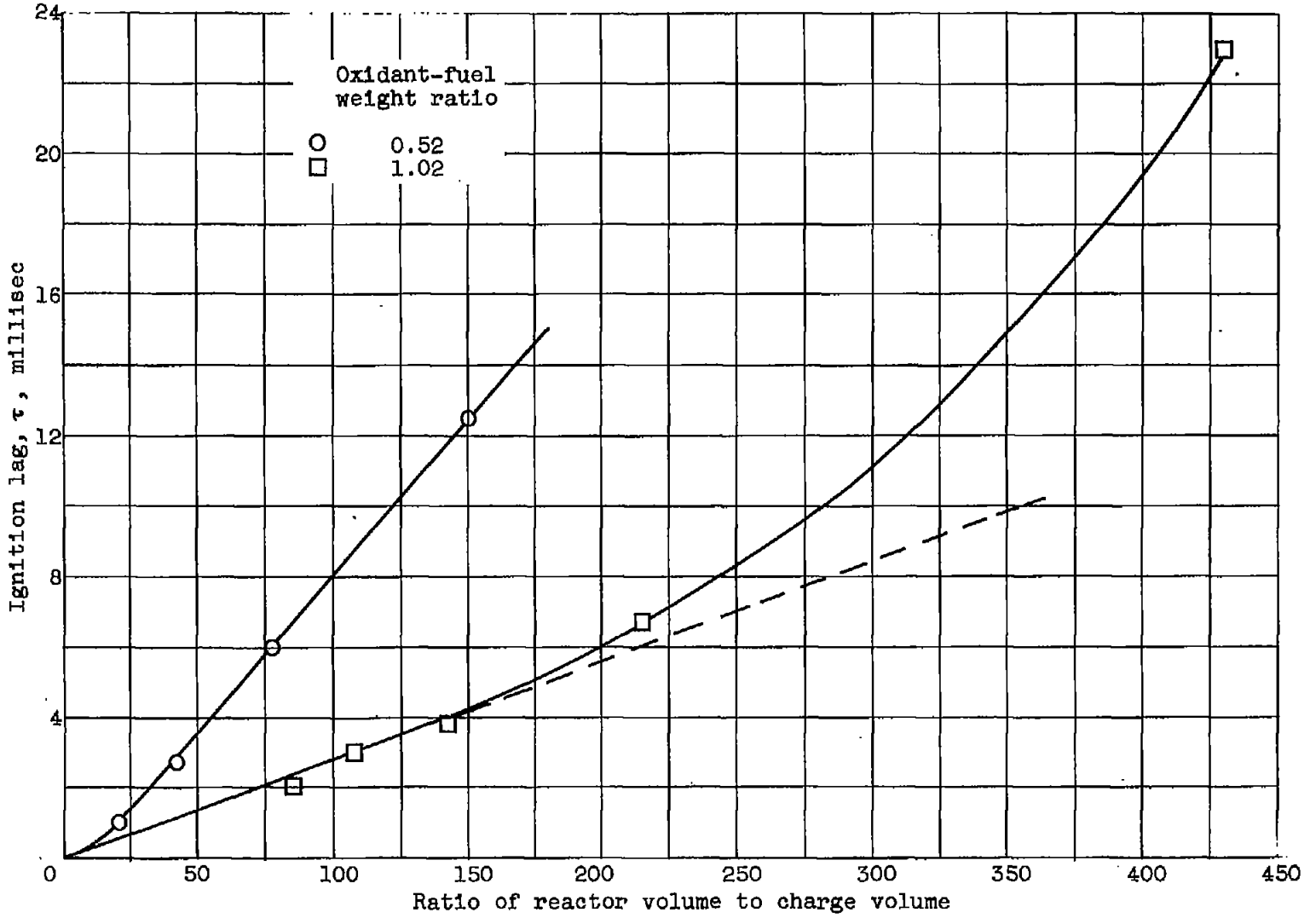

Figure 14. - Ignition lag of triethylamine - fuming nitric acid (2% H_2O, 0.5% NO_2) at approximately 70° F as function of concentration in closed reactor (ref. 9).

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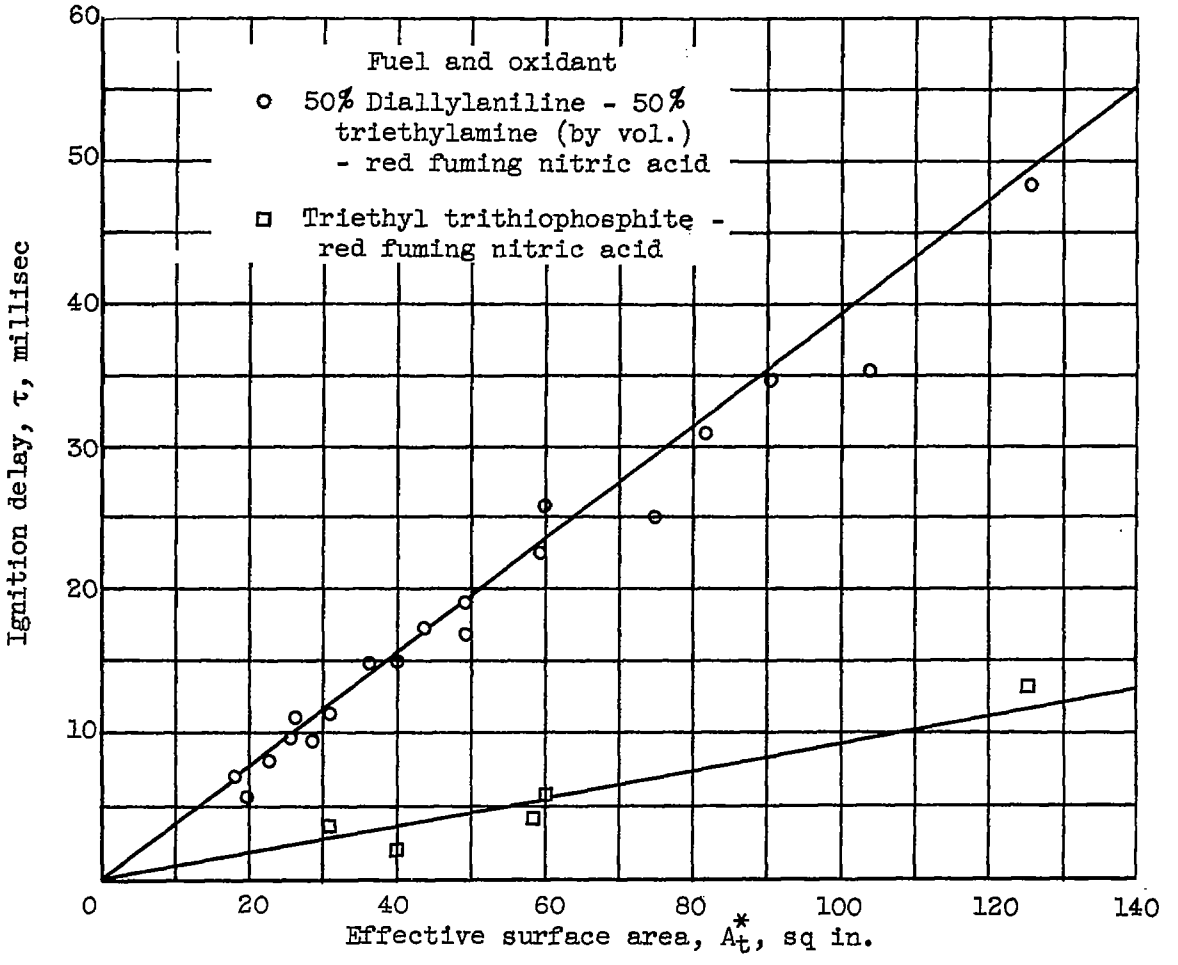

Figure 15. - Comparison of ignition-delay - effective surface area relation for two propellant combinations (ref. 19). Propellant temperature, 120° F; exhaust-nozzle diameter, 0.4 inch.

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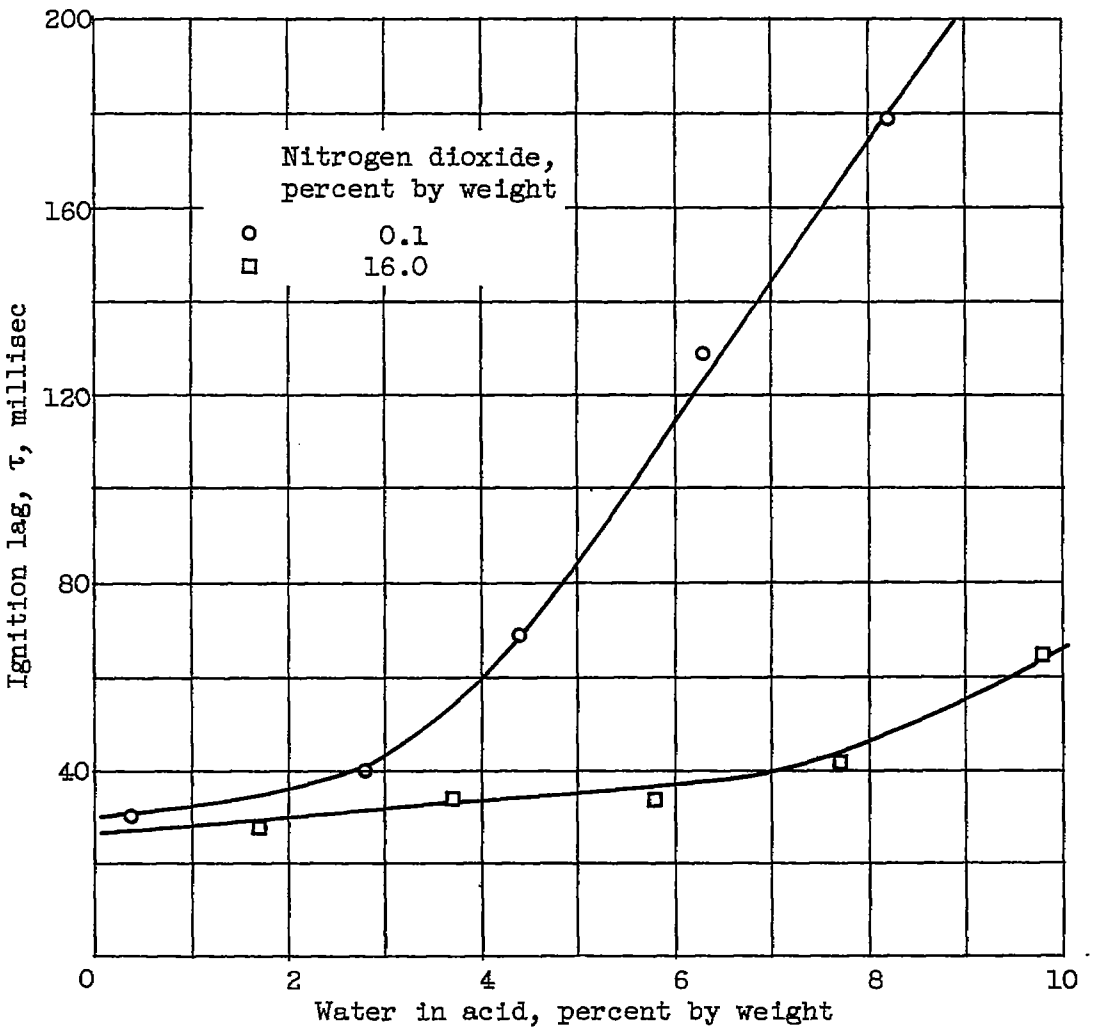

Figure 16. - Effect of water and nitrogen dioxide in fuming nitric acid on ignition lag of o-toluidine-triethylamine (3:7 by vol.) at -40° F.

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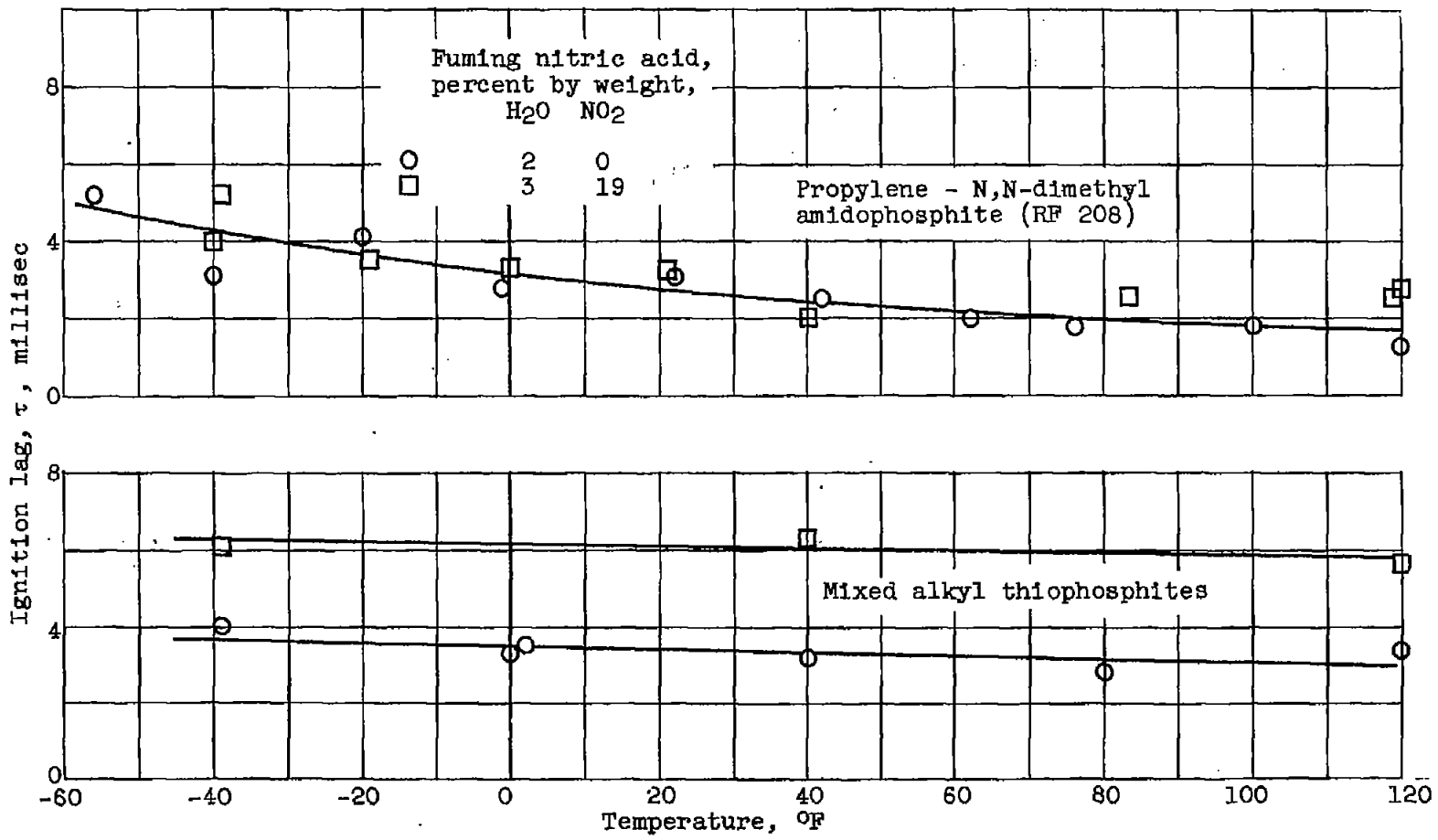

Figure 17. - Effects of acid composition on ignition lag of organophosphorus compounds (ref. 18, engine).

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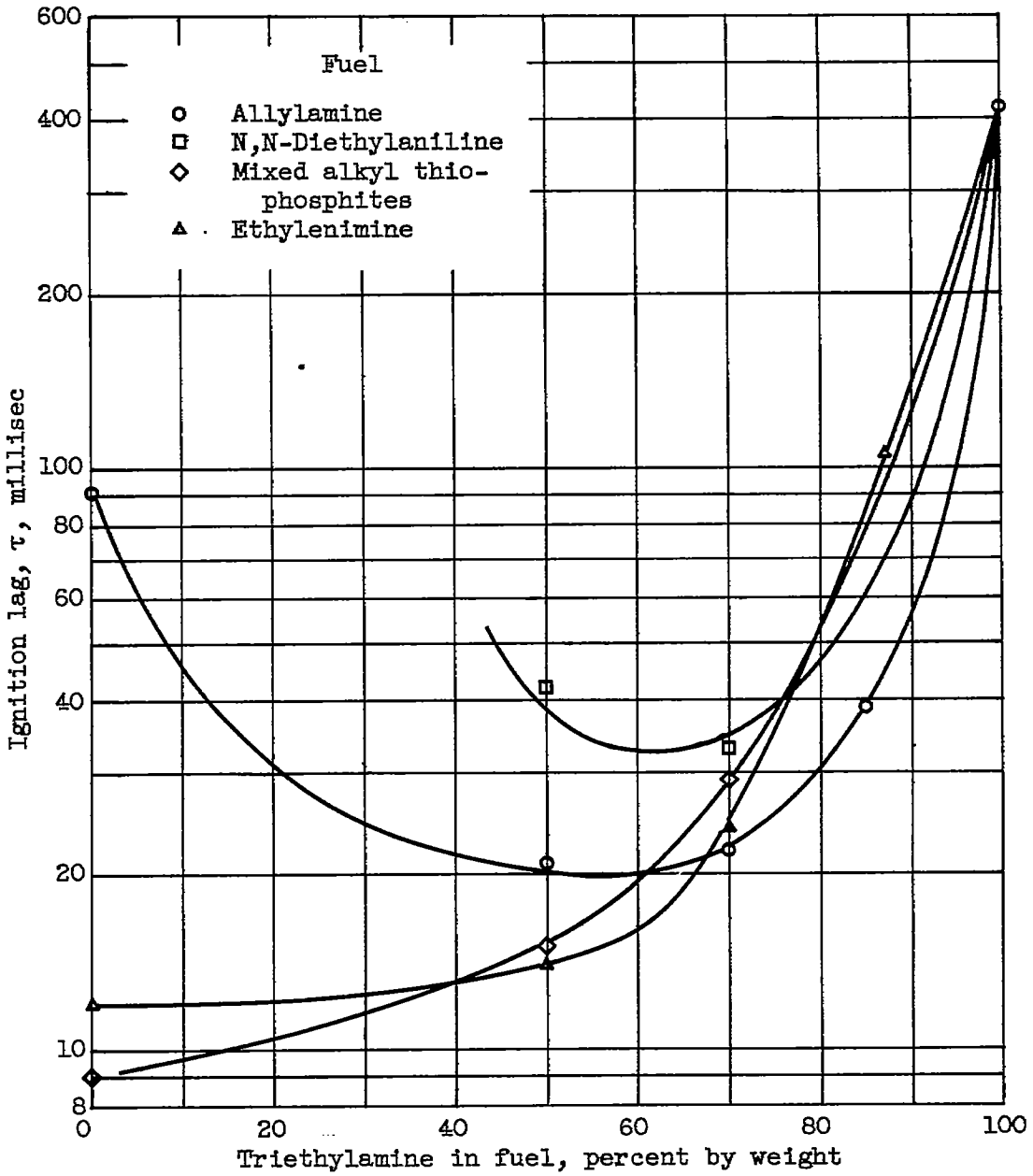

Figure 18. - Effects of triethylamine blending on ignition lag of several fuels (refs. 13 and 15, open tube).

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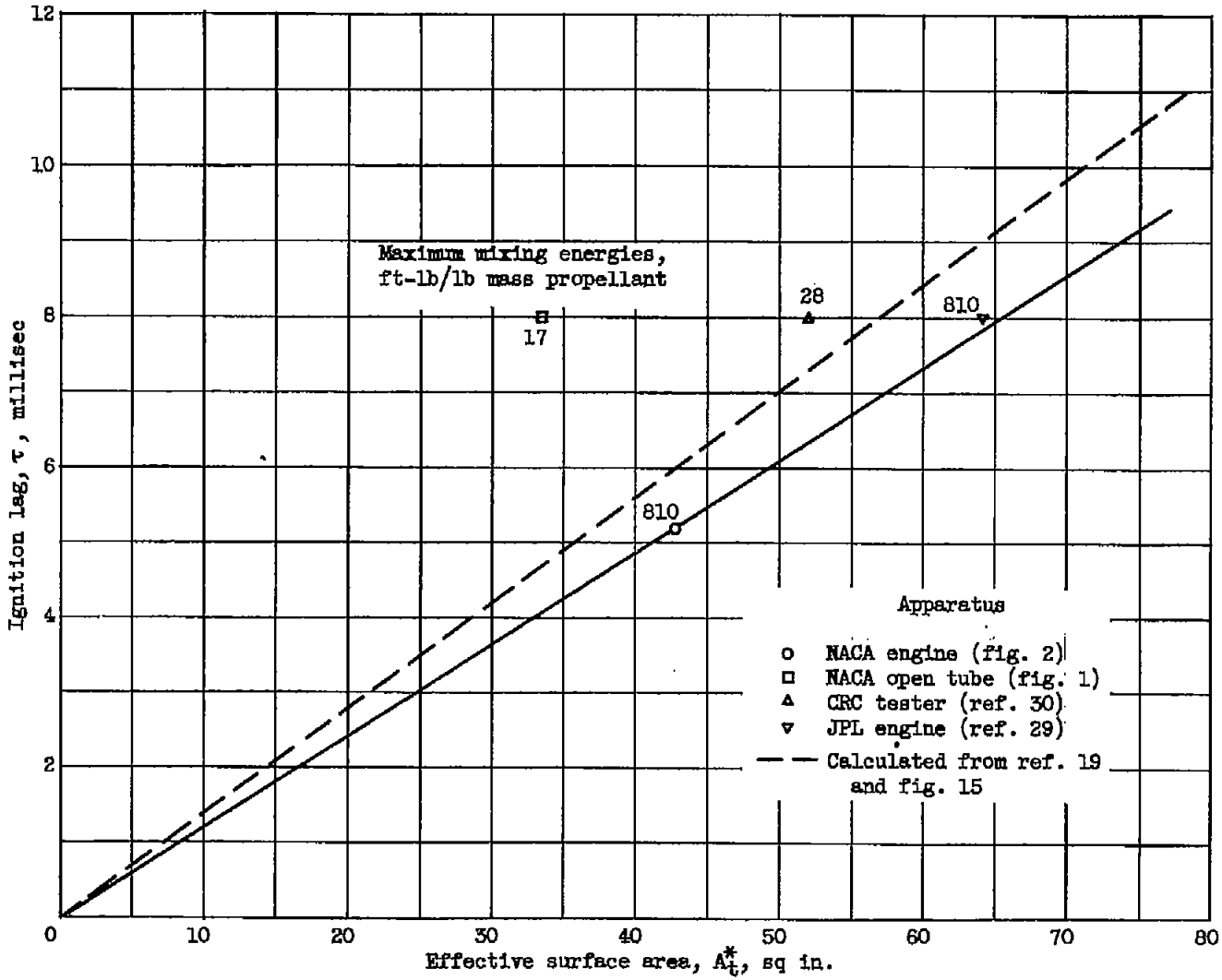

Figure 19. - Comparison of ignition lag - effective surface area relations for several apparatus. Triethyl trithiophosphite - fuming nitric acid (2% H_2O, 0% N_2O); temperature, 75° F; (refs. 18 and 26).

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