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RESEARCH MEMORANDUM

IGNITION DELAYS OF ALKYL THIOPHOSPHITES WITH WHITE AND RED FUMING NITRIC ACIDS WITHIN TEMPERATURE RANGE 80° TO -105° F

By Riley O. Miller and Dezso J. Ladanyi

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NATIONAL ADVISORY COMMITTEE
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SUMMARY

From experimental and published ignition delay data, an appraisal was made of the self-igniting properties of alkyl thiophosphites. Data presented herein indicate that at -40° F mixed alkyl thiophosphites ignite satisfactorily with white fuming nitric acids containing small amounts of water, and with red fuming nitric acids of widely varying water content (2 to 10 percent) containing 8 percent or more nitrogen tetroxide. Data herein also indicate that triethyl trithiophosphite diluted with as much as 40 percent n-heptane will ignite with satisfactory average delays (≈50 milliseconds) at temperatures of -40° F and higher. Dilution with n-heptane appears to have nearly the same effect on ignition delay of triethyl trithiophosphite at -40° F as dilution with mixed butyl mercaptans when white fuming nitric acid is used. At -40° F, triethyl trithiophosphite diluted with n-heptane indicates approximately the same ignition behavior as ethylenimine blended with the same diluent. With suitable acid, mixed alkyl thiophosphites ignites satisfactorily at temperatures as low as -76° F.

INTRODUCTION

Considerable interest exists in alkyl thiophosphites as possible rocket fuels because not only do they ignite readily at low temperatures with white fuming nitric acids (references 1 to 3), white fuming nitric acid plus potassium nitrate (reference 1), and low-freezing red fuming nitric acid (reference 4), but also they can be produced from petroleum products (reference 1).

A self-igniting fuel to be of maximum value should ignite rapidly over a wide range of acid compositions and temperatures. (Rapid ignition is desirable to assure quick and reliable engine starting.) Ignition with acids of varying compositions is desirable because future specifications for nitric acids used in rockets may depend upon the application (reference 5); and, under extreme service conditions, compositions of acids may deviate from specifications. Two decomposition products of fuming nitric acid are water and nitrogen tetroxide, and the relative amounts

of these in rocket acids may vary either by design or by accident. Although recent experiments (reference 4) have extended the ignition delay data (time from first contact of fuel and oxidant to start of flame) of mixed alkyl thiophosphites to low-freezing red fuming nitric acid at very low temperatures (-40 to -105° F), no ignition data have been published showing the specific effects of either water or nitrogen tetroxide in the acid.

The effects on low-temperature ignition delays of blending alkyl thiophosphites with two other fuels, mixed butyl mercaptans (reference 2) and triethylamine (reference 4), have been studied. No data, however, have been published on the effect of hydrocarbons as blending agents. Hydrocarbons may be used either as diluents in self-igniting fuels or as the propellant fuel to be ignited by a momentary flow of ignitor fuel. In the latter case the ignitor fuel may become diluted with hydrocarbon in the rocket chamber. The ignition behavior of mixtures of alkyl thiophosphites with hydrocarbon is an important consideration in their evaluation as self-igniting fuels. The Bureau of Aeronautics of the Navy has initiated a cooperative program in which specific samples of triethyl trithiophosphite, n-heptane, and white fuming nitric acid are to be evaluated at specific temperatures in the ignition delay apparatus of various organizations, and has requested the participation of the NACA Lewis laboratory.

The investigation described herein was undertaken: (1) to determine the effects of water and nitrogen tetroxide in nitric acid on the ignition of mixed alkyl thiophosphites at 70° and -40° F; (2) to determine the effect of dilution of triethyl trithiophosphite by n-heptane on its ignition with a white fuming nitric acid at 75°, 32°, and -40° F; (3) as a sidelight, to study the ignition behavior of phosphorous trichloride; and (4) in light of these and other data, some of which are reviewed, to form an appraisal of the self-igniting properties of alkyl thiophosphites as fuels and blending agents. The experiments were conducted with a modified open-cup apparatus (references 6 and 7), and a small-scale rocket engine (reference 8). In the appraisal, ignition delays of 50 milliseconds and less were considered desirable, although delays of the order of 70 milliseconds in the open-cup apparatus may be acceptable.

PROCEDURE

Apparatus

Modified open-cup apparatus. - Most of the ignition data were obtained in a modified open-cup apparatus (fig. 1), the details of which are discussed in references 6 and 7. In this apparatus, the fuel sealed in a glass ampule is submersed in acid contained in a 1- by 8-inch

ignition-type test tube maintained at a desired temperature in a constant-temperature bath. The ampule is broken by an electrically insulated weight striking a stainless steel rod resting on top of the ampule; and the ignition delay is taken to be the measured time between the instant the weight strikes the rod and the start of continuous flames. The ignition delay data are taken from cathode ray oscillograms of light emission as a function of time. The delay intervals are also measured by an electronic timer which is stopped by an appearance of light, and in case of malfunction of the oscillograph these intervals are sometimes accepted although they may indicate short flashes of light instead of continuous flames. The oscillograms also include a record from a microphone, which is sometimes helpful in interpreting the data. Unless otherwise specified, the ignition data reported herein from the modified open-cup apparatus are taken from oscillograms of light emission against time.

Small-scale rocket engine apparatus. - The small-scale rocket engine apparatus used in one of the mixed alkyl thiophosphites - red fuming nitric acid series reported herein is a modification of the one described in detail by reference 8. The changes most pertinent to the experiments reported herein were in the method of propellant injection. Essentially, the new system consisted of yoke-connected propellant valves actuated by a fast-acting pneumatic cylinder. The injection system consisted of two oxidant jets impinging on one fuel jet to obtain a resultant stream that was coincidental with the axis of the combustion chamber. The engine had a thrust of approximately 50 pounds. Figure 2(a) is a diagrammatic sketch of the apparatus.

The rocket engine assembly consisted of an injector head, a transparent cylindrical combustion chamber, a plate with a convergent exhaust nozzle, and propellant tanks. A diagrammatic cut-away view and a close-up assembly photograph are shown by figures 2(a) and 2(b), respectively.

The two 0.040-inch-diameter oxidant-injector holes were drilled in the injector head with an included angle of 90°. The 0.040-inch-diameter fuel injector hole was located directly in the center of the head. The three propellant streams ejected from these orifices each traveled about 1/2 inch before impinging 1/4 inch from the main face of the injector head.

The propellant tanks were loaded in place on the engine assembly. Inlet lines were then connected to individual gas pressure supply sources. For all runs, the propellant-injection pressures were 450 pounds per square inch gage. Just before a run, each propellant tank was pressurized to the desired value.

The actual operation of the apparatus was almost completely automatic, being controlled by a preset electrical program timer. When the propellant valves were snapped open, the propellants were forced into the combustion chamber where the ensuing events were recorded by a high-speed camera.

Materials

Acids. - Acids used in the water and nitrogen tetroxide studies were prepared by blending three stock solutions: (1) an approximately absolute nitric acid containing traces of water and nitrogen tetroxide, (2) a nearly anhydrous red fuming nitric acid containing 42 percent nitrogen tetroxide, and (3) a 70 percent concentrated nitric acid virtually free of nitrogen tetroxide. The stock acids were c.p. grade or were prepared from c.p. grade acids and were stored in pyrex containers. The stock acids were analyzed by the methods prescribed in Air Force specifications (references 9 and 10). The compositions of the samples used in the ignition experiments were established by weighing calculated quantities of the stock solutions. Spot checks of the analysis of some of the samples indicated satisfactory control of water content, but for samples containing large amounts of nitrogen tetroxide, the amount of oxide analyzed was of the order of 1 percent less than that expected from the weighed stock solutions. Some nitrogen tetroxide, presumably, was lost during the transfer and handling although this was minimized by precooling the stock solution. The acid compositions reported herein are the values indicated from the weights of the stock solutions and are deemed to be within the accuracy of the ignition delay data.

The acid used in the Bureau of Aeronautics cooperative program was received in soft glass bottles and composition of the acid was adjusted at this laboratory to approximately 1 percent water and 0.5 percent nitrogen tetroxide. The nitrogen tetroxide content was adjusted by blending part of the original sample with a part which was blown with dry carbon-dioxide-free air for 2 days at room temperature and atmospheric pressure. The water content was adjusted by adding a calculated quantity of water to the cold blended acid.

The low-freezing red fuming nitric acid used in the small-scale rocket engine was prepared by blending commercial white and red fuming nitric acids and adding a small amount of water. Analysis showed 3.8 percent water and 19.6 percent nitrogen tetroxide. This acid was stored in an aluminum drum.

Fuels. - The fuel, mixed alkyl thiophosphites, was procured from the U. S. Air Force and the triethyl trithiophosphite and n-heptane were supplied as part of a Bureau of Aeronautics cooperative project. The phosphorous trichloride was reagent grade.

RESULTS AND DISCUSSION

Summaries of the ignition (or reaction) data are contained in tables I to IV and some trends are illustrated in figures 3 to 8.

Effect of Water and Nitrogen Tetroxide Content of Nitric Acid on the Ignition of Mixed Alkyl Thiophosphites at 70° and -40° F in Modified Open-Cup Apparatus

Water in acid. - The effects of water in white fuming nitric acid on the ignition of mixed alkyl thiophosphites are shown by figure 3 in which average ignition delay (table I) is plotted as function of water content at 70° and -40° F. At both temperatures these data show that the ignition delay increased with increased water in acid, and the average delays were 4 to 7 times longer at -40° than at 70° F. At 70° F, mixed alkyl thiophosphites appears to ignite satisfactorily (35 millisec average) with acid containing as much as 10 percent water although considerable variation (10 to 80 millisec) was encountered with this acid (table I). At -40° F, ignition of mixed alkyl thiophosphites showed considerable sensitivity to water content in acid; 6 percent water resulted in considerable variation in delays (37 to 107 millisec). With white fuming nitric acid containing 2 percent water, however, the mixed thiophosphites gave very short delays (8 millisec average) at -40° F.

Nitrogen tetroxide in acids containing 2 and 10 percent water. - The undesirable effects of excess water in the acid on the ignition of mixed alkyl thiophosphites apparently can be overcome by the addition of nitrogen tetroxide to the acid. As shown by figure 4 (and table I), at -40° F the presence of 8 percent nitrogen tetroxide reduced the average delay of acid containing 10 percent water from 185 to 26 milliseconds, and 24 percent nitrogen tetroxide produced comparable but somewhat higher delays (48 millisec average). Presence of nitrogen tetroxide in the acid had little effect when the ignition delays were initially short (less than 40 millisec) as in acids containing 10 percent water at 70° F and acids containing 2 percent water at both 70° F and -40° F.

Qualitative observations. - With the mixed alkyl thiophosphites, shattering explosions were encountered with all acids containing 2 and 6 percent water; the presence of nitrogen tetroxide in acids containing 2 percent water did not modify this effect (table I). The acids containing 10 percent water generally gave short bright flames designated as "snappy"; after ignition little adhesive residue was found in the reaction chamber. In order to minimize damage to equipment, repeat experiments were omitted at conditions favoring explosions.

Reaction of Phosphorous Trichloride with White and Red Fuming Nitric Acids at 70° and -40° F in Modified Open-Cup Apparatus

Phosphorous trichloride, a reactant sometimes used in the preparation of thiophosphites having desirable low-temperature fluid properties, was investigated as a possible ignitor fuel with acids approaching the white and red fuming nitric acids currently specified by the U. S. Air Force. Phosphorous trichloride did not produce flames, but under certain conditions the sound records did indicate a delayed reaction. These results are shown in table II. The reactions were mild at -40° F, but at 70° F vigorous flameless reactions occurred with well defined delay periods of 23 ±2 milliseconds for nitric acids containing 2 percent water and 0 or 8 percent nitrogen tetroxide.

Ignition of Mixed Alkyl Thiophosphites and Its Triethylamine Blends at 80 to -105° F with Low-Freezing Nitric Acid

The results of an investigation (reference 4) of the ignition of mixed alkyl thiophosphites and its triethylamine blends with low-freezing red fuming nitric acid (3 percent water - 19 percent nitrogen tetroxide) are shown in figure 5. These data, from the modified open-cup apparatus, show that mixed alkyl thiophosphites can be diluted with as much as 70 percent triethylamine and still ignite at -76° F with an average delay of approximately 40 milliseconds. At -105° F (acid supercooled), however, the ignition was considerably impaired; delays were either longer than 1 second or no ignition occurred.

Small-scale rocket engine experiments. - The ignition of mixed alkyl thiophosphites with low-freezing red fuming nitric acid also has been investigated at sea-level pressure in a small-scale rocket engine. These data are presented in table III and are shown plotted in figure 6 along with data (reference 4) obtained in the modified open-cup apparatus. The ignition delays from the small engine ranged linearly from about 11 milliseconds at 80° F to about 18 milliseconds at -70° F. Mechanical difficulties prevented procurement of ignition delay values at -95° F, but satisfactory ignitions were obtained in all three runs conducted at that temperature. It is possible that the increase in ignition delays remained linear to -95° F because of the lack of a marked viscosity effect at that temperature, as with an orthotoluidine-triethylamine and red fuming nitric acid combination (reference 11). The fuel viscosity of about 200 centistokes at -95° F apparently does not affect the mixing efficiency, and consequently the ignition delay, so much as in the modified open-cup apparatus (see reference 11). The combustion chamber after each run was found to be as clean as in runs made with hydrazine and white fuming nitric acid.

Ignition of Triethyl Trithiophosphite and Its n-Heptane Blends at 75°, 32°, and -40° F with White Fuming Nitric Acid in Modified Open-Cup Apparatus

Ignition delays of the blends of triethyl trithiophosphite with n-heptane are shown by table IV and the averages are plotted in figure 7. The average ignition delays of triethyl trithiophosphite increased as concentration of n-heptane was increased, and this trend was most pronounced at -40° F. The effect of blending appears to be least at 75° F. The data (fig. 7) show that triethyl trithiophosphite can be diluted with as much as 40 percent n-heptane and still give short ignition delays (54 millisec average at -40° F). The quality of the reaction of triethyl trithiophosphite was very similar to that observed with the mixed alkyl thiophosphites. The flames were short and bright (snappy). As is noted in table IV, explosions frequently resulted. The reactions became more violent both as concentration of n-heptane was decreased and as temperature was increased.

A comparison of n-heptane and mixed butyl mercaptans as blending agents with triethyl trithiophosphite is shown by figure 8(a). Within the range of comparison, the average ignition delays with n-heptane as diluent appeared to be nearly as short as the delays with mixed butyl mercaptans as determined in reference 2. In this comparison, n-heptane may be favored by the fact that the white fuming nitric acid contained only 1 percent water whereas the acid used for the butyl mercaptans may have contained more water, perhaps 2 percent. The apparatus in which the delays were determined were also different, but experiments with similar fuel-oxidant combinations have shown comparable results, for example mixed butyl mercaptans - mixed acid (references 6 and 12).

A comparison of the ignition delays (fig. 8(b)) of n-heptane blends of triethyl trithiophosphite and ethylenimine is of interest. With acids of low water content, ignition delays for mixed alkyl thiophosphites were independent of nitrogen tetroxide content (fig. 4) and would be about the same with either white or red fuming nitric acid. The data plotted in figure 8(b), therefore, show that at -40° F the effects of blending triethyl trithiophosphite or ethylenimine with n-heptane are similar. At a very low temperature (-105° F), however, ethylenimine ignited much more readily than did mixed alkyl thiophosphites (reference 4).

General Appraisal

Although a final appraisal of alkyl thiophosphites will depend upon full-scale rocket engine experiments, some inferences may be drawn from ignition delay experiments. At the low temperatures of current interest

(-40° F), alkyl thiophosphites ignite satisfactorily with white fuming nitric acids containing small amounts of water and red fuming nitric acids of widely varying composition. Ignition data also indicate that alkyl thiophosphites have a considerable tolerance for dilution with hydrocarbons, mercaptans, and aliphatic amines. At extremely low temperatures other fuels may ignite with shorter delays than alkyl thiophosphites. At -105° F, for example, with low-freezing nitric acid, 1:1 blends of ethylenimine or allylamine in triethylamine were found in the modified open-cup apparatus to ignite with delays much shorter than those of mixed alkyl thiophosphites (reference 4).

The quality of the reactions of alkyl thiophosphites with nitric acid indicates the possibility of rapid burning rates. Although the modified open-cup apparatus used in these experiments was often damaged by the vigorous reactions, damage to a rocket engine is not necessarily implied, as is shown by experience with other fuels. No explosions occurred in the series of runs made with the small-scale rocket engine apparatus and reported herein.

SUMMARY OF RESULTS

With a modified open-cup apparatus, studies were made of the effect of varying water and nitrogen tetroxide content in nitric acid on the ignition delays of mixed alkyl thiophosphites, and of the effect on ignition delay of diluting triethyl trithiophosphite with n-heptane when white fuming nitric acid was used as the oxidant. Ignition delays of mixed alkyl thiophosphites with low-freezing red fuming nitric acid were also measured in a small-scale rocket engine apparatus. On the basis of these and published ignition delay data, the self-igniting properties of alkyl thiophosphites were appraised. The results of these studies are as follows:

1. At 70° F, white fuming nitric acid containing as much as 10 percent water gave an average ignition delay of only 35 milliseconds with mixed alkyl thiophosphites. At -40° F, however, the maximum amount of water permissible in white fuming nitric acid appears to be less than 6 percent.

2. At -40° F, in nitric acid containing 10 percent water, the presence of 8 percent nitrogen tetroxide reduced the average ignition delay from 185 to 26 milliseconds. At 70° F, the amount of nitrogen tetroxide in acid containing either 2 or 10 percent water had little effect; the same applied at -40° F for acid containing 2 percent water.

3. Addition of n-heptane to triethyl trithiophosphite increased the ignition delays at 75°, 32°, and -40° F; this effect was most pronounced at -40° F. At -40° F, however, blends containing as much as 40 percent n-heptane gave an average ignition delay of only 54 milliseconds.

4. Phosphorous trichloride did not produce flames with either white or red fuming nitric acid at either 70° or -40° F, although delayed non-burning reactions were obtained at 70° F.

5. With white fuming nitric acid at -40° F, dilution with n-heptane up to 40 percent had about the same effect as dilution with mixed butyl mercaptans on the ignition of triethyl trithiophosphite; and at this temperature, triethyl trithiophosphite diluted with n-heptane appeared to have about the same ignition characteristics as ethylenimine diluted with n-heptane.

6. Data from modified open-cup and small-scale rocket engine apparatus show that with suitable acid, mixed alkyl thiophosphites have satisfactory short ignition delays at temperatures as low as -76° F. On the basis of data from the modified open-cup apparatus, dilution of mixed alkyl thiophosphites with up to 70 percent by volume triethylamine does not seriously impair its self-igniting properties at -76° F.

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TABLE I - IGNITION DELAYS OF MIXED ALKYL THIOPHOSPHITES WITH NITRIC ACIDS CONTAINING VARIED CONCENTRATIONS OF WATER AND NITROGEN TETROXIDE AT 70° AND -40° F

[Modified open-cup apparatus.]

Acid composition percent by weight			Number of trials	Ignition delay millisec			Reaction quality
H_2O	N_2O_4	HNO_3		Min.	Max.	Av.	
-40° F							
2	0	98	2	3	13	8	Explosions
2	8	90	3	1	2	2	Sporadic explosions
2	24	74	2	2	4	3	Explosions
6	0	94	2	37	107	72	Explosions
10	0	90	4	163	224	185	Snappy
10	8	82	2	23	29	26	Snappy
10	24	66	2	38	58	48	Mild
70° F							
2	0	98	2	2	2	2	Explosions
2	8	90	1	11	11	11	Explosion
2	24	74	1	8	8	8	Explosion
6	0	94	1	10	10	10	Explosion
10	0	90	3	10	80	35	Sporadic explosions
10	8	82	4	22	35	28	Snappy
10	24	66	4	27	45	34	Snappy

TABLE II - DELAY INTERVALS OF FLAMELESS REACTIONS OF PHOSPHOROUS TRICHLORIDE WITH WHITE AND RED FUMING ACIDS

[Modified open-cup apparatus. Delays based on appearance of noise indicated by microphone records.]

Acid composition percent by weight			Number of trials	Reaction delay millisec			Remarks
H_2O	N_2O_4	HNO_3		Min.	Max.	Av.	
-40° F							
2	0	98	3	520	742	612	Mild reactions
2	8	90	4	---	---	---	No delay indicated
70° F							
2	0	98	4	22	25	24	Vigorous reactions
2	8	90	4	21	24	23	Vigorous reactions

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TABLE III - IGNITION DELAYS OF MIXED ALKYL THIOPHOSPHITES AND LOW-FREEZING RED FUMING NITRIC ACID AT 80° TO -95° F IN SMALL-SCALE ROCKET ENGINE

Average propellant temperature °F	Lead propellant into combustion chamber	Time between jet entries into combustion chamber millisec	Ignition delay millisec
80	Oxidant	1.5	11.3
20	Fuel	.9	13.8
-40	Fuel	2.1	16.6
-70	Fuel	18.3	17.9
-95	-------	----	a
-95	-------	----	a
-95	-------	----	a

[a]Satisfactory ignition. Delay not measured.

TABLE IV - IGNITION DELAYS OF TRIETHYL TRITHIOPHOSPHITE AND ITS n-HEPTANE BLENDS WITH WHITE FUMING NITRIC ACID AT 75°, 32°, AND -40° F

[Modified open-cup apparatus.]

Fuel percent by volume		Number of trials	Ignition delay millisec			Reaction quality
Triethyl trithio-phosphite	n-Heptane		Min.	Max.	Av.	
-40° F						
60	40	3	45	68	54	Mild
70	30	3	31	49	37	Mild
80	20	4	15	20	18	Snappy
90	10	1	9	9	9	Explosion
100	0	1	2	2	2	Flameless explosions
32° F						
60	40	3	20	40	33	Moderate
70	30	2[a]	18	20	19	Snappy
80	20	2[a]	2	4	3	Explosion
90	10	1[a]	5	5	5	Explosion
75° F						
60	40	6	15	39	27	Snappy
70	30	3	16	34	22	Sporadic explosions
80	20	1	11	11	11	Explosion
90	10	1	12	12	12	Explosion
100	0	2[a]	7	9	8	Explosions

[a]Data from electronic timer.

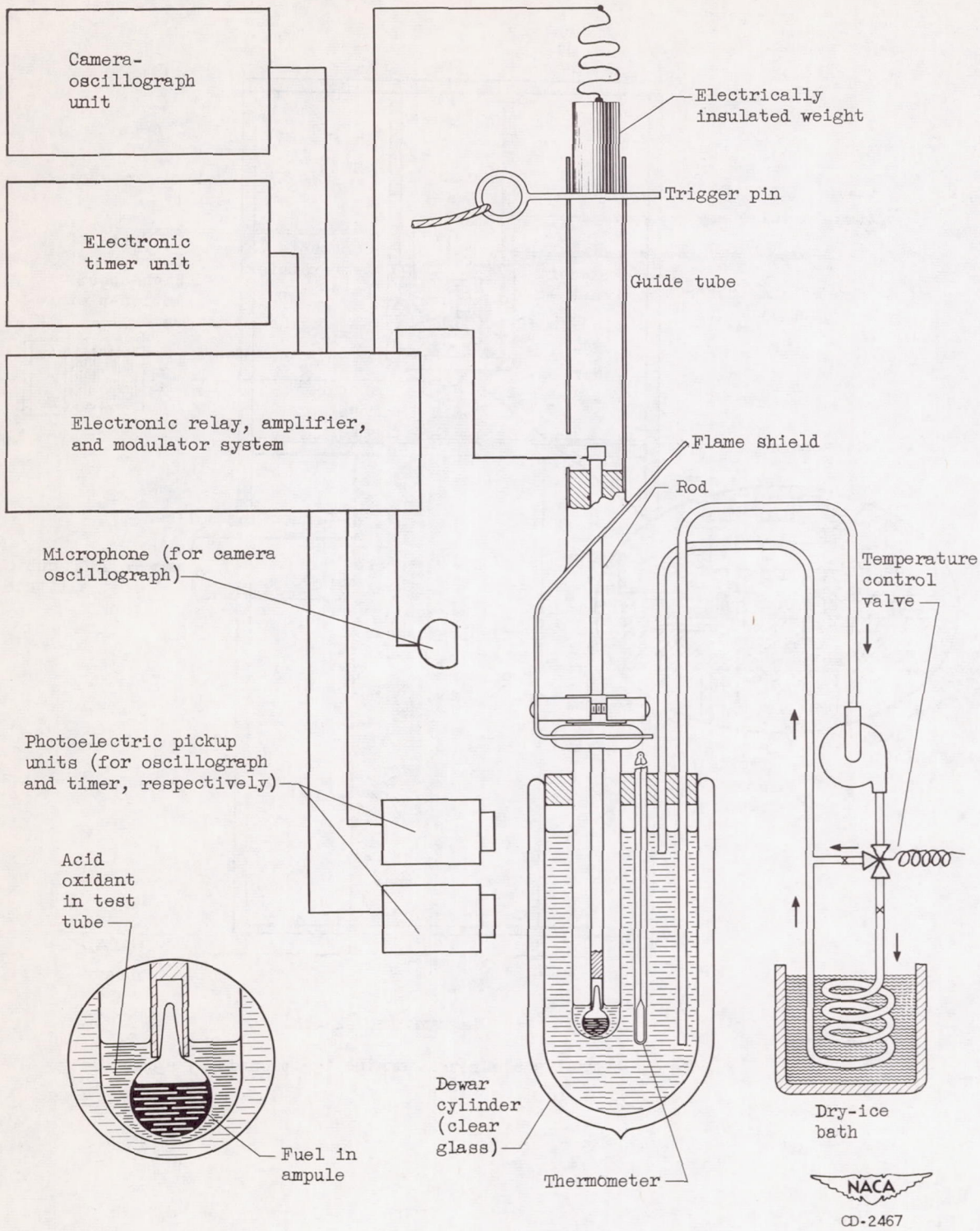
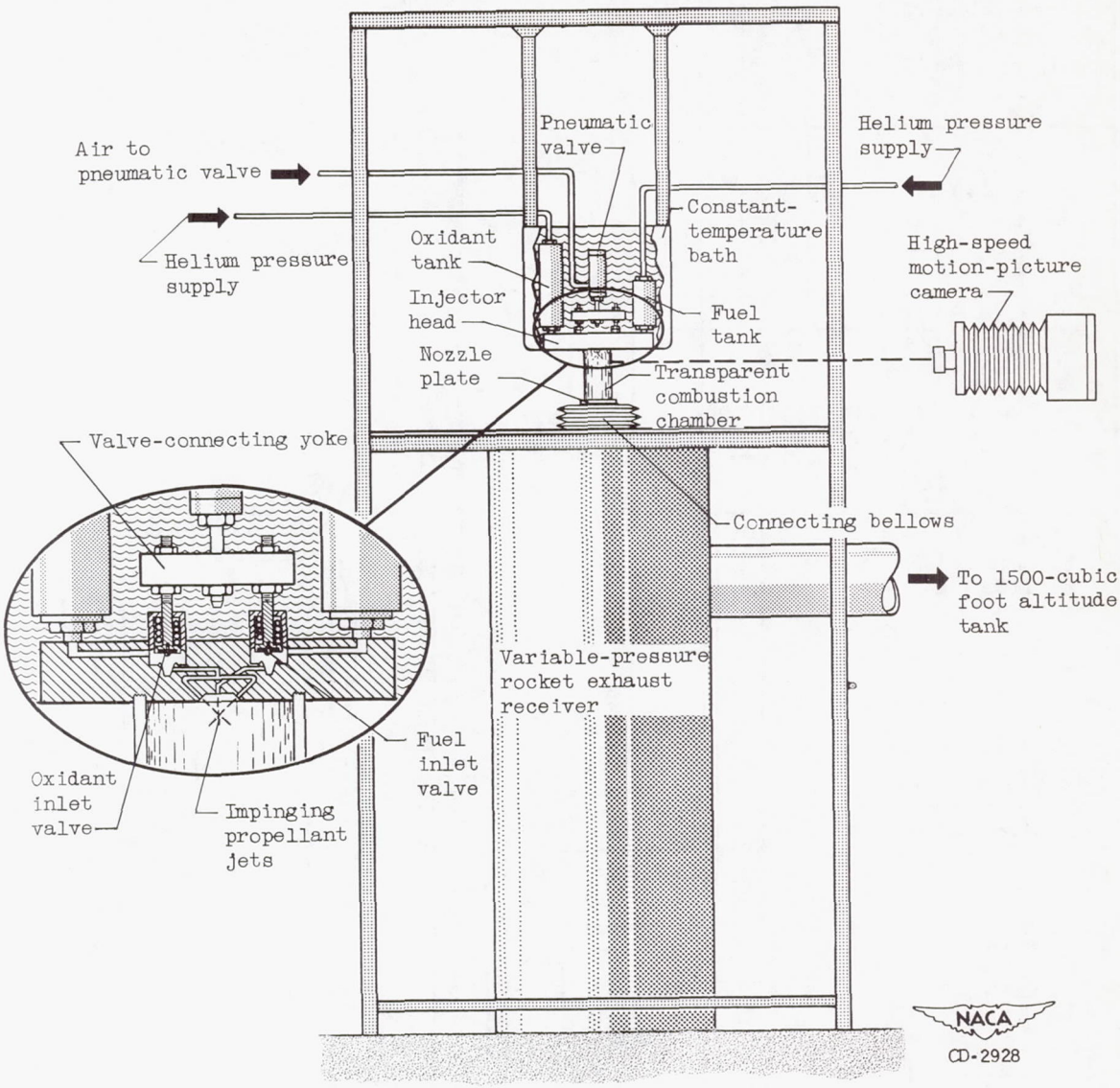
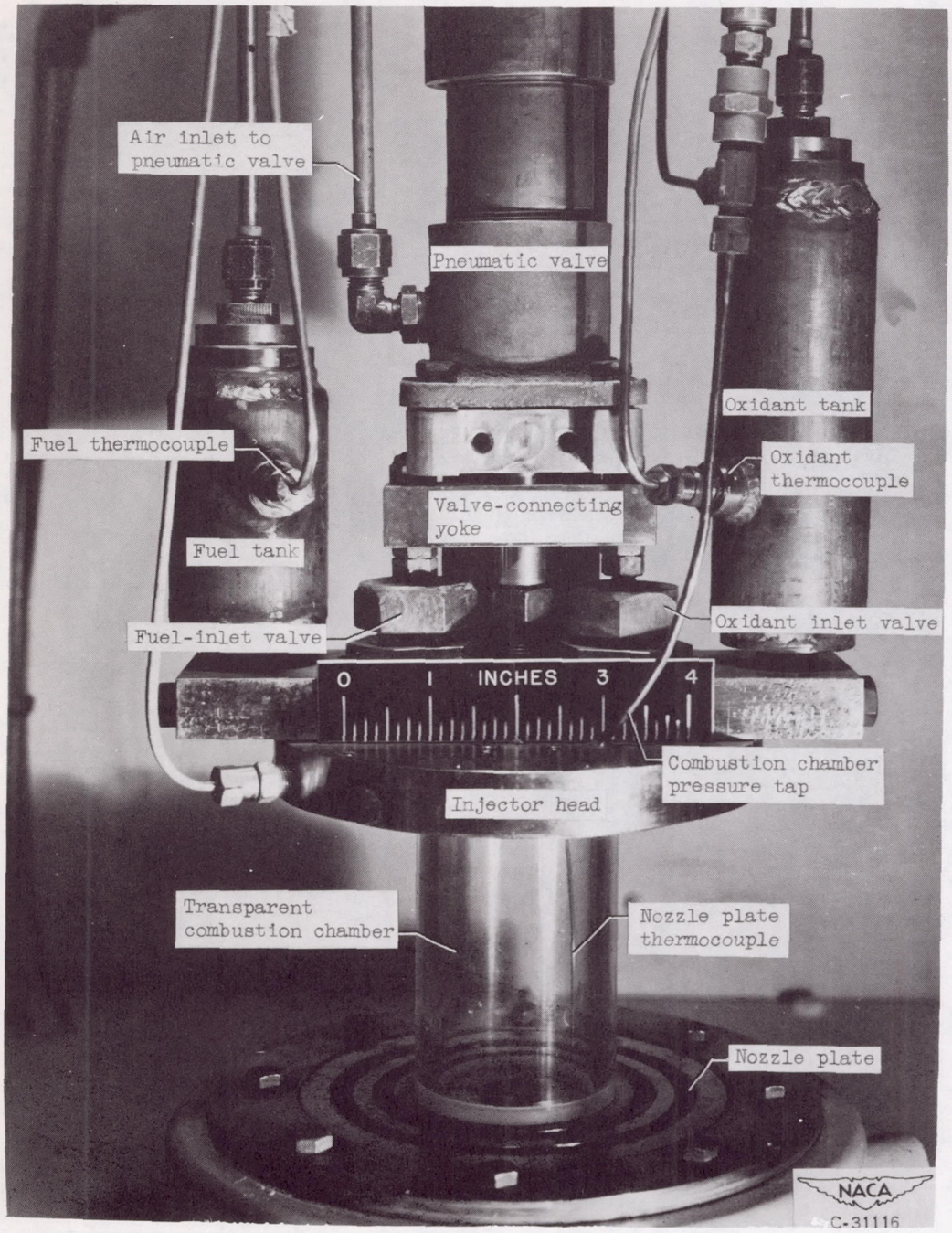


Figure 1. - Modified open-cup ignition delay apparatus.



(a) Diagrammatic sketch.

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



(b) Engine assembly.

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

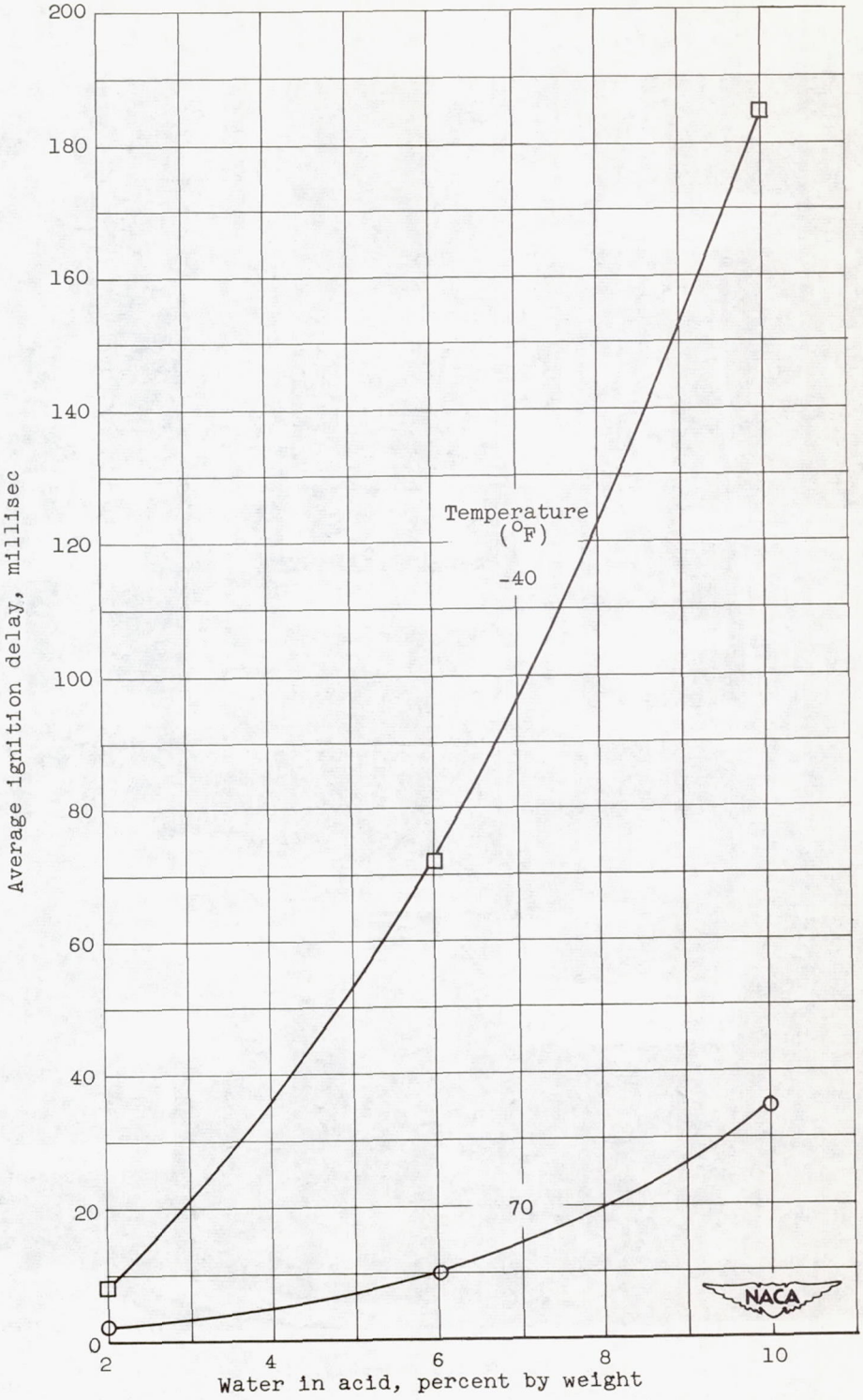


Figure 3. - Effect of water in white fuming nitric acid on ignition delays of mixed alkyl thiophosphites in modified open-cup apparatus.

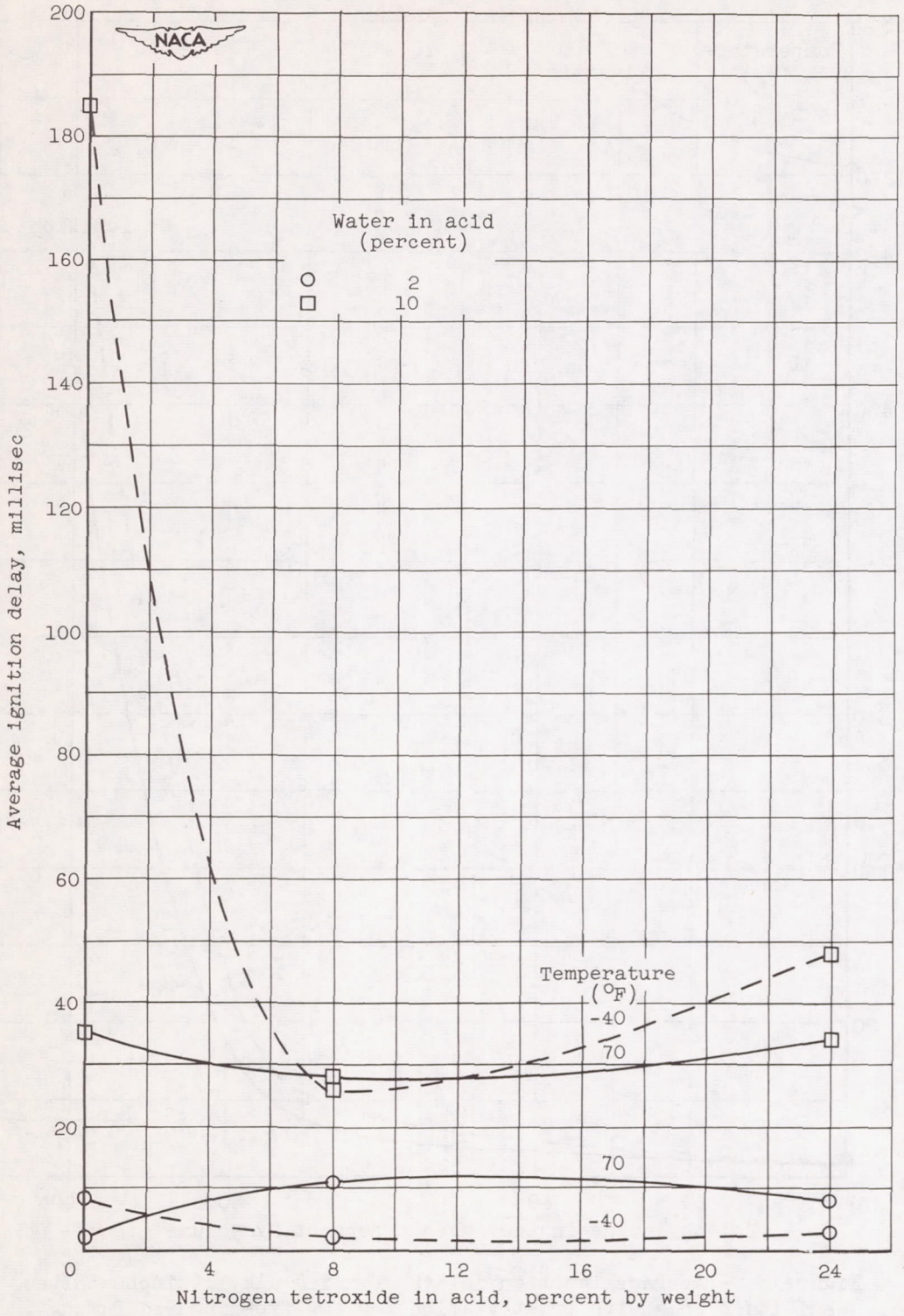


Figure 4. - Effect of nitrogen tetroxide in nitric acids containing 2 and 10 percent water on ignition delays of mixed alkyl thiophosphites in modified open-cup apparatus.

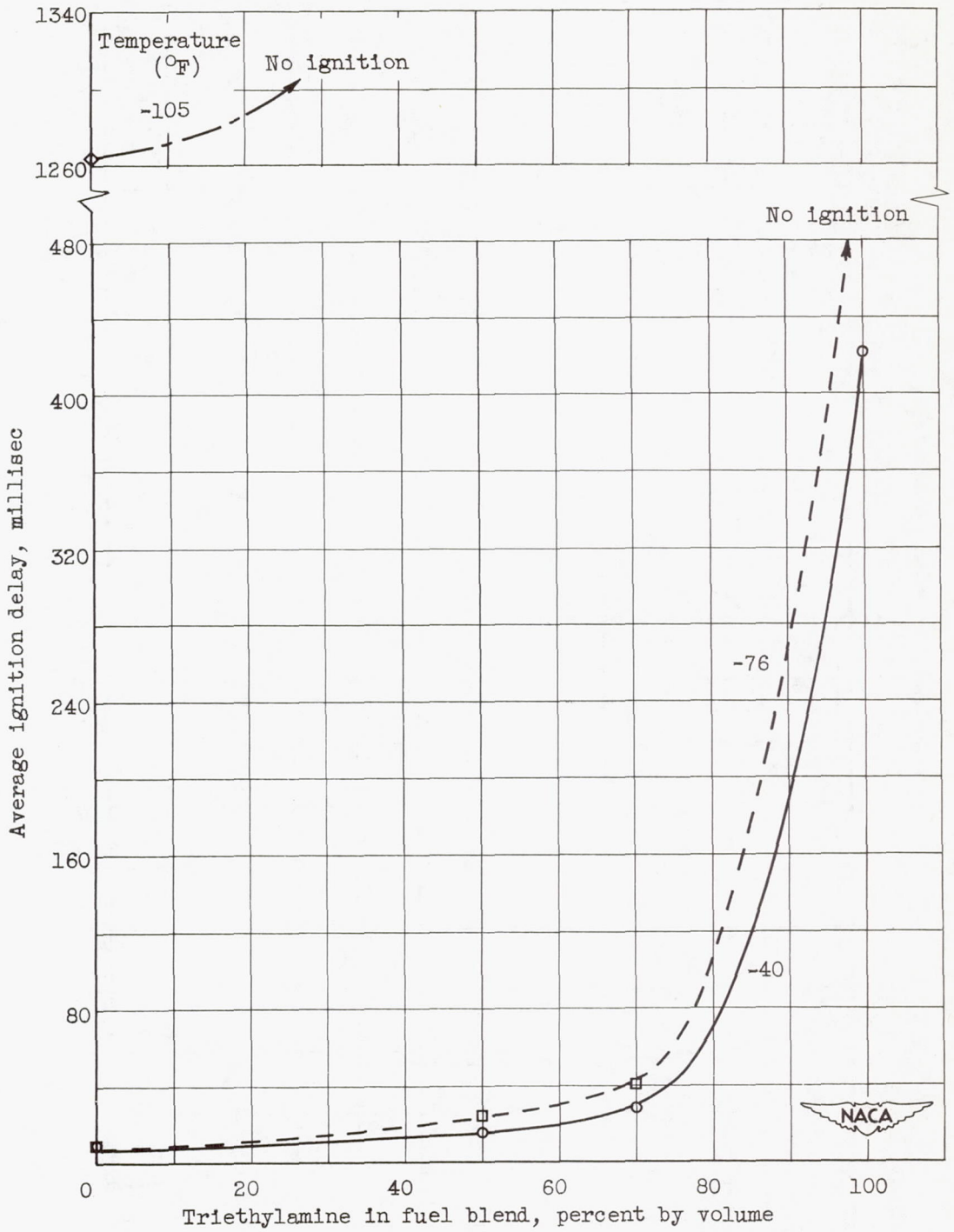


Figure 5. - Average ignition delays of mixed alkyl thiophosphites and its blends with triethylamine for low-freezing red fuming nitric acid in modified open-cup apparatus (reference 4). (Acid supercooled at -105° F.)

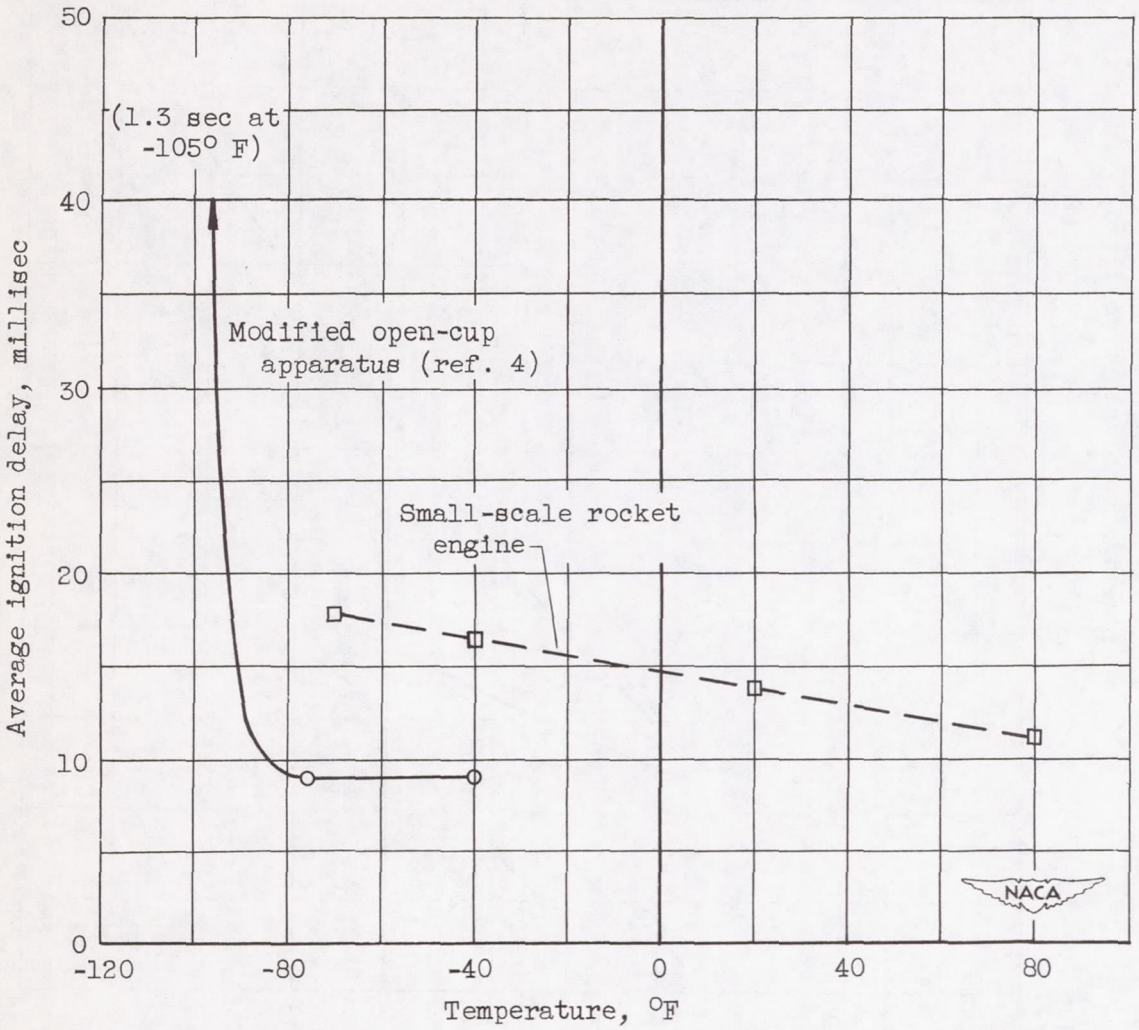


Figure 6. - Ignition delays of mixed alkyl thiophosphites with low-freezing red fuming nitric acid. (Acid supercooled at temperatures below -88° F.)

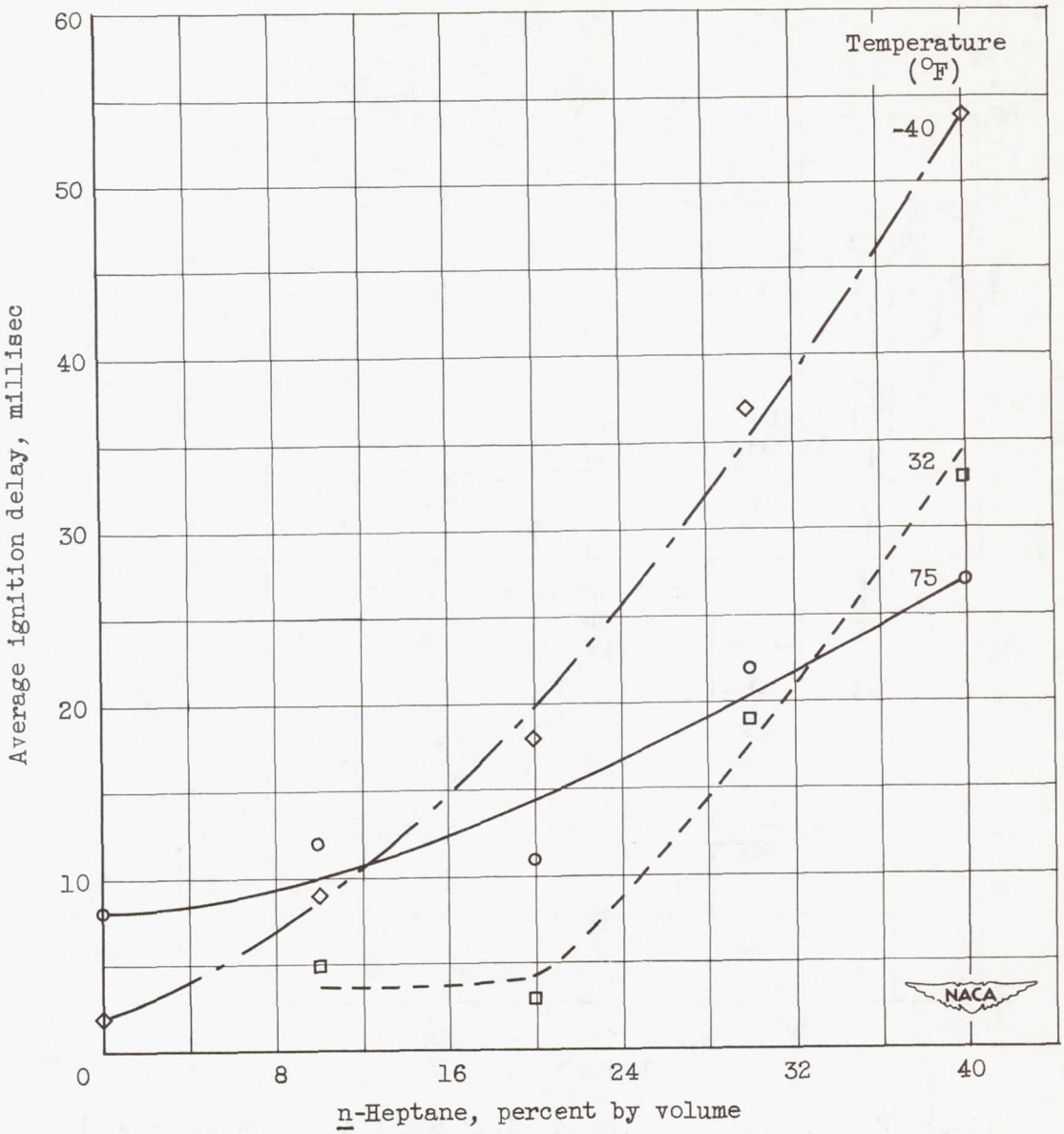
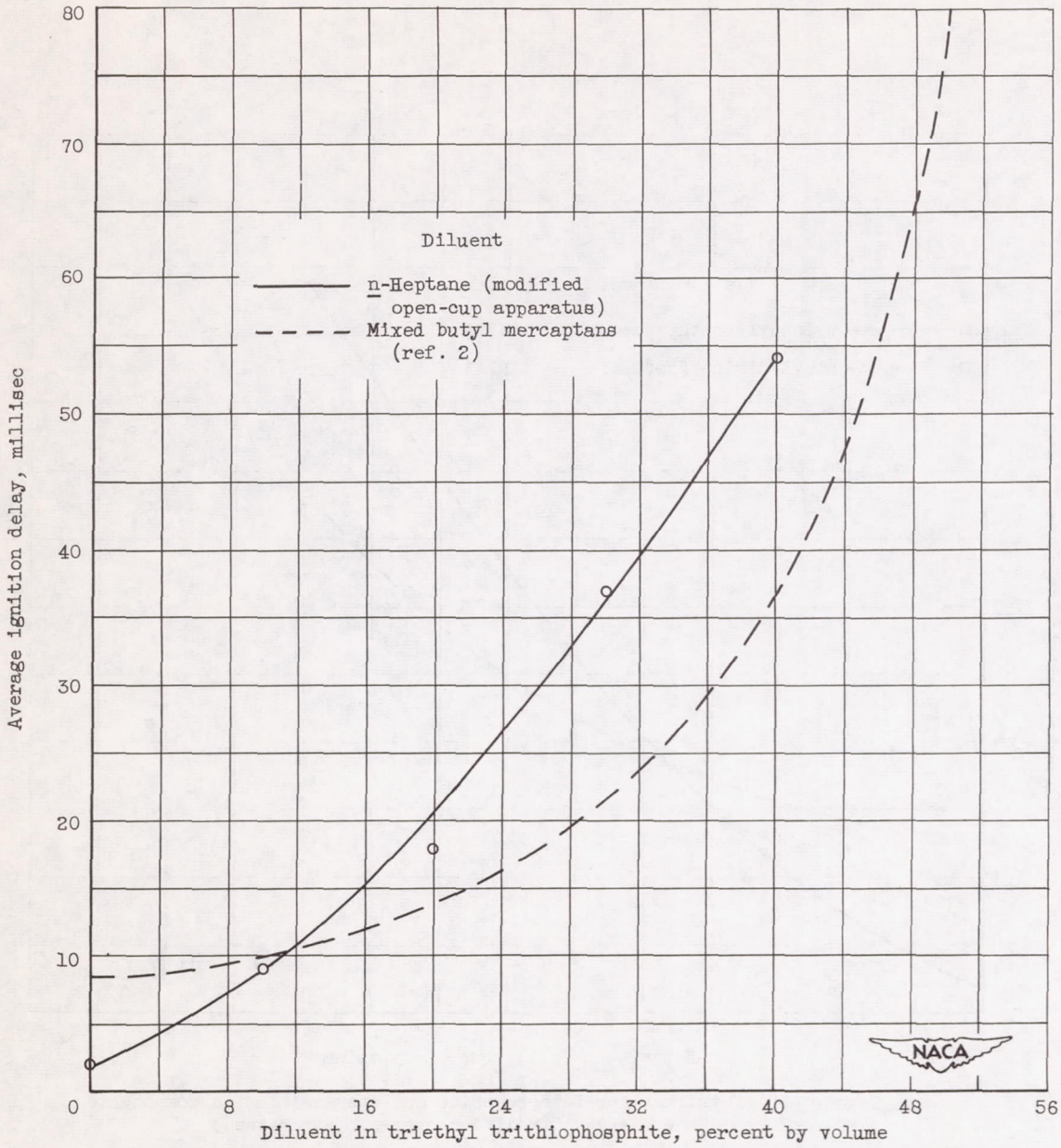
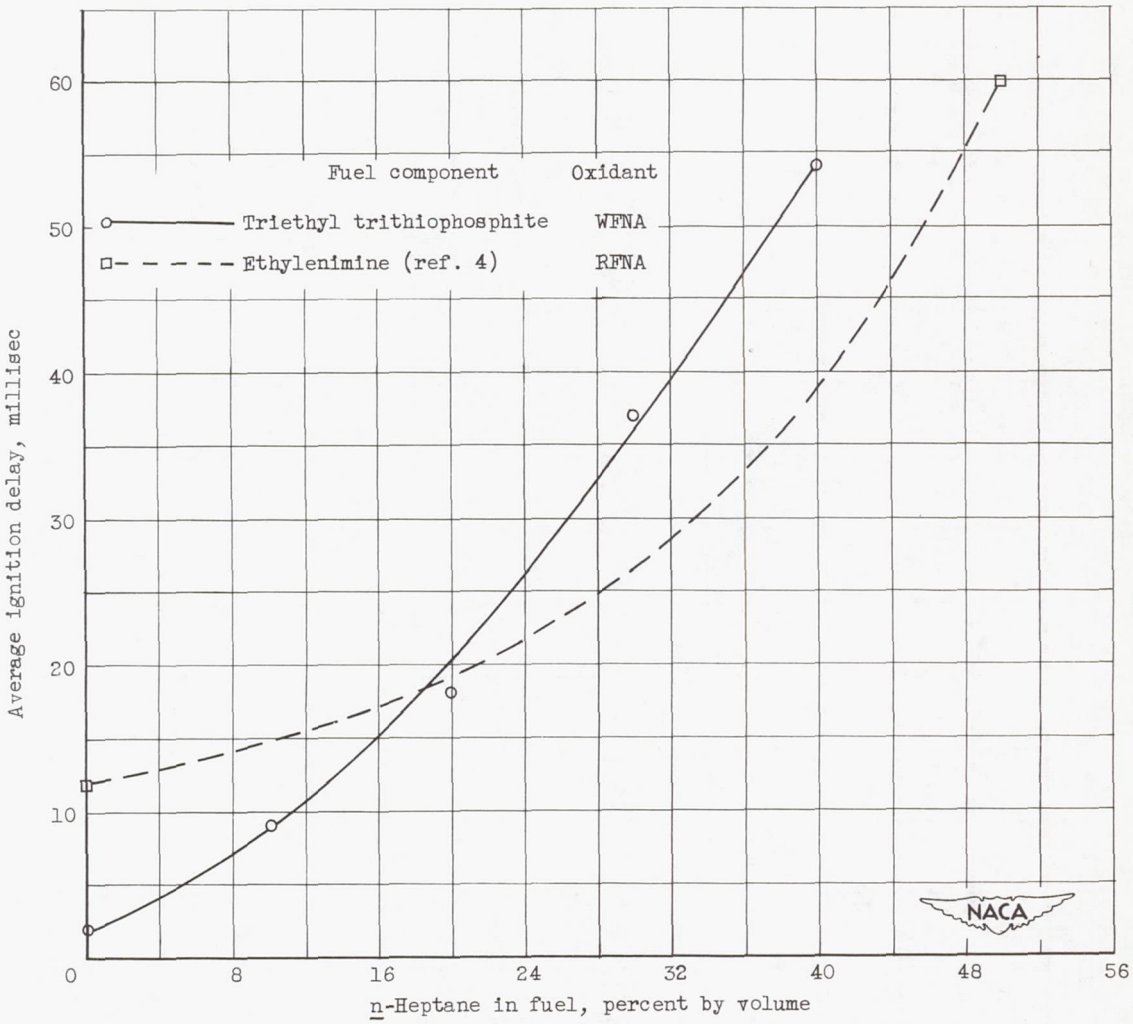


Figure 7. - Average ignition delays of triethyl trithiophosphite and its blends with n-heptane for white fuming nitric acid in modified open-cup apparatus.



(a) Comparison of n-heptane and mixed butyl mercaptans as diluents in triethyl trithiophosphite; oxidant, white fuming nitric acid.

Figure 8. - Comparison of average ignition delays at -40° F of triethyl trithiophosphite - n-heptane blends with those of other fuel blend systems.



(b) Comparison of triethyl trithiophosphite and ethylenimine as components of n-heptane blends. (Modified open-cup apparatus.)

Figure 8. - Concluded. Comparison of average ignition delays at -40° F of triethyl trithiophosphite - n-heptane blends with those of other fuel blend systems.