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RESEARCH MEMORANDUM

ORTHOTOLUIDINE AND TRIETHYLAMINE IN ROCKET ENGINE APPLICATIONS

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NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS
WASHINGTON
January 26, 1953

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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

RESEARCH MEMORANDUM

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SUMMARY

The literature pertaining to the use of orthotoluidine and triethylamine in rocket propellant combinations was surveyed and summarized with particular emphasis on ignition delay investigations and fuel mixture applications.

In addition, experimental ignition delay determinations of two orthotoluidine-triethylamine mixtures (1:1 and 3:7 by volume) and a low-freezing-point red fuming nitric acid were conducted at simulated altitude conditions utilizing a small-scale rocket engine of approximately 50 pounds thrust. The delays varied almost linearly from about 12 milliseconds at 120° F to about 28 milliseconds at -70° F for both propellant combinations. At -95° F, the ignition delays for the 1:1 and 3:7 fuel blends were about 101 and 29 milliseconds, respectively. Experiments at pressure altitudes of about 90,000 feet at the two temperature extremes indicated no significant effect of low initial ambient pressure on ignition delay. An explosion occurred after ignition in some of the tests at sea-level pressure and 80° to 120° F.

The literature survey and the experimental data of this investigation were examined and evaluated with respect to the utilization of orthotoluidine and triethylamine in rocket engine applications. Mixtures of these two compounds, especially the 3:7 blend by volume, appear promising as rocket starting fuels over a wide range of temperatures and initial ambient pressures. These mixtures can also be used as main fuels in applications where the cost is reasonable and where slight residues after operation are not detrimental. The addition of orthotoluidine to nonhypergolic fuels to make them self-igniting is not recommended because other additives reportedly are better in this respect.

INTRODUCTION

Of various methods used in the starting of rocket engines, especially at conditions of high altitude, ignition by chemical means continues to receive considerable attention because of the need for a reliable system that is independent of any external electrical or thermal source. Several propellant combinations with satisfactory ignition characteristics from room temperature to about -100° F have already been

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investigated (e.g., references 1 and 2); however, the search persists for fuels and oxidants that are even better with respect to desirable qualities such as low cost, ready availability, high viscosity index, high fluidity at low temperatures, short and reproducible ignition delays over a wide temperature range, good handling properties, nonresidue-forming characteristics, and moderate transient pressures at ignition.

Some mixtures of orthotoluidine and triethylamine have many of these desirable qualities. As part of a general investigation of the ignition characteristics of self-igniting rocket propellant combinations conducted at the NACA Lewis laboratory (references 1 to 4), a literature survey of orthotoluidine and triethylamine (unblended and as components of various mixtures) pertinent to rocket applications was made and is reported herein. In addition, ignition delay determinations of two orthotoluidine-triethylamine blends with a low-freezing-point red fuming nitric acid (RFNA) were made at simulated altitude conditions utilizing a small-scale rocket engine of approximately 50 pounds thrust and are also reported herein.

LITERATURE SURVEY

Unblended Orthotoluidine

General review. - Of the three isomeric toluidines, only orthotoluidine can be considered to have practical value as a fuel at the present time. Metatoluidine is produced only on a relatively small scale, and paratoluidine is a solid at ordinary room temperatures.

Unblended orthotoluidine has been of interest as a rocket fuel for at least 10 years. In early open-cup tests, it was found to ignite spontaneously with mixed acid (references 5 and 6) and also with red fuming nitric acids containing 6.5 to 25 percent nitrogen dioxide by weight (references 5 to 7). Ignition delays of approximately 60 milliseconds were obtained with the red fuming acid containing 6.5 percent NO_2 (reference 7). Successful self-ignition was obtained with the same propellant combination in a 50 pound thrust rocket engine (reference 7). At about the same time, German investigators found that toluidine (probably the ortho isomer) was self-igniting with nitric acid, nitrogen tetroxide, and mixed acid with added catalyst (reference 8).

Recent laboratory tests with an impinging-jet apparatus yielded an average ignition delay of 45 milliseconds for an orthotoluidine-RFNA combination (reference 9). With metatoluidine and RFNA, the average delay at the same conditions was 110 milliseconds. The ignition delay for both combinations was reduced to about 10 milliseconds when a small amount of ammonium metavanadate was added to the oxidant. Orthotoluidine has also been tested with anhydrous nitric acid (references 10 and 11). In an impinging-jet apparatus, the ignition delay was found to decrease from 112 to 64 milliseconds as the injection pressure was increased from 2.5 to 25 pounds per square inch (reference 10). In a simple open-cup apparatus, ignition delays of 700-800 milliseconds were obtained with orthotoluidine and absolute nitric acid (reference 11). When a catalyst, $FeCl_3 \cdot 6H_2O$ (60 grams per liter), was added to the acid, "immediate" ignition resulted.

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Investigations of orthotoluidine with oxidants other than the nitric acid type have also been made. In open-cup tests, there was no immediate decomposition when hydrogen peroxide (90 percent) was added to the fuel; however, spontaneous ignition occurred when the same oxidant contained dissolved cobaltous nitrate (reference 12).

Although not disclosed directly, all the studies just described were probably conducted at room temperatures. Unless noted otherwise, a similar assumption was made for all other investigations found in the literature and reported herein. This assumption is probably valid since the effect of temperature on ignition delay has been generally recognized and specifically indicated whenever it has been studied.

Summary. - Orthotoluidine ignites spontaneously with nitric-acid-type oxidants. Reduced ignition delays are obtained by the use of suitable catalysts in the acid. Spontaneous ignition can also occur with hydrogen peroxide if it contains a proper catalyst. Orthotoluidine, unsatisfactory for very low-temperature applications because of its relatively high final freezing point, has not been investigated extensively below room temperatures.

Unblended Triethylamine

General review. - Although triethylamine is used primarily as a blending agent in fuels to decrease the viscosity and often to improve the ignition characteristics, some studies have been made with this aliphatic amine to determine its usefulness in the unblended state. One of the earliest references to this substance in rocket applications is made in a German report issued about a decade ago which states that triethylamine is definitely better than diethyl- or monoethylamine with respect to ignition delay (reference 13). Later German tests indicate that triethylamine is self-igniting with nitric acid, mixed acid, and nitrogen tetroxide (reference 8). The same reference gives 47 milliseconds as the ignition delay at 20° C for triethylamine and nitric acid containing ferric nitrate. Ignition delays of 35 to 40 milliseconds were obtained in an open-cup apparatus with triethylamine and nitric acid (98 percent by weight) containing $FeCl_3 \cdot 6H_2O$ (reference 14). In another open-cup apparatus, triethylamine gave "immediate" ignition with both absolute nitric acid and nitric acid with hydrated ferric chloride added as a catalyst (reference 11). Simple drop tests have indicated that triethylamine ignites with nitric acid having as much as 10 percent water and sometimes with nitric acid having a 15 percent water content (reference 15).

In still another open-cup apparatus, long delays of greater than 700 milliseconds were obtained at -40° F with red fuming nitric acid containing 3 percent water and 19 percent nitrogen dioxide by weight (reference 1). With the same apparatus and at the same temperature, no ignition could be obtained with mixed acid and only sporadic ignition resulted with white fuming nitric acid containing 7 percent water by weight.

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The activity of triethylamine with oxidants other than the nitric acid type has also been investigated. German researchers have reported that triethylamine is self-igniting with hydrogen peroxide (80 percent) with added iron, copper, or cobalt catalyst (reference 8). On the other hand, a report of some American open-cup tests stated that ignition could not be obtained with hydrogen peroxide (90 percent) nor with this oxidant when copper, nickel, cobalt, iron, or vanadium catalysts were added (reference 12).

Summary. - Triethylamine is self-igniting with nitric acid oxidants at room temperatures. The ignition delays are decreased by the addition of catalysts to the acid. In spite of its low freezing point and high fluidity at low temperatures, triethylamine has unsatisfactory ignition characteristics with various nitric acids at -40° F. Suitability of the use of triethylamine with hydrogen peroxide, even with added catalysts, is controversial.

Orthotoluidine in Fuel Blends

General review. - There are several reasons for the use of orthotoluidine in fuel mixtures. If orthotoluidine is the primary component of the blend, a diluent may be used either to lower the freezing point, lower the cost, reduce the viscosity, or improve the ignition characteristics. If orthotoluidine is the secondary component, it is probably employed as an additive to give self-igniting properties to a fuel that is normally nonhypergolic with the common oxidants. Many of these two types of mixture have been investigated and are reported in the literature. Some of the blends include mixtures of orthotoluidine with *n*-hexane, *n*-octane, hexene-1, octene-1, octene-2, 2,2,4-trimethylpentane, 2-ethyl-1-hexene, 2-methyl-1-pentene, alkylate (mixed paraffin hydrocarbon isomers), benzene, toluene, mixed xylenes, ethyl benzene, diallylether, and methylal (reference 10). In this group, several of the diluents are unsuitable for low-temperature applications because of the appearance of a second phase. The phase relations at low temperatures are shown in table I. The limits for self-ignition with anhydrous nitric acid at room temperature vary and are also listed in table I. German open-cup ignition tests were conducted with several other orthotoluidine mixtures and nitric acid with added catalyst (reference 11). The diluents included methanol, ethanol, tetralin, solvent benzol, cyclohexane, benzine, benzol, and gas oil. The ignition delays for these blends, as well as the freezing points of the mixtures, are listed in table II. The ignition qualities of these orthotoluidine mixtures were found to be much better than those for similar aniline mixtures.

In another investigation, it was found, in partial contrast to reference 10, that the activity of all the nonhypergolic diluents tested had small effect on the maximum tolerable dilution of the hypergolic fuels studied (reference 16). Orthotoluidine, one of several self-igniting fuels tested with red fuming nitric acid, was diluted separately with gasoline, JP-3 fuel, kerosene, methanol, and isopropanol. In each case, it was possible to add up to 60 percent diluent and still maintain the self-igniting properties. Another source reports that it is possible to add as much as 69 percent gasoline (of total weight) to technical grade orthotoluidine and still get ignition with red fuming nitric acid containing 16 percent nitrogen dioxide (reference 7). A third laboratory found that the maximum tolerable dilution of toluidine (presumably ortho) with a refined petroleum fraction in the gasoline boiling range was 30 percent by volume (references 17 and 18). The oxidant was red fuming nitric acid.

Orthotoluidine fuel blends have also been investigated with hydrogen peroxide as the oxidant. Ignition was obtained when orthotoluidine containing a catalyst (acid cuprous chloride) and diluted with a large, but undisclosed, amount of acetone was tested with hydrogen peroxide (90 percent) in an open-cup apparatus (reference 12). Ignition also resulted when the same oxidant was mixed with orthotoluidine to which catalytic amounts of cobaltous chloride, cobalt sulfate, ferrous sulfate, or concentrated nitric acid had been added (reference 12).

Mixtures of orthotoluidine and triethylamine have been studied. Reference to these studies is made in the next section.

<u>Summary</u>. - Orthotoluidine can be diluted to a considerable extent with some nonhypergolic fuels and still maintain its self-igniting properties with nitric acid oxidants. Diluents are also added to orthotoluidine to reduce its freezing point and to improve other physical properties. Orthotoluidine and hydrogen peroxide are self-igniting when a suitable catalyst is added to the fuel.

Triethylamine in Fuel Blends

General review. - The use of triethylamine as an additive to a rocket fuel to enhance its ignition characteristics was first made about a decade ago. A German fuel, self-igniting with concentrated nitric acid and containing 96 percent gasoline and 4 percent of a mixture of triethylamine, tetrahydrofuran, and furfuryl alcohol, reached the laboratory stage at the end of the war (reference 19), but presumably no exploitation of this propellant combination has been made since that time. Most triethylamine blends that have been investigated contain much larger amounts of this compound. One example is a ternary fuel system of triethylamine, hydrazine, and aniline (20, 10, and 70 weight percent, respectively). Simple drop tests have indicated that this mixture would ignite spontaneously with nitric acid if its water content was less than about 4 percent (reference 15).

Fuel blends of triethylamine and xylidines have been considered important enough to receive the attention of many investigators in several countries. The British took cognizance of such blends when they referred to the practical possibilities of mixtures of aromatic and aliphatic amines (e.g., aniline, methylaniline, and xylidine with triethylamine or trimethylamine, in some cases with addition of hydrocarbons such as benzene, xylene, octane mixtures, and so forth) (reference 20). An important self-igniting fuel developed in Germany was Tonka 250, a mixture of triethylamine and xylidine (reference 19). Although furfuryl alcohol gave a shorter ignition delay, it was not used because of supply difficulties; moreover, Tonka 250 was able to ignite with lower concentrations of nitric acid (down to 85 percent HNO_3) and both its physical properties and its ignition delay were satisfactory at low temperatures. A 1:1 by volume mixture of triethylamine (97 percent pure) and mixed xylidines was found to have satisfactory low viscosities at low temperatures (reference 11). When tested on proving grounds, this blend showed such good ignition qualities that the use of a catalyst in the nitric acid could be abandoned. Information of a more detailed nature is available on a German propellant combination consisting of a fuel mixture of 50 percent triethylamine and 50 percent "m-xylidine" by weight and a concentrated nitric acid oxidant (reference 8). The ignition delay - temperature relations of this combination were determined in an open-cup apparatus at an initial ambient pressure of one atmosphere. The delays ranged from 14 milliseconds at 95° F to 21 milliseconds at 41° F. With the same fuel blend and with concentrated nitric acid containing added ferric nitrate, the same reference reports ignition delay values ranging from 13 milliseconds at 68° F to 41 milliseconds at -58° F. This fuel mixture produced average delays of 40 milliseconds with mixed acid at 68° F and 20-30 milliseconds with catalyst-containing mixed acid at the same temperature.

An ignition study of a blend of triethylamine with mixed xylidines (50-50 percent by volume) with 15 different nitric acid oxidants (mixed, anhydrous, red and white fuming acids) has been made at -40° F in a modified open-cup apparatus (reference 1). In this series, the greatest reactivity was indicated by the combinations employing the red fuming nitric acids (3-5 percent water, 16-35 percent nitrogen dioxide, by weight) and a mixed acid; the average ignition delays were about 30 milliseconds. These results are shown in table III. A similar study was made with a fuel blend of triethylamine and diallylaniline (50-50 percent by volume) and the results are also included in table III. In another investigation with the same apparatus and with various nitric acid oxidants, ignition delay determinations of several fuel mixtures in which triethylamine was a significant component were made at -40° F (reference 1). The resulting data are listed in table IV. Some of these propellant combinations were studied over a wide range of temperatures (70° to -105° F) and the ignition delay values are shown in table V (reference 1).

Similar investigations were made in a small-scale rocket engine (reference 2). Ignition delay measurements were made at -40° F with triethylamine-mixed xylidines and triethylamine-diallylaniline mixtures with anhydrous and white fuming nitric acids. The results are summarized in table VI. The latter fuel blend was also investigated over a wide range of temperatures and initial ambient pressures (reference 2). The results with both white and red fuming nitric acids are shown in figure 1.

Triethylamine has also been blended with pyrrole, and ignition delay determinations of this fuel mixture with various nitric acid oxidants have been made in an impinging-jet apparatus at temperatures from 70° to -65° F (reference 21) and are as follows:

Temperature (°F)	Ignition delay (millisec)				
	WFNA	WFNA + 8.5 percent additive (a)	WFNA + 12 percent additive (a)	RFNA (6 percent NO_2)	RFNA (13 percent NO_2)
70	11	15	19	14	11
-40	17	29	59	28	20
-65	(Frozen acid)	83	136	52	37

[a] Additive consisted of 50 percent KNO_3 and 50 percent H_2O.

Triethylamine blends have also been used with oxidants other than the nitric acid type. Ignition delay determinations were made with a mixture of 50 weight percent hydrazine hydrate and 50 weight percent methanol (plus a small quantity of $K_3Cu(CN)_4$) in which the hydrazine hydrate was progressively displaced by triethylamine substitution (reference 8). The experiments, conducted at 0° C in an open-cup apparatus with hydrogen peroxide (80 percent) as the oxidant, showed that the ignition delays varied nonlinearly from about 40 milliseconds with zero amount of triethylamine to 100 milliseconds with 30 percent triethylamine by weight. A minimum value of 28 milliseconds was obtained with 7 percent triethylamine.

Summary. - Triethylamine is used primarily as an additive to rocket fuels to enhance their physical and ignition properties. Of the many triethylamine mixtures investigated, fuel blends containing xylidines have been studied most extensively and have been found to ignite satisfactorily with nitric acid oxidants over a wide range of temperatures. Triethylamine blends having shorter ignition delays and a wider operating range of temperatures are known, but have had a more limited study. There are also some triethylamine mixtures that have satisfactory ignition characteristics with hydrogen peroxide.

Some Properties of Fuels Containing Orthotoluidine or Triethylamine

Besides scattered information available in chemical handbooks and similar sources, compilations of physical properties of orthotoluidine, triethylamine, and fuels containing these substances may be found in the rocket literature (references 1, 2, 5, 7, 8, 10, 11, 15, 22, and 23). Included among the listed properties are freezing points, boiling points, densities, viscosities, refractive indices, vapor pressures, heat capacities, flash points, surface tensions, and various heats of reaction. Some of these references also contain related pertinent rocket information such as handling and storage (reference 23), calculated and experimental products of reaction with various oxidants (reference 22), and toxicity (reference 23).

Availability and Cost of Orthotoluidine and Triethylamine

According to Frederick D. Bates, Jr. of the Chemical and Rubber Division, Office of Materials, Munitions Board, the present rate of production of orthotoluidine is 5,000,000 pounds per year. One-half this amount is for sale. Triethylamine is being produced at the rate of 1,500,000 pounds per year and all of it is for sale. As for the future, "no apparent limit to production is necessary."

For rocket starting applications, orthotoluidine may be purchased in drum quantities for approximately 23 cents per pound (reference 24). If used as a major component of the main fuel, tank car lots are available at about 22 cents per pound (reference 24). For similar applications, triethylamine can be obtained at about 44 cents per pound in either tank or carload quantities (reference 24).

IGNITION STUDIES WITH RED FUMING NITRIC ACID

Apparatus and Procedure

Ignition delay determinations over wide ranges of temperature and initial ambient pressure with orthotoluidine-triethylamine mixtures and red fuming nitric acid were made at the NACA Lewis laboratory with a small-scale rocket engine apparatus shown diagrammatically in figure 2 and described in detail in reference 2.

Propellants

Two orthotoluidine-triethylamine mixtures were investigated. One fuel blend contained a 1:1 volume ratio of orthotoluidine to triethylamine; the other, a 3:7 ratio. The oxidant used with each of these fuels was a red fuming nitric acid containing 3 percent water and 19 percent nitrogen dioxide by weight.

Results and Discussion

A total of 16 runs was made with the two propellant combinations at sea-level pressure and at temperatures from 120° to -95° F. Three runs resulted in explosions. A run was also made at a pressure altitude of about 90,000 feet at each of the temperature extremes. The results of the experiments are shown in table VII. A plot of ignition delay against temperature at various pressures for both propellant combinations is shown in figure 3.

The ignition delays of both fuels were substantially the same over most of the temperature range investigated. The delays ranged from about 12 milliseconds at 120° F to about 28 milliseconds at -70° F. Below -70° F, the viscosity of the 1:1 fuel mixture increased very rapidly as did its ignition delay, the latter reaching 101 milliseconds at -95° F. The more fluid fuel mixture continued its almost linear increase in ignition delay values to about 29 milliseconds at -95° F. Runs at pressure altitudes of about 90,000 feet at the two temperature extremes (runs 172 and 175) indicated no significant effect of low initial ambient pressures on ignition delay. Explosions occurred after ignition with both fuel blends (runs 167, 168, and 179); all these runs were made at sea-level pressure and 80° F or higher. As with other aromatic fuels, a carbonaceous residue remained in the combustion chamber after each run; however, the amount was small and less than that usually obtained with aniline at similar operating conditions.

These results were compared with those obtained with the modified open-cup apparatus (reference 1) and, as usual with propellant combinations with relatively short ignition delays (<50 milliseconds), were found to be very similar. In figure 4, open-cup ignition delay values for the orthotoluidine-triethylamine mixtures are superimposed on the curves of figure 3 representing small-scale engine data for the same mixtures. Data points for the open-cup apparatus all fall on or close to these curves. Open-cup ignition delays for the 3:7 fuel blend, however, seem to follow the small-scale engine values for the 1:1 fuel blend at temperatures below -75° F. This may be caused by a more rapid decrease in mixing efficiency with increasing viscosity as the temperature is lowered as compared with that obtained in the small-scale engine.

Summary of Results

With two orthotoluidine-triethylamine mixtures (1:1 and 3:7 by volume) and a low-freezing-point red fuming nitric acid, the ignition delays varied almost linearly from about 12 milliseconds at 120° F to about 28 milliseconds at -70° F for both propellant combinations. At -95° F, the ignition delays for the 1:1 and 3:7 fuel blends were about 101 and 29 milliseconds, respectively. An explosion occurred after ignition in some of the runs at 80° to 120° F.

CONCLUDING REMARKS

Orthotoluidine is about as good a rocket fuel as aniline with respect to cost, performance, and ignition characteristics, but it has a wider temperature application because of its lower freezing point. Present requirements, however, demand satisfactory operation at temperatures far below this limit. Such requirements can be satisfied by fuel mixtures of orthotoluidine and some suitable additive. Triethylamine, a fuel with relatively poor ignition characteristics by itself, is an excellent diluent. It is able to lower the freezing point of orthotoluidine considerably and also decreases its viscosity. A 3:7 by volume mixture of orthotoluidine and triethylamine freezes below -100° F and has a kinematic viscosity of only about 75 centistokes at that temperature. Its ignition delays with various nitric acid oxidants are lower than those of the unblended components. Use of triethylamine in the mixture, however, increases the total cost by 70 percent; the price of the blend in large quantities is, therefore, about 37 cents per pound, a cost that may still be satisfactory in many applications.

With these considerations taken into account, orthotoluidine-triethylamine mixtures, especially the 3:7 blend, appear promising as satisfactory rocket starting fuels. The high transient combustion chamber pressures encountered at ignition in some of the experimental tests can be eliminated by proper programming of the propellant flow rates. The slight residue usually found in the combustion chamber after ignition tests will be burned by the combustion of the ensuing main propellants. Application of these mixtures as main fuels can also be made in cases where the cost is considered reasonable and where small amounts of combustion-chamber residue after operation are not too objectionable. It can easily displace aniline in this respect, since it is superior in the several ways previously mentioned.

Orthotoluidine can be added to nonhypergolic fuels to make them self-igniting. Such application is not recommended, however, because a large percentage is usually required and because certain other additives have been reported to be superior in this respect (e.g., reference 19).

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TABLE I - LOW-TEMPERATURE PHASE RELATION AND MAXIMUM TOLERABLE DILUTION FOR SELF-IGNITION WITH ANHYDROUS NITRIC ACID AT ROOM TEMPERATURE OF SEVERAL ORTHOTOLUIDINE MIXTURES

(REFERENCE 10)

Diluent	Phase relation		Self-ignition limit at room temperature (mole fraction of diluent)
	Number of phases	Temperature (°C)	
n-Hexane	2	-40	0.6
n-Octane	2	-40	.2
Hexene-1	2	-30	.6
Octene-1	1	-20	.3
Octene-2	2	-20	.6
2,2,4-Trimethylpentane	2	-40	.7
2-Ethyl-1-hexene	2	-30	.8
2-Methyl-1-pentene	2	-20	.8
Alkylate	2	-40	.3
Benzene	2	-40	.5
Toluene	1	-40	.4
Mixed xylenes	2(<0.5 mole fraction diluent)	-40	.5
Ethyl benzene	2(<0.4 mole fraction diluent)	-40	.6
Diallylether	2(<0.2 mole fraction diluent)	-40	.7
Methylal	2(<0.3 mole fraction diluent)	-40	.5

TABLE II - IGNITION TESTS WITH SEVERAL ORTHOTOLUIDINE MIXTURES AND NITRIC ACID[a] IN EARLY GERMAN OPEN-CUP APPARATUS (REFERENCE 11)

Fuel diluent	Amount of diluent (percent by volume)	Freezing point (°C)	Ignition delay (millisec)
Methanol	10	<-65	Very short
Methanol	20	<-65	Very short
Methanol	25	<-65	300
Ethanol	10	<-65	Very short
Ethanol	30	<-65	300 - 400
Tetralin	80	<-50	Very short
Tetralin	85	<-50	600 - 700
Solvent benzol[b]	40	<-50	Very short - 300
Solvent benzol	50	<-50	300
Solvent benzol	60	<-50	400
Solvent benzol	70	<-50	500 - 600
Solvent benzol	80	<-50	800 - 900
Cyclohexane	50	-9	700
Cyclohexane	70	-7	(c)
Benzine	30	8[d]	500 - 600
Benzol	25	-15	500 - 800
Gas oil	50	-17[d]	500
Gas oil	60	-16[d]	600

[a] With added catalyst, $FeCl_3 \cdot 6H_2O$ (60 g/liter).

[b] Second cut.

[c] Number of nuclei.

[d] Phase separation.

TABLE III - SUMMARY OF DATA FOR TWO TRIETHYLAMINE MIXTURES AND SEVERAL NITRIC ACID OXIDANTS AT -40° F WITH MODIFIED OPEN-CUP APPARATUS

(REFERENCE 1)

Oxidant composition (percent by weight)				Average ignition delay (millisec)
HNO_3	N_2O	NO_2	Other	
50 percent triethylamine and 50 percent mixed xylidines (by volume at room temperature)				
81.3	1.6	----	17.1[a]	28
70.7	----	----	29.3[a]	48
80.8	3.4	15.8	----	31
78.0	3.0	19.0	----	31
67.6	3.2	29.2	----	31
60.1	5.2	34.7	----	34
97.1	.3	2.6	----	34
97.7	1.8	.5	----	42
93.0	6.8	.2	----	114
91.1	8.7	.2	----	(b)
92.8	1.7	.5	5.0[c]	92
87.9	1.6	.5	10.0[c]	151
85.9	7.7	.4	6.0[d]	(b)
83.9	9.0	----	6.7[e]	(b)
85.0	10.5	----	4.1[e]	(b)
50 percent triethylamine and 50 percent diallylaniline (by volume at room temperature)				
81.3	1.6	----	17.1[a]	27
70.7	----	----	29.3[a]	67
80.8	3.4	15.8	----	28
78.0	3.0	19.0	----	26
60.1	5.2	34.7	----	51
97.1	.3	2.6	----	17
97.7	1.8	.5	----	20
93.0	6.8	.2	----	(b)

[a] H_2SO_4.

[b] No ignition.

[c] NH_4NO_3.

[d] KNO_3.

[e] $HClO_4$.

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TABLE IV - SUMMARY OF DATA FOR SEVERAL TRIETHYLAMINE MIXTURES AND FOUR NITRIC ACID OXIDANTS AT -40° F WITH MODIFIED OPEN-CUP APPARATUS (REFERENCE 1)

Fuel diluent	Amount of diluent (percent by volume at room temperature)	Ignition delay (millisec)			
		Acid A[a]	Acid B[b]	Acid C[c]	Acid D[d]
Aniline	50	33	27	44	102
Aniline	30	38	21	23	380
N-Ethylaniline	50	45	54	(e)	(e)
N-Ethylaniline	30	48	36	105	(e)
N,N-Diethylaniline	50	35	42	33	(e)
N,N-Diethylaniline	30	65	33	94	(e)
N,N-Diallylaniline	50	27	26	(f)	
Orthotoluidine	50	36	27	42	(e)
Orthotoluidine	30	36	24	102	(e)
Mixed xylidines	50	32	31	114	(f)
Mixed xylidines	30	42	31	78	119

[a] 81.3 percent HNO_3, 1.6 percent H_2O, and 17.1 percent H_2SO_4 (by weight).

[b] 78.0 percent HNO_3, 3.0 percent H_2O, and 19.0 percent NO_2 (by weight).

[c] 93.0 percent HNO_3, 6.8 percent H_2O, and 0.2 percent NO_2 (by weight).

[d] 91.1 percent HNO_3, 8.7 percent H_2O, and 0.2 percent NO_2 (by weight).

[e] Sporadic ignition.

[f] No ignition.

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TABLE V - SUMMARY OF DATA FOR SEVERAL TRIETHYLAMINE MIXTURES AND RED FUMING NITRIC ACID CONTAINING 3 PERCENT WATER AND 19 PERCENT NITROGEN DIOXIDE (BY WEIGHT) AT VARIOUS TEMPERATURES WITH MODIFIED OPEN-CUP APPARATUS (REFERENCE 1)

Fuel diluent	Amount of diluent (percent by volume at room temperature)	Ignition delay (millisec)				
		70° F	-40° F	-76° F	-87° F	-105° F
Aniline	30	21	21	37	108	>1000
Orthotoluidine	50	19	24	38	61	210
Mixed xylidines	50	27	31	56		
Mixed xylidines	30	19	31	49	148	(a)
N-Ethylaniline	50	35	54	74		875
N-Ethylaniline	30	26	36	61		664
N,N-Diethylaniline	50	36	42	70		(a)
N,N-Diethylaniline	30	24	33	160		(a)
N,N-Diallylaniline	50	21	26	62	≈1000	(a)

[a] No ignition.

TABLE VI - SUMMARY OF DATA FOR TWO TRIETHYLAMINE MIXTURES WITH SEVERAL NITRIC ACID OXIDANTS AT -40° F WITH SMALL-SCALE ROCKET ENGINE APPARATUS (REFERENCE 2)

Oxidant composition (percent by weight)				Average ignition delay (millisec)
HNO_3	H_2O	NO_2	Other	
50 percent triethylamine and 50 percent mixed xylidines (by volume at room temperature)				
97.3	0.2	2.5	----	35
97.7	1.8	.5	----	42[a]
93.0	6.8	.2	----	423[a]
85.0	10.5	.4	4.1[b]	(c)
43 percent triethylamine and 57 percent diallylaniline (by weight)				
97.3	0.2	2.5	----	14
97.7	1.8	.5	----	17

[a] Ignition followed by explosion.
[b] $HClO_4$.
[c] No ignition.

[redacted]

[redacted]

TABLE VII - SUMMARY OF DATA FOR TWO ORTHOTOLUIDINE-TRIETHYLAMINE MIXTURES AND RED FUMING NITRIC ACID CONTAINING 3.0 PERCENT WATER AND 19 PERCENT NITROGEN DIOXIDE (BY WEIGHT)

[Small-scale rocket engine apparatus]

Run	Average propellant temperature (°F)	Initial pressure altitude (ft)	Initial ambient pressure (mm Hg)	Maximum combustion-chamber pressure (lb/sq in. gage)	Time to attain maximum combustion-chamber pressure (sec)	Temperature (°F)						Lead propellant into combustion chamber	Time between jet entries into combustion chamber (millisec)	Ignition delay (millisec)
						Fuel	Oxidant	Injector head	Constant temperature bath	Nozzle plate	Ambient air			
50 percent orthotoluidine and 50 percent triethylamine (by volume at room temperature)														
175	121	91,000	12.3	298	0.9	121	121	122	125	78	86	Oxidant	2.0	10.3
179	120	0	≈760	(a)	---	120	120	121	121	75	85	Fuel	2.0	[d]12.0
178	81	0	≈760	300	1.6	81	81	85	84	88	89	Fuel	1.2	13.6
168	80	0	≈760	(a)	---	81	80	80	80	85	82	Oxidant	.8	[e]14.3
177	20	0	≈760	299	1.7	21	20	21	18	57	61	Fuel	.6	19.8
169	-40	0	≈760	298	1.5	-40	-41	-38	-41	71	71	Fuel	.6	25.9
180	-40	0	≈760	291	1.6	-40	-40	-37	-39	48	65	Oxidant	1.2	22.8
174	-70	0	≈760	270	1.9	-70	-70	-67	-71	42	42	Oxidant	9.7	30.0
182	-70	0	≈760	(b)	---	-70	---	-67	-68	49	52	Fuel	[c]4	[c]27
170	-95	0	≈760	164	1.7	-95	-95	-93	-96	43	47	Oxidant	7.5	101.4
30 percent orthotoluidine and 70 percent triethylamine (by volume at room temperature)														
184	120	0	≈760	270	1.8	120	120	120	121	76	82	Fuel	0.3	15.3
187	110	0	≈760	(a)	---	110	110	111	112	72	77	Fuel	.4	[f]11.6
183	80	0	≈760	286	1.5	80	80	80	80	68	72	Oxidant	.6	11.9
181	20	0	≈760	299	1.5	20	20	21	20	60	63	Oxidant	5.1	17.2
176	-40	0	≈760	303	1.4	-40	-40	-36	-40	49	55	Oxidant	1.1	26.5
173	-70	0	≈760	266	1.3	-70	-70	-66	-70	55	54	Oxidant	.6	24.7
171	-95	0	≈760	278	2.0	-95	-93	-92	-96	56	52	Oxidant	4.6	27.7
172	-95	89,000	13.5	244	.7	---	-95	-93	-95	52	60	Oxidant	4.6	29.9

[a] Explosion occurred after ignition.
[b] Frozen combustion-chamber pressure tap.
[c] Estimated value; no direct time record.
[d] Time between ignition and explosion, <0.3 millisecond.
[e] Time between ignition and explosion, 0.7 millisecond.
[f] Time between ignition and explosion, 1.5 milliseconds.

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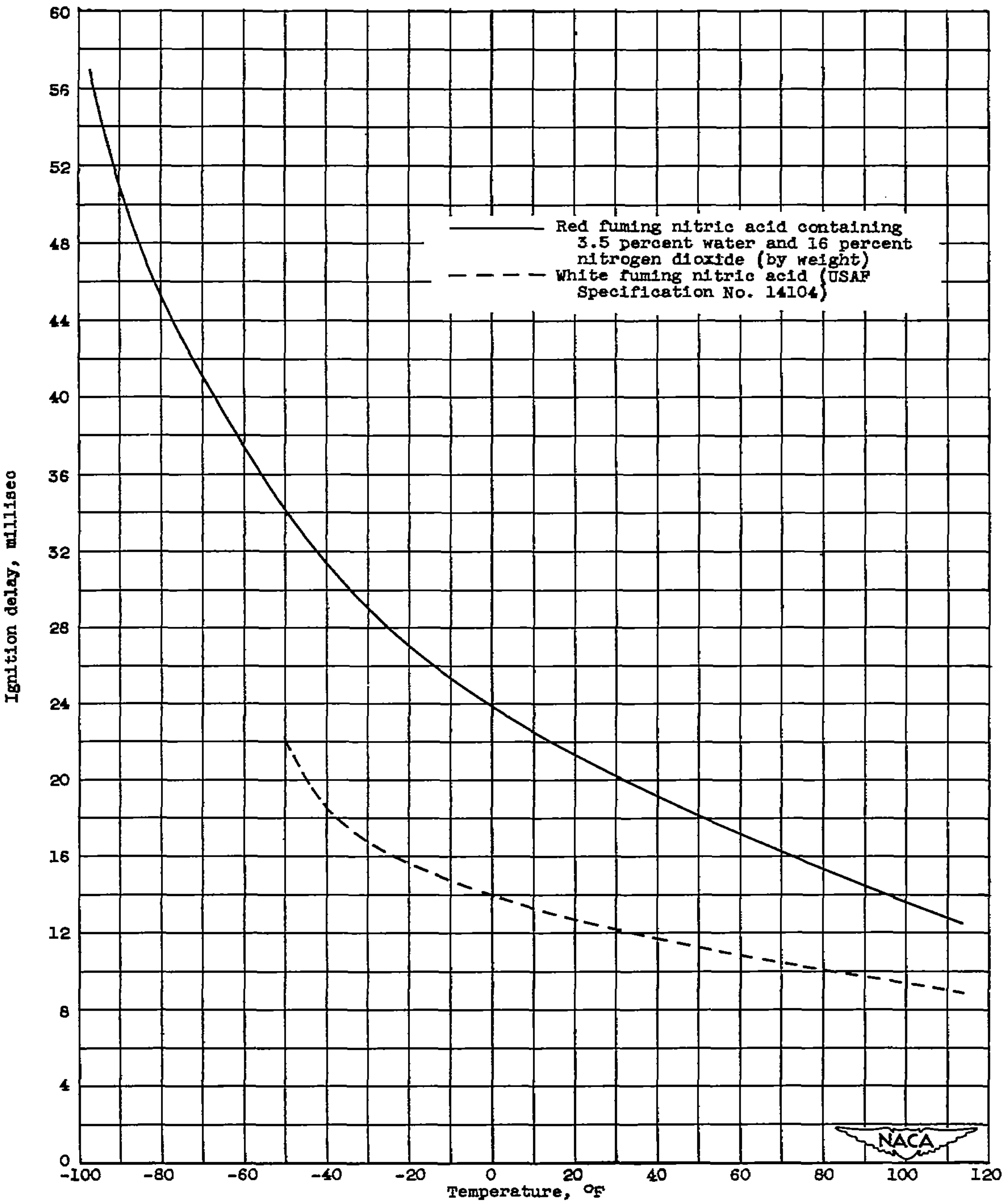

Figure 1. - Ignition delay of 43 percent triethylamine and 57 percent diallylaniline (by weight) and two nitric acid oxidants with small-scale rocket engine apparatus at initial ambient pressures from 760 to 11 millimeters of mercury (reference 2).

[redacted]

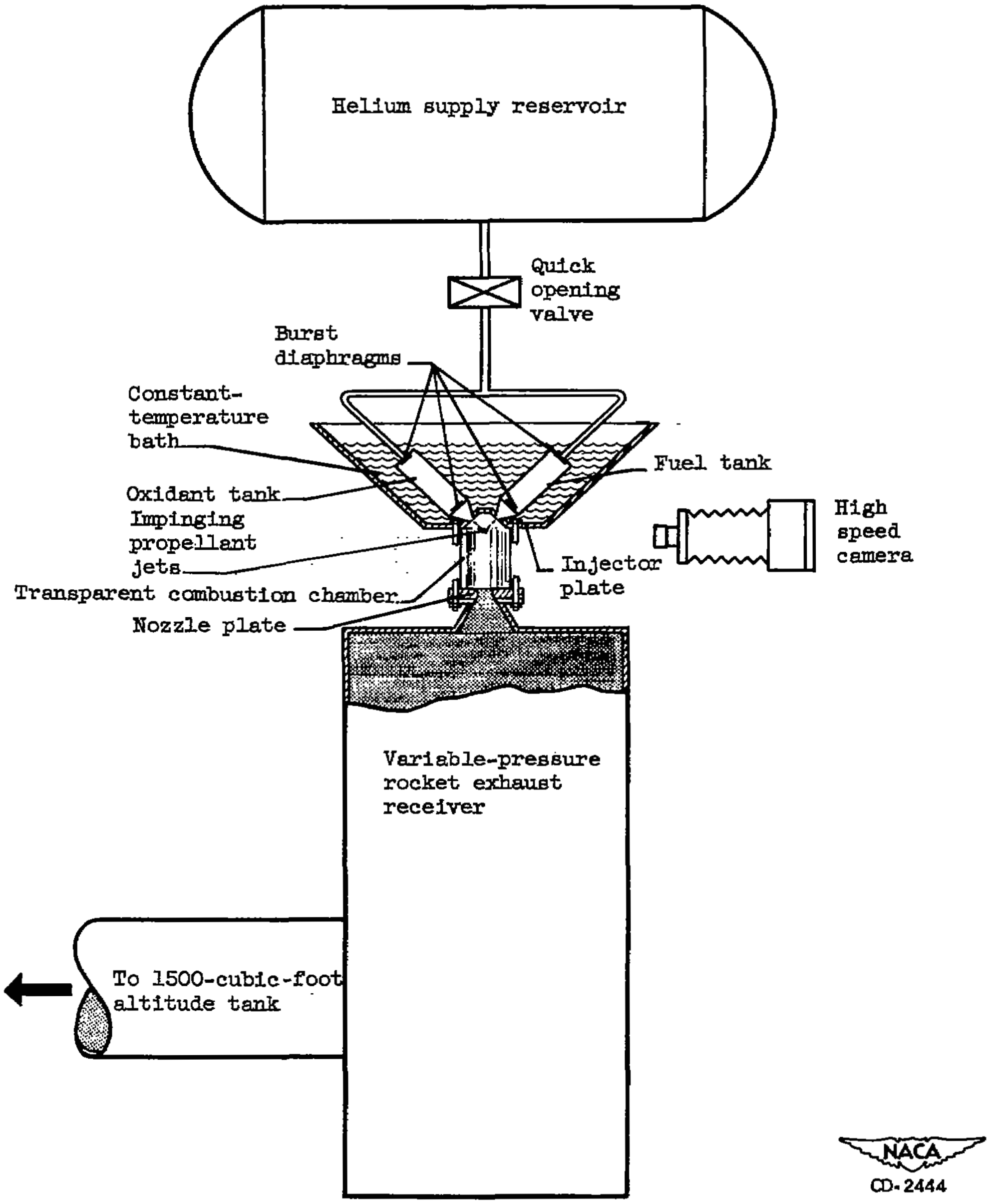

Figure 2. - Diagrammatic sketch of small-scale rocket engine ignition delay apparatus.

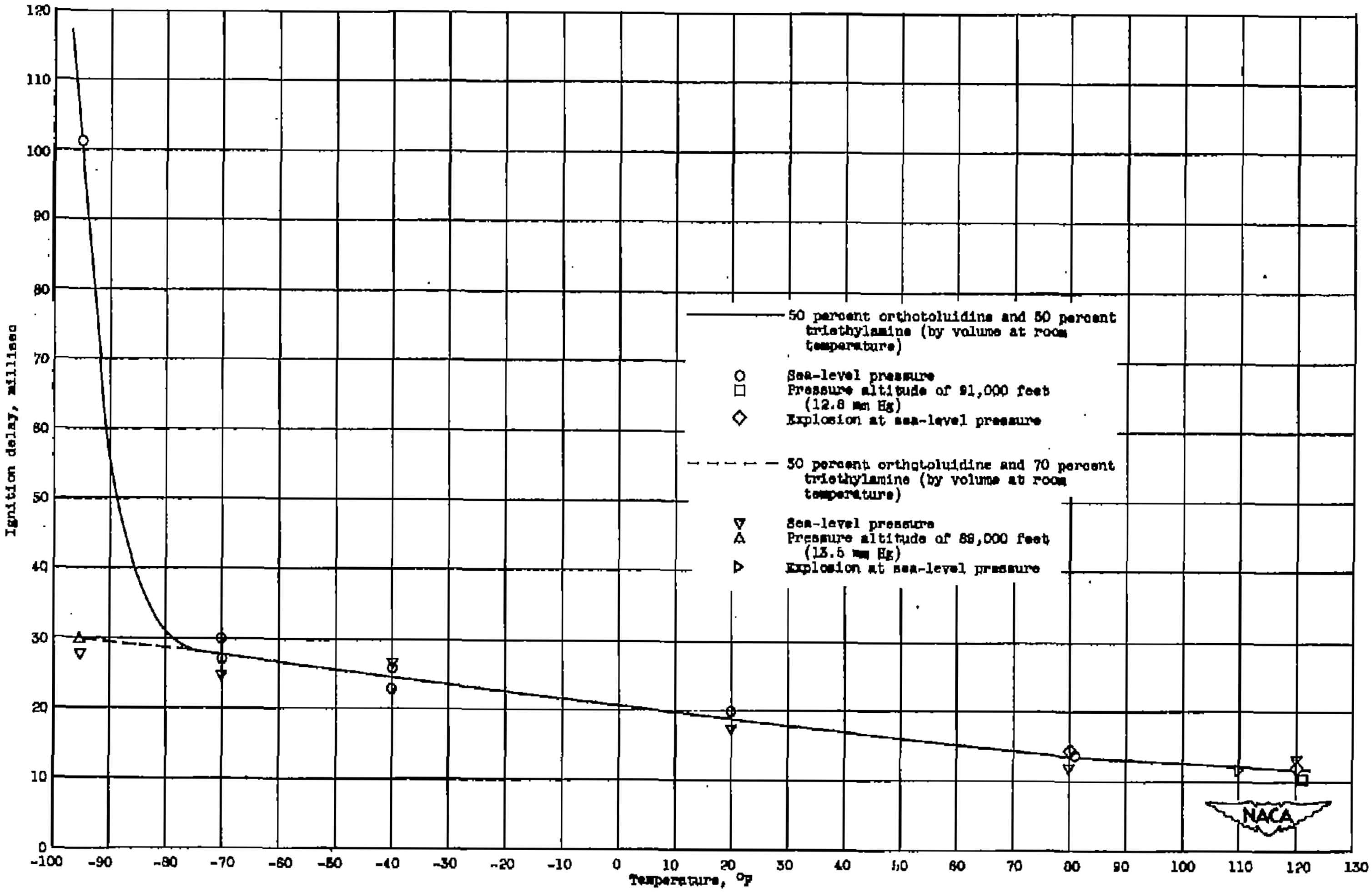

Figure 3. - Ignition delay of two orthotoluidine-triethylamine mixtures and red fuming nitric acid containing 3.0 percent water and 19 percent nitrogen dioxide (by weight)(small-scale rocket engine apparatus).

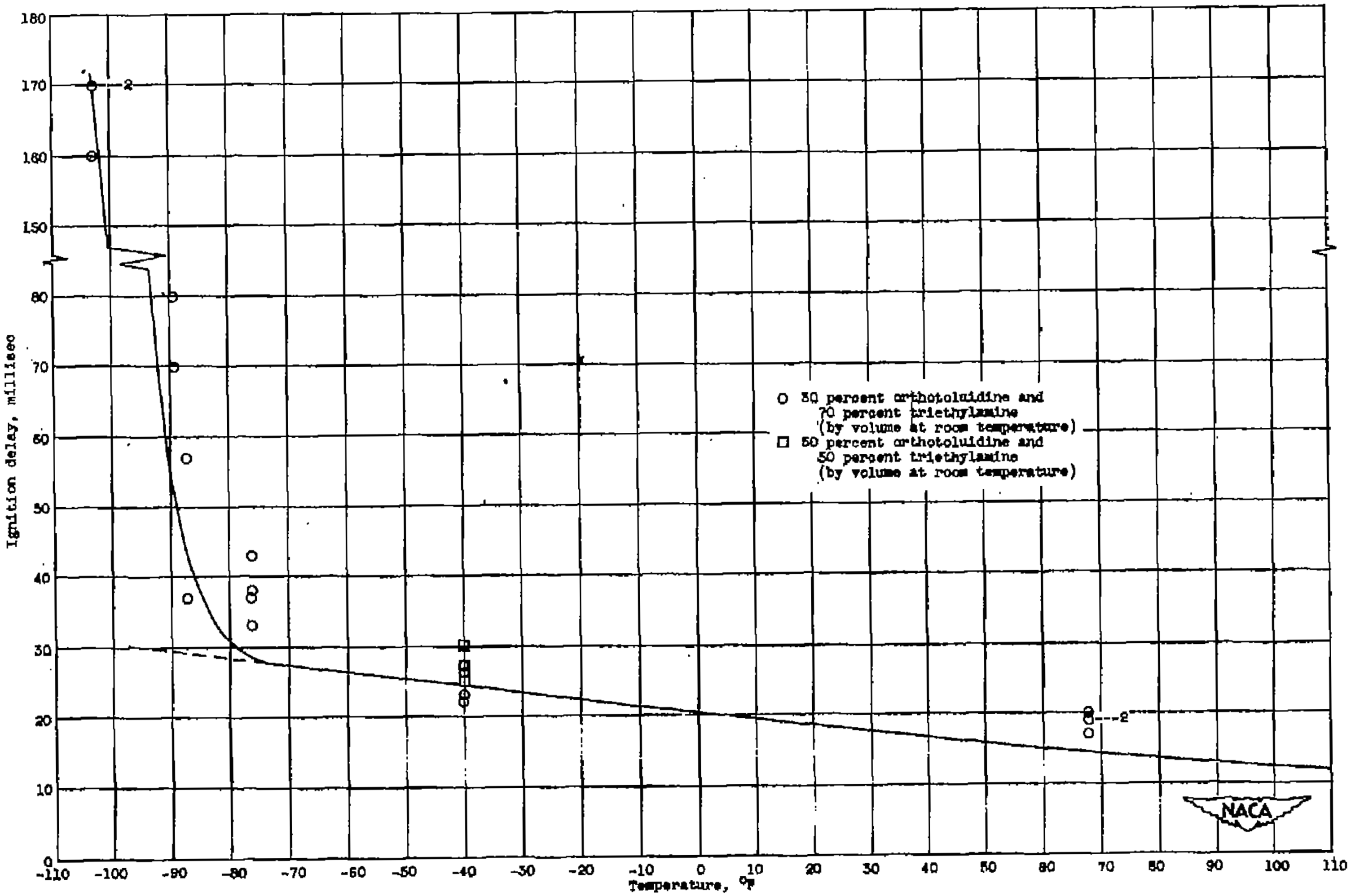

Figure 4. - Ignition delay of two orthotoluidine-triethylamine mixtures and red fuming nitric acid containing 3.0 percent water and 19 percent nitrogen dioxide (by weight) obtained with modified open-cup apparatus at sea-level pressure (reference 1) and superimposed on curves of data obtained with small-scale rocket engine apparatus (see fig. 3).

SECURITY INFORMATION

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