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RESEARCH MEMORANDUM

LOW-TEMPERATURE IGNITION-DELAY CHARACTERISTICS OF
SEVERAL ROCKET FUELS WITH MIXED ACID IN MODIFIED
OPEN-CUP-TYPE APPARATUS

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RESEARCH MEMORANDUM

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LOW-TEMPERATURE IGNITION-DELAY CHARACTERISTICS OF
SEVERAL ROCKET FUELS WITH MIXED ACID IN MODIFIED
OPEN-CUP-TYPE APPARATUS

By Riley O. Miller

SUMMARY

An investigation was conducted to determine possible rocket fuels that ignite spontaneously at low temperatures with mixed acid (nitric plus sulfuric) in a more reliable manner than crude N-ethylaniline (monoethylaniline), a rocket fuel in current use. By means of a bench-scale technique a number of fuels were determined to ignite with mixed acid at subzero temperatures; several of these fuels were investigated over a more extended temperature range.

With mixed acid, the following fuels showed generally shorter and less variable ignition-delay intervals than crude N-ethylaniline (over the temperature range of approximately 80° to -40° F): mixed butyl mercaptans, 70-percent (by volume) furfuryl alcohol plus 30-percent crude N-ethylaniline, 63-percent furfuryl alcohol plus 27-percent crude N-ethylaniline and 10-percent methanol, 70-percent furfuryl alcohol plus 30-percent xylene, 35-percent furfuryl alcohol plus 65-percent crude N-ethylaniline, 90-percent commercial gum turpentine plus 10-percent propylene oxide, pure N-ethylaniline, and commercial gum turpentine. Summaries of self-ignition data for these and other fuels are presented.

INTRODUCTION

Recent experiments in which the rocket propellant, crude N-ethylaniline (monoethylaniline) and mixed acid (nitric plus sulfuric), failed to ignite satisfactorily at low temperature (reference 1) indicate the necessity of a knowledge of the self-ignition properties of certain rocket propellants at low temperatures, as well as at moderate temperatures, inasmuch as rockets may be required to start at high altitudes or under arctic conditions.

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In the evaluation of rocket propellants to determine self-ignitability, optimum economy of materials and safety to personnel make small-scale experimental estimates of ignition characteristics desirable before full-scale experiments are undertaken. Care, however, must be exercised in making estimates of propellant ignitability from data obtained with small-scale ignition-delay apparatus because such factors as mixing and geometry tend to restrict numerical results to the apparatus used. The ignition-delay interval is, in general, an arbitrary quantity defined for a specific apparatus as the time interval between definite starting and ending conditions.

In spite of the geometry and mixing restrictions, previous investigations (reference 2) indicate that not only lengths but also degrees of variation of ignition-delay intervals obtained with small-scale apparatus are significantly characteristic of propellant combinations. Moreover, combinations of propellants that give comparatively short delay intervals and small variations in delay intervals in small-scale ignition-delay experiments also show desirable ignition characteristics in rocket engines.

Various investigations have been conducted in Germany, England, and the United States in which small-scale apparatus was used for the estimation of propellant self-ignition characteristics. The methods employed may be divided into three general classes: (1) open-cup methods in which one propellant is made to fall into or is injected into the other propellant; the ignition-delay interval is determined either by high-speed photography or by electronic equipment (references 2 to 6); (2) a method used in England in which the propellants are impinged as low-velocity jets in a horizontal plane in open air; the ignition-delay interval is calculated from the distance the propellants fall from the point of impingement to the point of ignition; and (3) methods in which the propellants are injected at high velocities into a chamber; the ignition delay is measured by high-speed photography or electronic equipment (references 7 to 9).

The open-cup methods are preferable to the impinging-jet methods for investigations of the comparative self-ignition properties of a number of propellant combinations according to reference 2. Although the open-cup methods tend to give considerable variation in ignition-delay intervals, the data appear to be more independent than data obtained by other methods of arbitrarily selected fuel-oxidant ratios, which may or may not have been optimum for any particular propellant combination (reference 2). Furthermore, the open-cup methods are more convenient to set up and less time-consuming in obtaining experimental results. Although some ignition-delay data from open-cup-type experiments are available for propellants at low temperatures (reference 4), most of the experiments in which these methods were used have been conducted at room temperature.

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An investigation of the self-ignition characteristics at moderate and low temperatures of possible rocket-propellant combinations was conducted at the NACA Lewis laboratory to suggest, for use in rocket engines (reference 1), several available fuels that remain fluid and ignite spontaneously with mixed acids at low temperatures in a more reliable manner than crude N-ethylaniline.

A modified open-cup method was used to obtain ignition-delay data for approximately 60 propellant combinations. Innovations in cooling the propellants and bringing them into contact and in timing the ignition delay provided an apparatus with which the data could be conveniently obtained.

Summaries of the ignition-delay data obtained are presented herein. Both lengths and variations in the ignition-delay intervals (the approximate period of time that elapses between the first contact of fuel and oxidant and the first detectable appearance of flame) have been considered in making estimates of the comparative ignitability of the fuels with mixed acids.

APPARATUS

The function of the apparatus was (1) to bring the fuel and the oxidant to a selected temperature (80° to -50° F), (2) to bring the fuel and the oxidant into mutual contact at this temperature, and (3) to measure the time interval between the start of this contact and the first appearance of detectable flame. The apparatus (fig. 1) consisted of a temperature control system, a firing mechanism, and a means for measuring ignition-delay intervals.

Temperature-control system. - The temperature-control system (fig. 1) consisted of a clear glass Dewar cylinder ($2\frac{3}{4}$ in. I. D.), a coolant pump, a dry-ice bath and heat exchanger, and the required piping and valves. At the beginning of the experiments, the temperature inside the Dewar cylinder was controlled by two manually operated needle valves but later the temperature was automatically controlled by an electric solenoid valve and an adjustable temperature-actuated switch. The Dewar cylinder contained a thermometer for indicating coolant temperature.

Firing mechanism. - The firing mechanism used is shown in figure 1. A 1- by 8-inch pyrex ignition-type test tube containing a glass ampule about $9/16$ inch in diameter was held partly submerged in the coolant in the Dewar cylinder. A stainless-steel rod when hit by a weight that fell 6 inches crushed the ampule, releasing the fuel under the surface

of the acid oxidant. A simple trigger pin was used to support the dropable weight (approximately 0.4 lb) in a guide tube before firing. The microswitch, which was mounted on the firing mechanism, actuated the timing apparatus when the weight hit the rod.

Ignition-delay measurement. - The instrumentation by which the ignition-delay data were obtained included a photoelectric pickup unit, an electronic-relay-amplifier unit, an oscillator, and an electronic counter. The circuit was so designed that the counter would register the total number of cycles from the oscillator (1000 or 10,000 cps) between the instant the weight hit the rod and microswitch and the instant a flash of light, sufficiently bright to affect the photoelectric pickup, appeared in the test tube.

A high-speed motion-picture camera capable of speeds up to 3000 frames per second was used to photograph and time the action of several firings. The camera was modified to permit the recording of timing marks on the edge of the film as it was exposed. This modification consisted of a small argon bulb inside the camera, connected to the output of a calibrated oscillator. Another argon bulb connected to a battery in series with the microswitch on the firing mechanism was photographed to indicate the instant the microswitch was tripped.

FUELS

Some of the fuels investigated were used as supplied, others were blends or mixtures.

Crude N-ethylaniline. - Crude N-ethylaniline (monoethylaniline) and mixtures of crude N-ethylaniline with furfuryl alcohol, 2,5-dimethylfuran, hydroxy benzenes, amines, or various other additives were investigated. The crude N-ethylaniline was a commercial product obtained from the Bureau of Aeronautics, Department of the Navy. The following analysis is the average of several samples of crude N-ethylaniline:

| | Percent by weight |
|---|----------------------|
| Aniline C ₆ H ₅ ·NH ₂ | 25.4 |
| N-Ethyylaniline C ₆ H ₅ ·NH·C ₂ H ₅ | 60.6 |
| N,N-Diethylaniline C ₆ H ₅ N(C ₂ H ₅) ₂ | 12.0 |
| Water H ₂ O | .25 |
| Difference | 1.75 |

Ignition characteristics of pure N-ethylaniline, pure N,N-diethylaniline (constituents of crude N-ethylaniline), and several pure N-ethylaniline - additive mixtures were also investigated.

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Furfuryl alcohol - xylene blends. - Because of the low viscosity and the availability of xylene, blends of xylene and furfuryl alcohol were investigated.

Commercial gum turpentine. - Ignition properties of commercial gum turpentine and mixtures of turpentine, respectively, with propylene oxide and other additives were investigated. A constituent of turpentine, α -pinene, was also investigated.

Mixed butyl mercaptans. - Because they are readily available from petroleum, mixed butyl mercaptans were investigated. The composition (reference 6) was approximately:

| Mercaptan | Percent by volume |
|--|----------------------|
| Isopropyl $(CH_3)_2CH \cdot SH$ | 1 |
| n-Propyl $CH_3 \cdot CH_2 \cdot CH_2 \cdot SH$ (and <u>tert</u> -butyl $(CH_3)_3C \cdot SH$) | 23 |
| sec-Butyl $CH_3(C_2H_5)CH \cdot SH$ | 37 |
| Isobutyl $(CH_3)_2CH \cdot CH_2 \cdot SH$ | 7 |
| n-Butyl $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot SH$ | 11 |
| Amyl $C_5H_{11}SH$ | 21 |

OXIDANTS

For most of this investigation, a mixed acid, which was used as an oxidant, was prepared from reagent-grade 95-percent white fuming nitric acid and chemically pure oleum (70-percent H_2SO_4 plus 30-percent SO_3). The composition of the acid approached the specifications of the commercial mixed acid used in rocket engines. This laboratory-prepared acid was used because it apparently was more desirable as a reference oxidant than commercial acid, inasmuch as commercial acids may more likely contain variable amounts of trace impurities that might act as catalysts or inhibitors. For more accurate comparison with rocket experiments (reference 1), commercial mixed acid was used for some of the firings with crude N-ethylaniline and with 70-percent furfuryl alcohol plus 30-percent crude N-ethylaniline and for all the firings with mixed butyl mercaptans.

The following are the average analyses of the mixed acids:

| Mixed acid | Percent by weight | |
|--|---------------------|------------|
| | Laboratory prepared | Commercial |
| Nitric acid HNO_3 and nitrous acid HNO_2 (as HNO_3) | 80.0 | 79.4 |
| Sulfuric acid, H_2SO_4 | 15.3 | 16.7 |
| Nonacidic components ^a (by difference) | 4.7 | 3.9 |

^aThe nonacidic components were presumed to be mostly water.

PROCEDURE

The tip of an ampule, in which 1 milliliter of the desired fuel had been sealed, was inserted into the drilled end of the smashing rod; and a test tube was slipped over the ampule and clamped in the firing mechanism. The test tube was partly submerged in the coolant in the Dewar cylinder and the trigger pin and the weight were set in place, as shown by figure 1. The acid (3 ml) was then transferred to the test tube by means of a remotely operated syringe. The acid and fuel were allowed to cool for about 15 minutes. (A mock-up of the apparatus with a thermocouple in an ampule of crude N-ethylaniline submerged in mixed acid in a test tube showed that the fuel reached equilibrium temperature at -40° F from room temperature within 10 min.) After the cooling period, the trigger pin was pulled out of the guide tube by means of a string, letting the weight fall on the rod and the microswitch actuator, breaking the ampule, and starting the timing sequence. The temperature of the coolant in the Dewar cylinder prior to the firing and the ignition-delay interval after the firing were recorded. After each firing, the apparatus was washed with water and with acetone.

EVALUATION OF METHOD

Lag in apparatus. - The method used was checked by high-speed motion pictures. Several films were taken of the test tube with an illuminated background to show the action of the propellants in the apparatus during the firing sequence. Other films were taken with no external illumination and with the instruments in operation in order to check the rate of response of the timing circuit. Most of the films were taken at approximately 1000 or 2000 frames per second. In order to obtain the best possible definition, these pictures of the apparatus were taken without the coolant bath; therefore, the propellants were at room temperature.

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The short interval during which the apparatus brought the propellants into contact is shown by the positive enlargements from high-speed motion-picture films (fig. 2), which are silhouette photographs of the apparatus taken during the first 0.003 second of the timed sequence. Two inert immiscible liquids taken at approximately 0.001-second intervals are photographed in figure 2(a). The viscosities of the liquids in the ampule and in the test tube were 80 and 6 centistokes, respectively, thus the viscosities of crude N-ethylaniline and mixed acid at low temperatures were approximately simulated. The action of 70-percent furfuryl alcohol plus 30-percent crude N-ethylaniline and commercial mixed acid, a combination that produced short ignition-delay intervals, is presented in figure 2(b). Figure 2(c) shows crude N-ethylaniline and commercial mixed acid, a combination that gave longer ignition-delay intervals. The first vertical column of photographs shows the apparatus just before the microswitch had been tripped by the weight. The second column shows the apparatus approximately 0.001 second later; the microswitch was tripped in each case. The next two columns show the apparatus 0.002 and 0.003 second, respectively, after the first photographs were taken. As shown by these photographs, the liquids were in contact with each other within 0.002 second after the microswitch was tripped; in the case of 70-percent furfuryl alcohol plus 30-percent N-ethylaniline, a preliminary nonburning reaction was already under way.

Other high-speed motion pictures taken with no external illumination showed that ignition often started with a series of intermittent flashes, which evidently caused scatter in the data obtained. The intensity and the length of flashes apparently increased during the early part of the ignition process and the measured ignition-delay interval was the interval between the tripping of the microswitch and a flash of sufficient intensity to affect the photocell and stop the timing circuit. A well-defined correlation of the instrument response with high-speed motion pictures was complicated by the frequent starting of ignition with this series of flashes. On four records, however, a flash on the film preceded the times recorded by the electronic timer by not more than 0.003 second. In each case the photocell apparently responded to either the first or second flash registered on the film. Photographic evidence thus indicates that the combined lag in the ampule breaking, the propellants contacting each other, and the instruments responding to a flash may be 0.002 to 0.005 second. The ignition-delay intervals reported herein are the uncorrected values read from the electronic counter.

Variations in ignition-delay data. - The data obtained from these experiments substantiate the hypothesis (reference 2) that degrees of variation as well as lengths of time lag in ignition-delay data may be functions of propellant combinations. Examples of these tendencies are

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illustrated by figure 3, where ignition-delay intervals of crude N-ethylaniline and a fresh solution of 70-percent furfuryl alcohol plus 30-percent crude N-ethylaniline with laboratory-prepared mixed acid are shown plotted as functions of temperature. The sporadic and variable nature of ignition-delay data from crude N-ethylaniline is illustrated by frequent instances of no ignition at subzero temperatures and by a maximum deviation from the faired curve of about 0.4 second, which occurred in the low temperature region. The ignition-delay data of the furfuryl alcohol plus crude N-ethylaniline blend were much less scattered with a maximum deviation of about 0.03 second from the faired curve. Comparisons of these and other propellant combinations indicate that the scatter of results was more a function of the propellant combination than of the ignition-delay timing instrumentation.

As a consequence of the tendency for ignition of certain propellant combinations to occur over a range of time, a large number of firings of each propellant combination at various temperatures would be required to eliminate all elements of uncertainty in comparing one combination with another. Because expediency required that a number of possible propellants be considered in a short time, a high degree of certainty was sacrificed in obtaining some of the data. The results, nevertheless, provide a choice from which propellant combinations may be selected for further research.

RESULTS AND DISCUSSION

Summaries of the ignition-delay data are so presented in tables I and II that estimates of the ignitability of the various propellant combinations may be made. For each propellant combination the maximum and minimum ignition-delay intervals at one or more temperatures are presented in order to indicate approximately a range in time over which ignition may be expected. As a further aid to such estimates, the geometric average of the ignition-delay intervals at each of these temperatures is presented and the number of firings is indicated. Geometric averages were used inasmuch as in some cases the ignition-delay intervals varied with temperature in an approximately exponential manner. The spreads in temperature over which the groups of data are averaged are small (less than 10° F total spread for 90 percent of the data). Approximate kinematic viscosities at -40° F and specific gravities of some of the fuels are given in table III.

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Comparison of propellants. - Several firings were made with crude N-ethylaniline and the laboratory-prepared acid at subzero and moderate temperatures in order to establish the behavior of a fuel known to have poor ignition characteristics at low temperatures in a rocket engine (reference 1). Ignition characteristics of a number of other fuels and fuel mixtures were investigated by two or more firings at approximately -40° F. Some of these fuels were selected because of (1) apparent ignitability at subzero temperatures, (2) probable commercial availability, and (3) fluidity (low viscosity) at subzero temperature; the selected fuels were then investigated more extensively over a temperature range of approximately 80° to -40° F.

With the laboratory-prepared mixed acid the following fuels (in estimated order of decreasing ignitability) investigated over the temperature range of approximately 80° to -40° F tended to ignite more readily than crude N-ethylaniline (composition is given in percent by volume):

70-percent furfuryl alcohol plus 30-percent crude N-ethylaniline
63-percent furfuryl alcohol plus 27-percent crude N-ethylaniline
and 10-percent methanol
70-percent furfuryl alcohol plus 30-percent xylene
35-percent furfuryl alcohol plus 65-percent crude N-ethylaniline
90-percent commercial gum turpentine plus 10-percent propylene
oxide
Pure N-ethylaniline
Commercial gum turpentine

In a limited number of experiments at low temperature (approximately -40° F) the following fuels also showed shorter average ignition-delay intervals than crude N-ethylaniline (composition is given in percent by volume unless otherwise noted):

Furfuryl alcohol
95-percent commercial gum turpentine plus 5-percent propylene
oxide
50-percent crude N-ethylaniline plus 50-percent 2,5-dimethylfuran
70-percent crude N-ethylaniline plus 30-percent 2,5-dimethylfuran
70-percent turpentine plus 30-percent propylene oxide
95-percent crude N-ethylaniline plus 5-percent pyrogallol (by
weight)
80-percent turpentine plus 20-percent vinyl isobutyl ether
85-percent crude N-ethylaniline plus 15-percent furfuryl alcohol
Turpentine saturated with p-phenylenediamine
95-percent pure N-ethylaniline plus 5-percent pyrogallol (by
weight)

95-percent pure N-ethylaniline plus 5-percent di-tert-butyl peroxide (by weight)
35-percent furfuryl alcohol plus 65-percent xylene

The following fuels, investigated with commercial mixed acid, (table II) ignited more readily than crude N-ethylaniline with commercial acid at both room and subzero temperatures:

Mixed butyl mercaptans

70-percent furfuryl alcohol plus 30-percent crude N-ethylaniline

As shown by tables I and II, crude N-ethylaniline ignited in a more reliable manner with commercial mixed acid than with the laboratory-prepared mixed acid. With commercial mixed acid (table II) mixed butyl mercaptans and 70-percent furfuryl alcohol plus 30-percent N-ethylaniline showed tendencies toward shorter ignition-delay intervals at subzero temperatures than at room temperatures. Differences in the behavior of crude N-ethylaniline and 70-percent furfuryl alcohol plus 30-percent crude N-ethylaniline with commercial mixed acid and the laboratory-prepared mixed acid, respectively, indicate that significant effects on ignition-delay characteristics may be produced by small differences in the composition of the acids.

Although tendencies for ignition-delay intervals of propellant combinations to decrease with decreasing temperature (table II) are unusual, such trends for 70-percent vinyl-ethyl ethers plus 30-percent aniline and 85-percent vinyl ethyl ethers plus 15-percent aniline, respectively, with nitric acid have been reported in generally unavailable German literature. Data of reference 10 show that the reaction rate of gaseous propane and oxygen at low pressure increased with decreasing temperature within a definite temperature range; suppression of chain reactions at high temperatures may be a possible explanation. In the case of certain rocket propellants, however, a preliminary gaseous evolution (fig. 2(b)) possibly accentuated at higher temperatures may disperse or expel a portion of the propellants from the reaction vessel before they are completely in contact, thereby creating conditions that may increase the ignition-delay intervals as they are measured.

Viscosities. - The data presented indicate that a number of possible rocket fuels exist that at temperatures as low as -40° F not only appear to ignite more reliably with mixed acids than crude N-ethylaniline (tables I and III), but also (as indicated by the kinematic-viscosity data of table III) are more fluid. Examples of such fuels are mixed butyl mercaptans, commercial gum turpentine, pure N-ethylaniline, and 70-percent furfuryl alcohol plus 30-percent xylene. Blends of 30- and

50-percent 2,5-dimethylfuran in crude N-ethylaniline and 35-percent furfuryl alcohol in xylene also showed relatively low viscosities at low temperature.

Applications. - Rocket-engine starting experiments (reference 1) qualitatively substantiate some of the results presented. The sporadic behavior of crude N-ethylaniline with mixed acid at low temperatures, as observed from the ignition-delay experiments, was also apparent in reference 1. The short ignition delays, as determined by these experiments for mixed butyl mercaptans, 70-percent furfuryl alcohol plus 30-percent crude N-ethylaniline, and commercial gum turpentine with mixed acid as oxidant, were confirmed by the rocket starting experiments wherein all these fuels gave satisfactory starting at low pressures and temperatures.

SUMMARY OF RESULTS

The ignition-delay intervals of a number of possible rocket fuels with mixed acid (nitric plus sulfuric) at subzero temperatures were experimentally investigated. Several fuels, which appeared to ignite more satisfactorily than crude N-ethylaniline (monoethylaniline) at temperatures approximately -40° F, were investigated at various other temperatures over the extended range of approximately 80° to -40° F. The following trends were observed:

1. With a laboratory-mixed acid the following fuels, investigated over the temperature range of approximately 80° to -40° F, tended to ignite more satisfactorily than crude N-ethylaniline (fuels listed in estimated order of decreasing ignitability):

70-percent furfuryl alcohol plus 30-percent crude N-ethylaniline
63-percent furfuryl alcohol plus 27-percent crude N-ethylaniline
and 10-percent methanol
70-percent furfuryl alcohol plus 30-percent xylene
35-percent furfuryl alcohol plus 65-percent crude N-ethylaniline
90-percent commercial gum turpentine plus 10-percent propylene
oxide
Pure N-ethylaniline
Commercial gum turpentine

2. Of the fuels investigated with commercial mixed acid, mixed butyl mercaptans and 70-percent furfuryl alcohol plus 30-percent crude N-ethylaniline produced shorter average-ignition-delay intervals at both room and subzero temperatures than did crude N-ethylaniline.

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REFERENCES

1. Ladanyi, Dezso J., Sloop, John L., Humphrey, Jack C., and Morrell, Gerald: Starting of Rocket Engine at Conditions of Simulated Altitude Using Crude Monoethylaniline and Other Fuels with Mixed Acid. NACA RM E50D20, 1950.
2. Noeggerath, Wolfgang: Summary of German Methods for Testing Hypergolic Rocket Propellants. Tech. Rep. F-TR-1130-ND, ATI (Wright-Patterson Field), Oct. 1946. (Available from CADO as ATI 2385.)
3. Kaplan, Nathan: Investigation of New Liquid Fuels for Jet Propulsion. Prog. Rep. No. 10, GALCIT Proj. No. 1, Air Corps Jet Prop. Res., GALCIT, Nov. 16, 1943. (Available from CADO as ATI 31217.)
4. Clarke, Fredric B., and Sappington, Merrill H.: Study of the Ignition Lag of Spontaneous Rocket Propellants. Memo No. 9-3, Jet Prop. Lab., C.I.T., June 15, 1947. (Proj. TU2-1, Contract No. W-04-200-ORD-1482.) (Available from CADO as ATI 40175.)
5. Warner, B. F.: Studies in Self-igniting Liquid Propellants. Part I. The Measurement of Ignition Delays by the Falling Drop Method. Part II. Ignition Delays of Propellants Based on Nitric Acid-aniline. Rep. No. 201/R/47, Chem. Res. & Development Dept., British M.O.S., Nov. 1946.
6. Condit, P. C.: Liquid Rocket Fuels. Final Rep., 1948-1949, on Navy Contract NOa(s) 9947, Calif. Res. Corp. (Standard Oil Co. Calif.), Oct. 31, 1949. (Available from Bur. Aero.)
7. Kavanagh, G. M., Leffler, J. E., and St. John, R. C.: Self-Igniting Fuels for Use with Hydrogen Peroxides. Rep. No. 8, Div. Ind. Cooperation, M.I.T., July 1, 1946. (Bur. Ord. Contract No. NOrd-9107, Task C.)

CONFIDENTIAL

- ~~CONFIDENTIAL~~
8. Aleck, B. J., Forbes, J., Healy, R., Meerbaum, S., and Rappolt,
J. P.: Rep. SPD 126, The M. W. Kellogg Co., Oct. 1, 1947. (Bi-
Monthly Rep. No. 1, Contract W-33-038-ac-13916, Suppl. No. 2.)
(Available from CADO as ATI 13685.)
9. Anon.: Combined Bimonthly Summary No. 7 - July 20, 1948 to Aug. 20,
1948. Jet Prop. Lab., C.I.T., Sept. 15, 1948.
10. Pease, Robert N.: The Negative Temperature Coefficient in the Rate
of Propane Oxidation. Jour. Am. Chem. Soc., vol. 60, no. 9,
Sept. 7, 1938, pp. 2244-2246.
11. Anon.: Handbook of Chemistry and Physics, Charles D. Hodgman, ed.
Chem. Rubber Pub. Co. (Cleveland), 28th ed., 1944.
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TABLE I - SUMMARY OF IGNITION-DELAY DATA OF SEVERAL FUELS WITH LABORATORY-PREPARED MILLED ACID AT VARIOUS TEMPERATURES

| Fuel (percent by volume) | Number of firings | Average temp- erature (°F) | Ignition-delay interval (sec) | | | NACA |
|--|-------------------------|-------------------------------------|----------------------------------|----------------------|----------------------|--|
| | | | Minimum | Maximum | Geometric average | |
| Crude N-ethylaniline (monoethyl-aniline) | 3 | -45 | 300×10^{-3} | 839×10^{-3} | 500×10^{-3} | No ignition, 9 trials between -10 and -50° F |
| | 4 | -37 | 62 | 732 | 238 | |
| | 5 | -29 | 89 | 258 | 132 | |
| | 2 | -7 | 239 | 265 | 252 | |
| | 2 | 22 | 61 | 231 | 119 | |
| | 6 | 79 | 50 | 340 | 144 | |
| Crude N-ethylaniline dried over potassium hydroxide | 2 | -35 | 346 | 584 | 450 | |
| Crude N-ethylaniline, batch distilled | 2 | -36 | ----- | ----- | ----- | No ignition |
| Crude N-ethylaniline, batch distilled and dried over potassium hydroxide | 2 | -36 | ----- | ----- | ----- | No ignition |
| 85-percent crude N-ethylaniline plus 15-percent furfuryl alcohol | 4 | -38 | 18 | 298 | 90 | |
| 85-percent crude N-ethylaniline plus 35-percent furfuryl alcohol | 2 | -42 | 56 | 93 | 72 | |
| | 3 | -26 | 57 | 48 | 41 | |
| | 2 | 31 | 41 | 43 | 42 | |
| | 2 | 73 | 33 | 47 | 39 | |
| 30-percent crude N-ethylaniline plus 70-percent furfuryl alcohol (fresh solution) | 3 | -49 | 85 | 106 | 97 | |
| | 5 | -41 | 18 | 86 | 43 | |
| | 3 | -32 | 21 | 46 | 28 | |
| | 2 | -6 | 15 | 22 | 17 | |
| | 4 | 15 | 19 | 51 | 26 | |
| | 5 | 79 | 16 | 43 | 23 | |
| (6 and 10 days after mixing) | 8 | -36 | 38 | 109 | 56 | |
| 27-percent crude N-ethylaniline plus 63-percent furfuryl alcohol and 10-percent methanol | 5 | -41 | 20 | 80 | 47 | |
| | 3 | -24 | 21 | 40 | 27 | |
| | 3 | 31 | 16 | 31 | 24 | |
| | 2 | 81 | 14 | 26 | 19 | |
| 90-percent crude N-ethylaniline plus 10-percent 2,5-dimethylfuran | 4 | -40 | ----- | ----- | ----- | Sporadic ignition |
| 70-percent crude N-ethylaniline plus 30-percent 2,5-dimethylfuran | 2 | -36 | 55 | 81 | 67 | |
| 50-percent crude N-ethylaniline plus 50-percent 2,5-dimethylfuran | 3 | -41 | 54 | 91 | 67 | |
| 30-percent crude N-ethylaniline plus 70-percent 2,5-dimethylfuran | 2 | -42 | ----- | ----- | ----- | Flameless explosions |

| | | | | | | NACA |
|---|---|-----|---------------------|----------------------|---------------------|-------------------|
| 95-percent crude N-ethylaniline plus 5-percent pyrogallol (by weight) | 3 | -36 | 52×10^{-5} | 155×10^{-5} | 80×10^{-5} | |
| 90-percent crude N-ethylaniline plus 10-percent pyrogallol (by weight) | 3 | -38 | 271 | 492 | 334 | |
| 90-percent crude N-ethylaniline plus 10-percent catechol (by weight) | 3 | -36 | 174 | 235 | 215 | |
| 95-percent crude N-ethylaniline plus 5-percent resorcinol (by weight) | 2 | -35 | ----- | ----- | ----- | Sporadic ignition |
| 98-percent crude N-ethylaniline plus 2-percent 2,4,6-trinitroresorcinol (by weight) | 2 | -42 | ----- | ----- | ----- | No ignition |
| Crude N-ethylaniline saturated with p -phenylenediamine | 4 | -42 | ----- | ----- | ----- | Sporadic ignition |
| 90-percent crude N-ethylaniline plus 10-percent ethanolamine (by weight) | 2 | -40 | ----- | ----- | ----- | Sporadic ignition |
| 90-percent crude N-ethylaniline plus 10-percent 2-amino-2-methyl- 1-propanol (by weight) | 2 | -42 | ----- | ----- | ----- | Sporadic ignition |
| 90-percent crude N-ethylaniline plus 10-percent pyridine (by weight) | 2 | -42 | ----- | ----- | ----- | Sporadic ignition |
| 95-percent crude N-ethylaniline plus 5-percent morpholine (by weight) | 2 | -40 | ----- | ----- | ----- | Sporadic ignition |
| 95-percent crude N-ethylaniline plus 5-percent methylal (by weight) | 2 | -40 | ----- | ----- | ----- | Sporadic ignition |
| 95-percent crude N-ethylaniline plus 5-percent di- <i>tert</i> butyl peroxide (by weight) | 2 | -31 | ----- | ----- | ----- | No ignition |
| 95-percent crude N-ethylaniline plus 5-percent azoxybenzene (by weight) | 3 | -36 | ----- | ----- | ----- | No ignition |
| 90-percent crude N-ethylaniline plus 10-percent propylene oxide (by weight) | 2 | -38 | ----- | ----- | ----- | No ignition |

TABLE I - CONCLUDED. SUMMARY OF IGNITION-DELAY DATA OF SEVERAL FUELS WITH LABORATORY-PREPARED MIXED ACID AT VARIOUS TEMPERATURES

| Fuel (percent by volume) | Number of firings | Average temp- erature (°F) | Ignition-delay interval (sec) | | | NACA Remarks |
|---|-------------------------|-------------------------------------|----------------------------------|----------------------|----------------------|----------------------|
| | | | Minimum | Maximum | Geometric average | |
| 95-percent crude N-ethylaniline plus 5-percent picric acid (by weight) | 2 | -38 | ----- | ----- | ----- | Sporadic ignition |
| 98-percent crude N-ethylaniline plus 2-percent aluminum ethoxide (by weight) | 2 | -36 | ----- | ----- | ----- | Sporadic ignition |
| 50-percent crude N-ethylaniline plus 70-percent turpentine | 2 | -36 | ----- | ----- | ----- | Flameless explosions |
| Pure N-ethylaniline | 8 | -40 | 64×10^{-3} | 128×10^{-3} | 83×10^{-3} | |
| | 4 | -4 | 43 | 68 | 54 | |
| | 6 | 34 | 39 | 78 | 60 | |
| | 3 | 73 | 34 | 63 | 50 | |
| 95-percent pure N-ethylaniline plus 5-percent pyrogallol (by weight) | 5 | -38 | 54 | 178 | 96 | |
| 95-percent pure N-ethylaniline plus 5-percent resorcinol (by weight) | 3 | -32 | 98 | 209 | 145 | |
| 95-percent pure N-ethylaniline plus 5-percent di- <u>tert</u> -butyl peroxide (by weight) | 2 | -37 | 62 | 148 | 96 | |
| Pure N,N-diethylaniline | 2 | -36 | 153 | 175 | 164 | |
| Furfuryl alcohol | 2 | -35 | 35×10^{-3} | 56×10^{-3} | 44×10^{-3} | |
| 70-percent furfuryl alcohol plus 30-percent xylene | 7 | -40 | 9 | 100 | 31 | |
| | 5 | -2 | 26 | 188 | 48 | |
| | 2 | 25 | 26 | 43 | 33 | |
| | 2 | 74 | 39 | 52 | 45 | |
| 35-percent furfuryl alcohol plus 65-percent xylene | 3 | -32 | 92 | 111 | 101 | |
| Xylene | 2 | -36 | ----- | ----- | ----- | No ignition |
| | 2 | 75 | ----- | ----- | ----- | No ignition |

| | | | | | | |
|---|---|-----|---------------------|---------------------|---------------------|---|
| Commercial gum turpentine | 2 | -56 | ----- | ----- | ----- | Flameless explosions |
| | 3 | -39 | 62×10^{-3} | 99×10^{-3} | 77×10^{-3} | |
| | 2 | -3 | 78 | 85 | 81 | |
| | 3 | 24 | 54 | 191 | 87 | |
| | 4 | 73 | 29 | 69 | 44 | |
| 98-percent turpentine plus 2-percent propylene oxide | 3 | -58 | ----- | ----- | ----- | Sporadic ignition and flameless explosions |
| 85-percent turpentine plus 5-percent propylene oxide | 2 | -35 | 53 | 62 | 57 | |
| 90-percent turpentine plus 10-percent propylene oxide | 4 | -40 | 47 | 81 | 63 | |
| | 2 | -7 | 49 | 57 | 53 | |
| | 3 | 74 | 40 | 64 | 54 | |
| 70-percent turpentine plus 30-percent propylene oxide | 2 | -39 | 67 | 91 | 78 | |
| 90-percent turpentine plus 10-percent 2,5-dimethylfuran | 2 | -42 | ----- | ----- | ----- | Sporadic ignition |
| | 2 | -13 | 76 | 94 | 85 | |
| 70-percent turpentine plus 20-percent 2,5-dimethylfuran and 10-percent propylene oxide | 2 | -38 | ----- | ----- | ----- | Flameless explosions |
| 70-percent turpentine plus 15-percent 2,5-dimethylfuran and 15-percent propylene oxide | 4 | -40 | ----- | ----- | ----- | Sporadic ignition and flameless explosions |
| 80-percent turpentine plus 10-percent 2,5-dimethylfuran and 10-percent propylene oxide | 2 | -40 | 72 | 136 | 99 | |
| 75-percent turpentine plus 15-percent 2,5-dimethylfuran and 10-percent vinyl isobutyl ether | 2 | -38 | ----- | ----- | ----- | Flameless explosions |
| 80-percent turpentine plus 20-percent vinyl isobutyl ether | 2 | -40 | 79 | 86 | 83 | |
| Turpentine saturated with p-phenylene- diamine | 2 | -44 | 79 | 102 | 90 | |
| α -Pinene (containing inhibitor) | 3 | -55 | ----- | ----- | ----- | Flameless explosions |
| | 2 | -20 | 107 | 117 | 112 | |

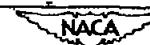


TABLE II - SUMMARY OF IGNITION-DELAY DATA OF SEVERAL FUELS WITH COMMERCIAL MIXED ACID AT VARIOUS TEMPERATURES

| Fuel (percent by volume) | Number of firings | Average tempera- ture (°F) | Ignition-delay interval (sec) | | |
|---|-------------------------|-------------------------------------|----------------------------------|----------------------|----------------------|
| | | | Minimum | Maximum | Geometric average |
| Crude N-ethylaniline | 11 | -36 | 144×10^{-3} | 341×10^{-3} | 220×10^{-3} |
| | 11 | -30 | 138 | 350 | 222 |
| | 10 | -14 | 129 | 242 | 176 |
| | 9 | 11 | 126 | 406 | 178 |
| | 6 | 25 | 120 | 198 | 152 |
| | 6 | 31 | 82 | 134 | 112 |
| | 8 | 76 | 64 | 97 | 78 |
| 70-percent furfuryl alcohol plus 30-percent crude N-ethylaniline | 10 | -36 | 9 | 91 | 31 |
| | 11 | -30 | 7 | 43 | 24 |
| | 2 | -22 | 19 | 35 | 26 |
| | 18 | 75 | 23 | 97 | 43 |
| Mixed butyl mercaptans | 3 | -55 | 16 | 39 | 22 |
| | 8 | -39 | 9 | 57 | 23 |
| | 16 | -30 | 9 | 62 | 23 |
| | 6 | 66 | 28 | 49 | 36 |
| dl-Limonene | 2 | -51 | (a) | (a) | (a) |
| | 2 | -23 | (b) | (b) | (b) |
| | 2 | 70 | 95 | 119 | 106 |

^aNo ignition.

^bSporadic ignition.

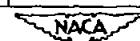


TABLE III - APPROXIMATE KINEMATIC VISCOSITIES AT TEMPERATURE OF
 -40° F AND SPECIFIC GRAVITIES AT ROOM TEMPERATURE OF SEVERAL
 ROCKET FUELS

| Fuel (percent by volume) | Kinematic viscosity at -40° F (centistokes) | Specific gravity at room tem- perature |
|--|---|---|
| Crude N-ethylaniline | 90 | 0.97 |
| Mixed butyl mercaptans | 1.3 ^a | .83 ^a |
| Commercial gum turpentine | 8.8 | .87 |
| 35-percent furfuryl alcohol plus 65-percent xylene | 9.2 | .96 ^b |
| 70-percent furfuryl alcohol plus 30-percent xylene | 51 | 1.05 ^b |
| 50-percent 2,5-dimethylfuran plus 50-percent crude N-ethylaniline | 11 | .94 ^b |
| 30-percent 2,5-dimethylfuran plus 70-percent crude N-ethylaniline | 20 | .95 ^b |
| Pure N-ethylaniline | 44 | .96 ^c |
| 63-percent furfuryl alcohol plus 27-percent crude N-ethylaniline and 10-percent methanol | 125 | 1.05 ^b |
| 15-percent furfuryl alcohol plus 85-percent crude N-ethylaniline | 130 | .99 ^b |
| 35-percent furfuryl alcohol plus 65-percent crude N-ethylaniline | 180 | 1.03 ^b |
| 70-percent furfuryl alcohol plus 30-percent crude N-ethylaniline | 228 | 1.08 ^b |
| Furfuryl alcohol | 224 | 1.13 ^c |

^aData from reference 6.

^bEstimated from data of reference 11.

^cData from reference 11.



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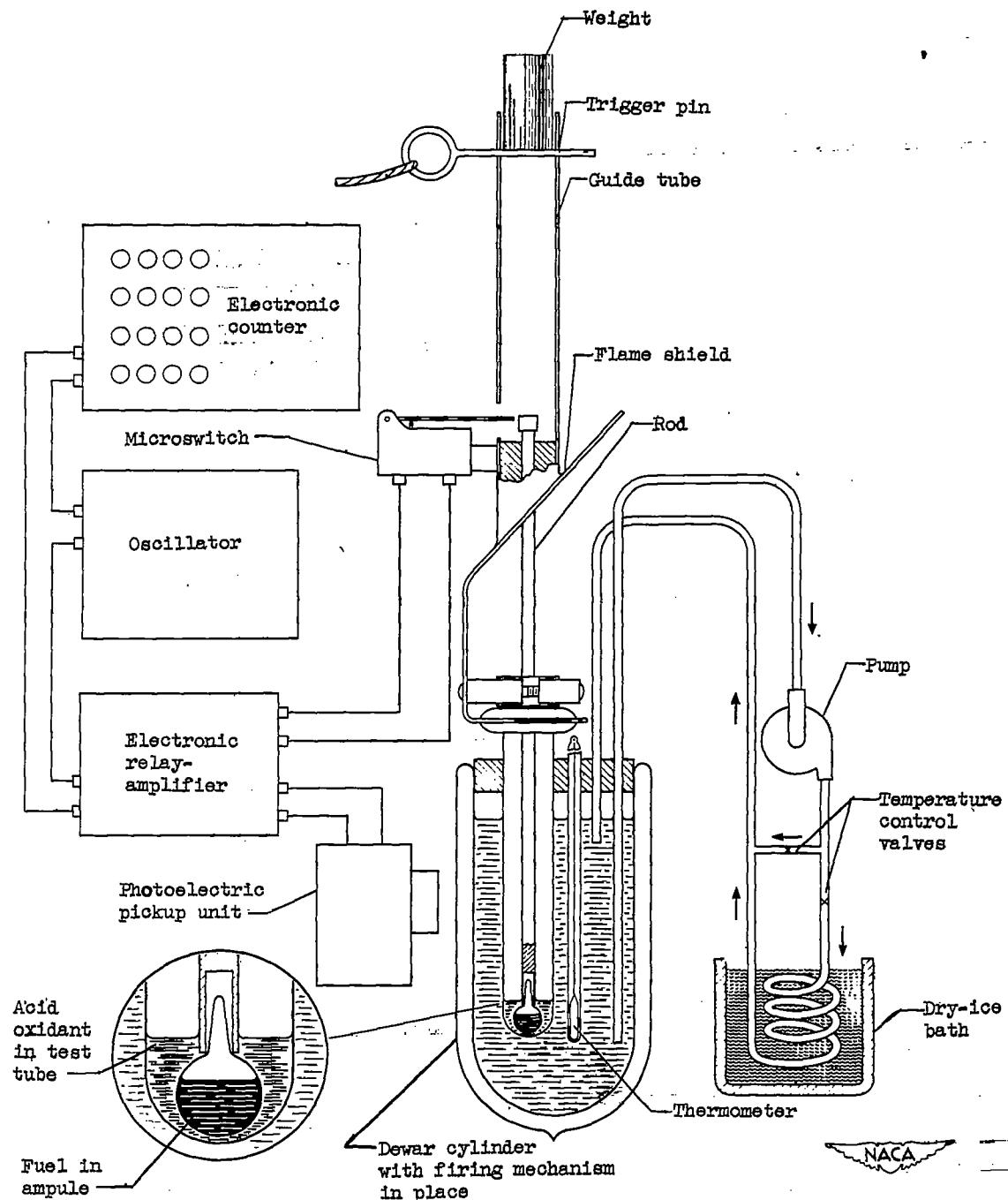


Figure 1. - Apparatus for determination of spontaneous ignition-delay interval of rocket fuel-oxidant combinations at various initial temperatures.

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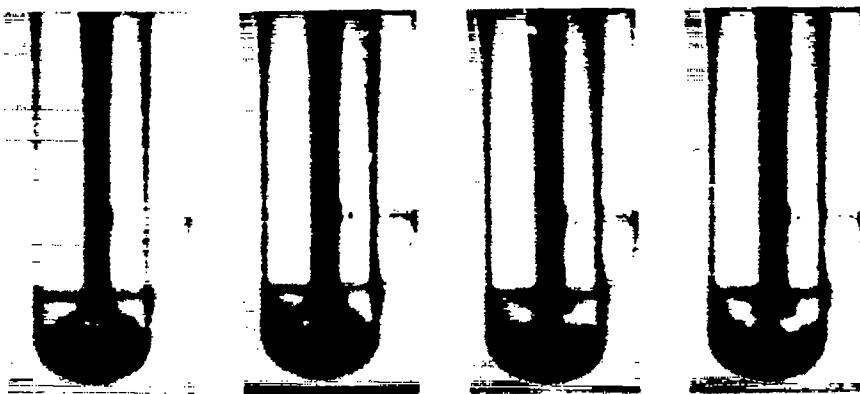
Time, sec.

0

0.001

0.002

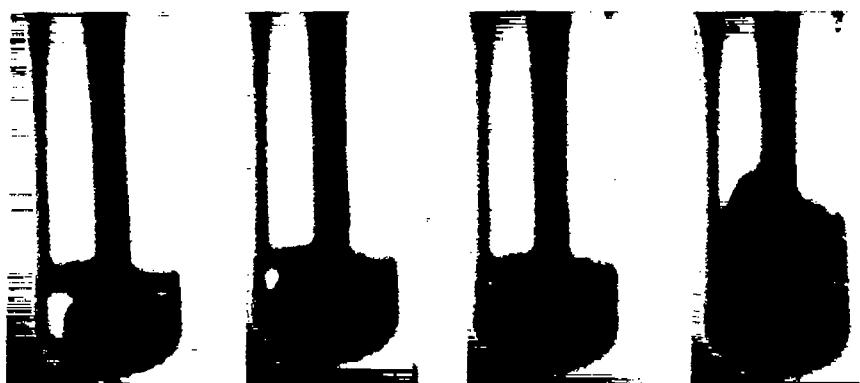
0.003



(a) Inert liquids.



(b) 70-percent furfuryl alcohol plus 30-percent crude N-ethylaniline with commercial mixed acid.




C-25160

(c) Crude N-ethylaniline with commercial mixed acid.

Figure 2. - Positive enlargements from frames of high-speed silhouette motion pictures showing behavior of inert liquids and rocket propellants at room temperature during first 0.003 second of timed interval. (Ignition occurred some time after beginning of preliminary nonburning reactions shown.)

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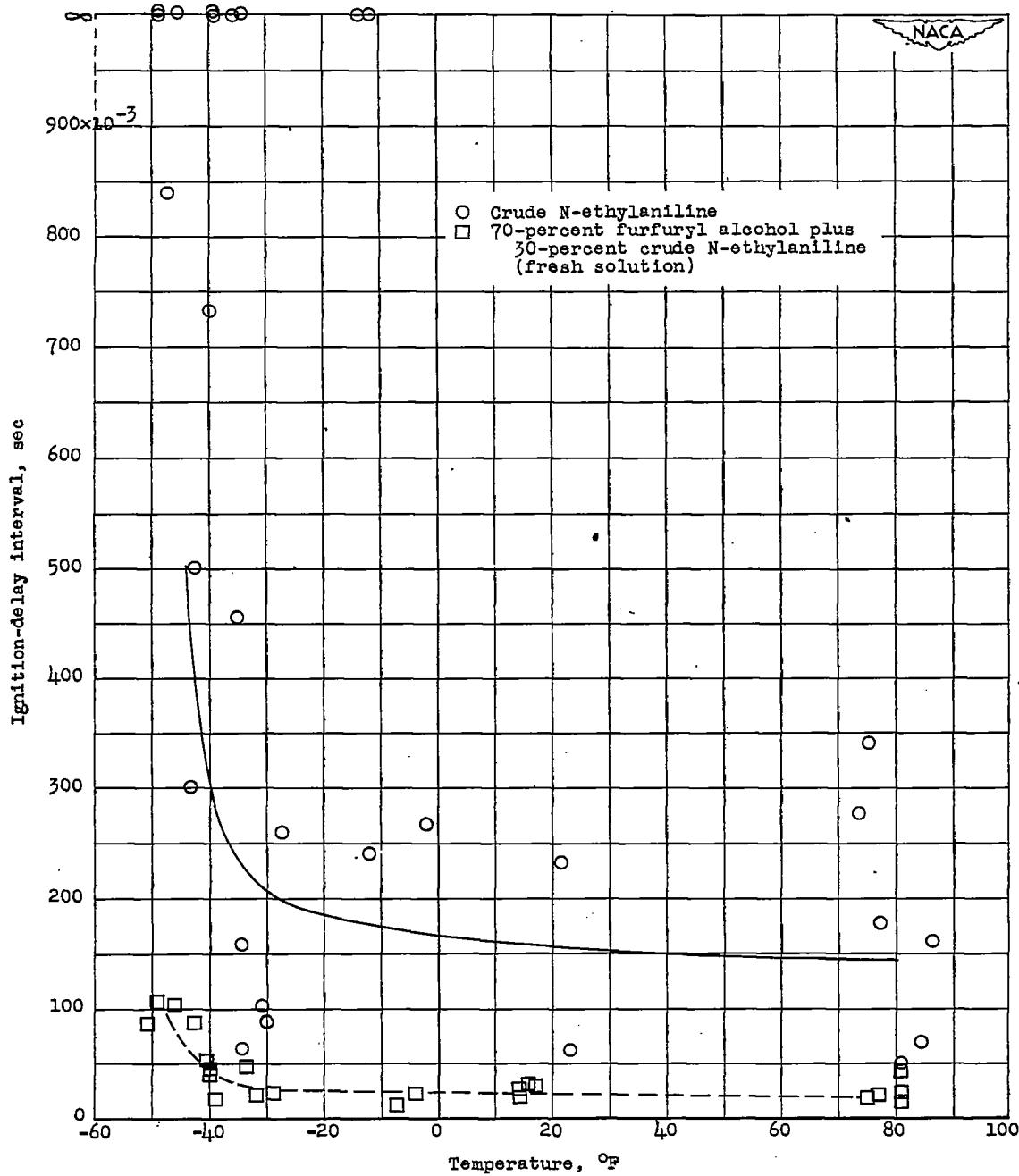


Figure 3. - Comparison of ignition-delay intervals of crude N-ethylaniline and 70-percent furfuryl alcohol plus 30-percent crude N-ethylaniline with laboratory-prepared mixed acid as functions of temperature.