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THE THERMAL STABILITY OF UNSYMMETRICAL DIMETHYLHYDRAZINE

By Adolph E. Spakowski

Lewis Research Center
Cleveland, Ohio

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SUMMARY

The thermal stability of unsymmetrical dimethylhydrazine was investigated in a static system simulating conditions in an almost-empty fuel tank. The self-ignition temperature and spontaneous decomposition temperature of the pure fuel were determined at atmospheric pressure to be 454° and 740° F, respectively, with the larger (740° F) value, obtained in an inert atmosphere of nitrogen, representing the minimum temperature that would cause a rapid exothermic reaction. The addition of 40 weight percent diethylenetriamine to unsymmetrical dimethylhydrazine did not significantly affect these properties.

INTRODUCTION

Rocket-powered flight of recoverable vehicles with the attendant reentry problem has raised the question of the thermal stability of propellant fuels during the reentry portion of the flight path when the temperature of the fuel tanks would be raised due to high aerodynamic heating rates. Both the residual fuel and its vapors will be exposed to the high wall temperatures of the tank. If the wall temperature was higher than the self-ignition temperature of the fuel vapor or liquid, ignition would occur with accompanying rapid increase in both temperature and pressure. A part of this hazard can be eliminated by flushing the fuel tank with an inert gas, like helium or nitrogen; however, the question still remains whether or not the fuel would decompose spontaneously.

Propellant combinations like unsymmetrical dimethylhydrazine - nitrogen tetroxide and hydrazine - nitrogen tetroxide have been proposed for rocket systems. On decomposing, these fuels release large quantities of gas, and even in a vented system could produce considerable pressure buildup. It has been suggested that mixing diethylenetriamine with unsymmetrical dimethylhydrazine will significantly raise the temperature of decomposition.

An investigation was undertaken at the NACA Lewis laboratory to determine the self-ignition and spontaneous decomposition temperatures of pure unsymmetrical dimethylhydrazine and of a mixture of unsymmetrical dimethylhydrazine and diethylenetriamine.

APPARATUS AND PROCEDURE

Self-Ignition Temperature

The self-ignition temperatures were determined in the standard apparatus developed at the National Bureau of Standards (ref. 1). The apparatus is shown diagrammatically in figure 1. The three independently controlled electrical heaters were regulated by variable transformers to establish uniform heating of the glass flask. Two sizes of flasks were used, 1000 and 125 milliliters. Thermocouples to indicate the temperature of the heaters and flask were connected to an indicating Brown potentiometer. During any particular test the heaters were controlled so that the flask was uniformily heated as indicated by the thermocouples located on the outer surface and inside the flask.

The self-ignition temperature was determined by first heating the glass flask to a predetermined temperature near the expected self-ignition temperature and following with a small charge of the fuel, then observing whether or not an ignition occurred. The temperature was varied over small intervals until a temperature was found below which ignition did not occur. After each test the flask was flushed with an airstream to remove the combustion products and to provide a fresh atmosphere for the next test. When solid combustion products were formed, the flask was replaced with a clean flask and the temperature was rechecked. Fuel charges for each test were varied from 0.1 to 0.3 milliliter in the 1-liter flask and from 0.05 to 0.1 milliliter in the 125-milliliter flask.

Spontaneous Decomposition Temperature

The spontaneous decomposition temperatures were determined in the self-ignition temperature apparatus with the modification shown in figure 2. By passing an inert gas through the stainless-steel tube, air could be kept from diffusing into the flask. Before each test the flask was flushed with the inert gas while the neck of the flask was continually purged with the same gas. Analyzed gas samples taken from the flask at various times showed this to be a satisfactory method of exluding oxygen. The tests were all made at atmospheric pressure using the self-ignition temperature procedure but using an inert atmosphere of either nitrogen or helium. Fuel charges for each test were 0.2 milliliter in the 1-liter flask and 0.05 milliliter in the 125-milliliter flask. While the ignitions in air were easily identified by the characteristic flames and reports, the decomposition tests were not accompanied by any visible flames, and the sounds produced by the reactions were audible only at the higher temperatures. These findings do not preclude the possibility that flames of low luminosity were produced since most of these tests were conducted in a lighted room and observations into the flask were extremely limited. The reactions were noted by observing the temperature change in the flask, a rapid temperature increase indicated a reaction. Time-temperature plots were made of both the ignition reactions and decompositions by connecting the thermocouple inside the flask to a General Electric recording potentiometer. Greater sensitivity was obtained by recording only the temperature difference between the thermocouple inside of the flask and a thermocouple at the outer surface.

MATERIALS

The commercial-grade unsymmetrical dimethylhydrazine (UDMH) and technical-grade diethylenetriamine (DETA) were obtained from manufacturers. Several physical properties of UDMH are listed in the following table:

Fuel boiling point, $^{\circ}F$	
Percent evaporated	
10	145
90	147
Density at 77° F, g/ml	0.7856
Refractive index at 77° F	1.4062
Assay, weight percent	98.6

RESULTS AND DISCUSSION

The self-ignition temperature of pure unsymmetrical dimethylhydrazine (UDMH) and 60-percent unsymmetrical dimethylhydrazine - 40-percent diethylenetriamine (this mixture is called UDETA) were determined in the National Bureau of Standards apparatus. The data are listed in table I and indicate several things, such as the small effect due to flask size. The self-ignition temperature of the pure UDMH in the 125-milliliter flask was only a few degrees higher than that found in the liter flask; the reverse is true for the two sets of UDETA data. Such small differences, however, may well be within the reproducibility of the method when used with this type of fuel. Table I also shows that a small inhibiting effect can be attributed to the addition of 40-percent DETA as the self-ignition temperature of UDMH was raised 2° to 15°.

All of the self-ignition temperature runs were evidenced by flames and loud reports while some of the reactions were violent enough to blow the stopper and thermocouple completely out of the flask. In figures 3(a) and (b) time-temperature histories of typical self-ignition runs are plotted. After the fuel was injected into the flask (at time zero), the temperature in the flask dropped because of the cooling effect of vaporizing fuel, then started to increase slowly as some reaction began. In the cases where no ignition occurred (no flame or noise), the time-temperature curve passed through a maximum of the type shown by the dashed curves in figure 3. As a comparison, when water was injected into the flask under similar conditions, only the temperature drop due to vaporization and then the slow rise to the initial temperature were observed. In every case where an ignition did occur, a sharp increase in temperature was simultaneously recorded. The thermocouples only showed that a rapid exothermic reaction occurred, but did not indicate true peak temperatures. In figure 3(b) the effect of initial temperature on the ignition delay time is illustrated by a series of runs at 480°, 481°, and 486° F with 0.05 milliliter of fuel in the 125-milliliter flask.

The spontaneous decomposition temperatures of pure UDMH and UDETA, determined in the modified apparatus, are listed in table I. Runs were made using either helium or nitrogen as the inert atmosphere. In each case the same gas was used for both flushing the flask after each run and continually flushing the neck of the flask during the subsequent run. There does not appear to be much, if any, significant effect due to either differences in flask size or inert gas on the decomposition temperature of pure UDMH. The addition of 40-weight percent DETA to UDMH increases the decomposition temperature of UDMH by several degrees. Here again the small differences may well be within the uncertainty of the method.

The decomposition reactions were very difficult to detect since no visible flames were produced and the only sound was barely audible except at higher temperatures. The criterion used to determine whether or not a reaction had taken place was a rapid temperature increase indicated by the thermocouple inside the flask. Typical time-temperature traces obtained from decomposition runs are shown in figures 4(a) and (b). These curves also exhibit the characteristic temperature drop due to vaporization of the fuel sample. The temperature peaks were similar to, but lower than those obtained from the ignition reactions.

From the data obtained in this study it appears that the addition of 40-percent DETA to UDMH does not materially change either the spontaneous decomposition or self-ignition temperature of pure UDMH. Actually the self-ignition temperature of UDMH was increased up to 15° F. Therefore, the addition of DETA had a small inhibiting effect.

The self-ignition and spontaneous decomposition temperatures of UDMH at atmospheric pressure were investigated in reference 2 in a constant-volume apparatus that has a 200-milliliter Erlenmeyer reaction flask as part of the specially designed equipment. The self-ignition temperature of 482° F determined in this test was associated with an ignition delay of 12 seconds. The UDMH vapor did not explosively decompose below 1112° F in an inert atmosphere of nitrogen. In this series of tests no audible sounds, flames, or sudden pressure rises were experienced to indicate decomposition reactions (data obtained from J. A. Herickes). The differences between the data obtained in reference 2 and this investigation can be explained by the two criteria set up to measure decomposition. In reference 2 the vapors of UDMH must "explosively decompose" while in this study a rapid exothermic reaction must occur.

The static conditions in the experiments discussed herein were intended to simulate the conditions existing in an almost-empty fuel tank. The data obtained in this study would seem to indicate that a potentially dangerous situation could exist at fuel-tank skin temperatures above 450° F in an uninerted system and above 740° F in a system inerted with nitrogen or helium. These temperatures might vary considerably if the tank walls either inhibited or catalyzed the reactions in any way.

The experiments conducted in this study do not, of course, indicate the violence of the decomposition reaction nor the extent of pressure buildup in a closed vessel, such as an aircraft fuel tank. Further experimentation would be required to determine whether or not fuel decomposition would rupture a tank under the conditions prevailing in high-altitude high-speed flight.

SUMMARY OF RESULTS

A preliminary investigation of the thermal stability of unsymmetrical dimethylhydrazine was made in both air and inert atmospheres of nitrogen and helium. In order to improve the stability characteristics of unsymmetrical dimethylhydrazine in a static system, the effect of an additive, namely, diethylenetriamine, was studied. Results from the series of tests are summarized as follows:

1. The self-ignition and spontaneous decomposition temperatures of pure unsymmetrical dimethylhydrazine were 454° and 740° F, respectively.

2. The addition of diethylenetriamine, 40 percent by weight, did not significantly raise either the self-ignition temperature or the spontaneous decomposition temperature of unsymmetrical dimethylhydrazine.

3. The use of either fuel in an inert atmosphere for extended periods of time in the temperature regime above 740° F might result in a hazardous operating condition.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, September 10, 1958

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1. Setchkin, Nicholas P.: Self-Ignition Temperatures of Combustible Liquids. Jour. Res. Nat. Bur. Standards, vol. 53, no. 1, July 1954, pp. 49-66.

2. Herickes, Joseph A., Damon, Glenn H., and Zabetakis, Michael G.: Determination of the Safety Characteristics of Unsymmetrical Dimethylhydrazine. Summary Rep. 3565, Bur. Mines, Jan. 15, 1957.

TABLE I. - THE SELF-IGNITION AND SPONTANEOUS DECOMPOSITION TEMPERATURES OF UNSYMMETRICAL DIMETHYLHYDRAZINE AND 60-PERCENT UNSYMMETRICAL DIMETHYLHYDRAZINE - 40-PERCENT DIETHYLENETRIAMINE AT ATMOSPHERIC PRESSURE

Compound	Flask, ml	Self-ignition temperature, °F	Spontaneous decomposition temperature, °F
UDMH	1000	454	[a]746
	125	[b]457	[b,c]740
		[b]460	[a]748
		[b]464	[b,c]744
UDETA	1000	469	[a]748
			[b,c]748
	125	466	[b,c]753

[a] In helium atmosphere.

[b] Redistilled under nitrogen.

[c] In nitrogen atmosphere.

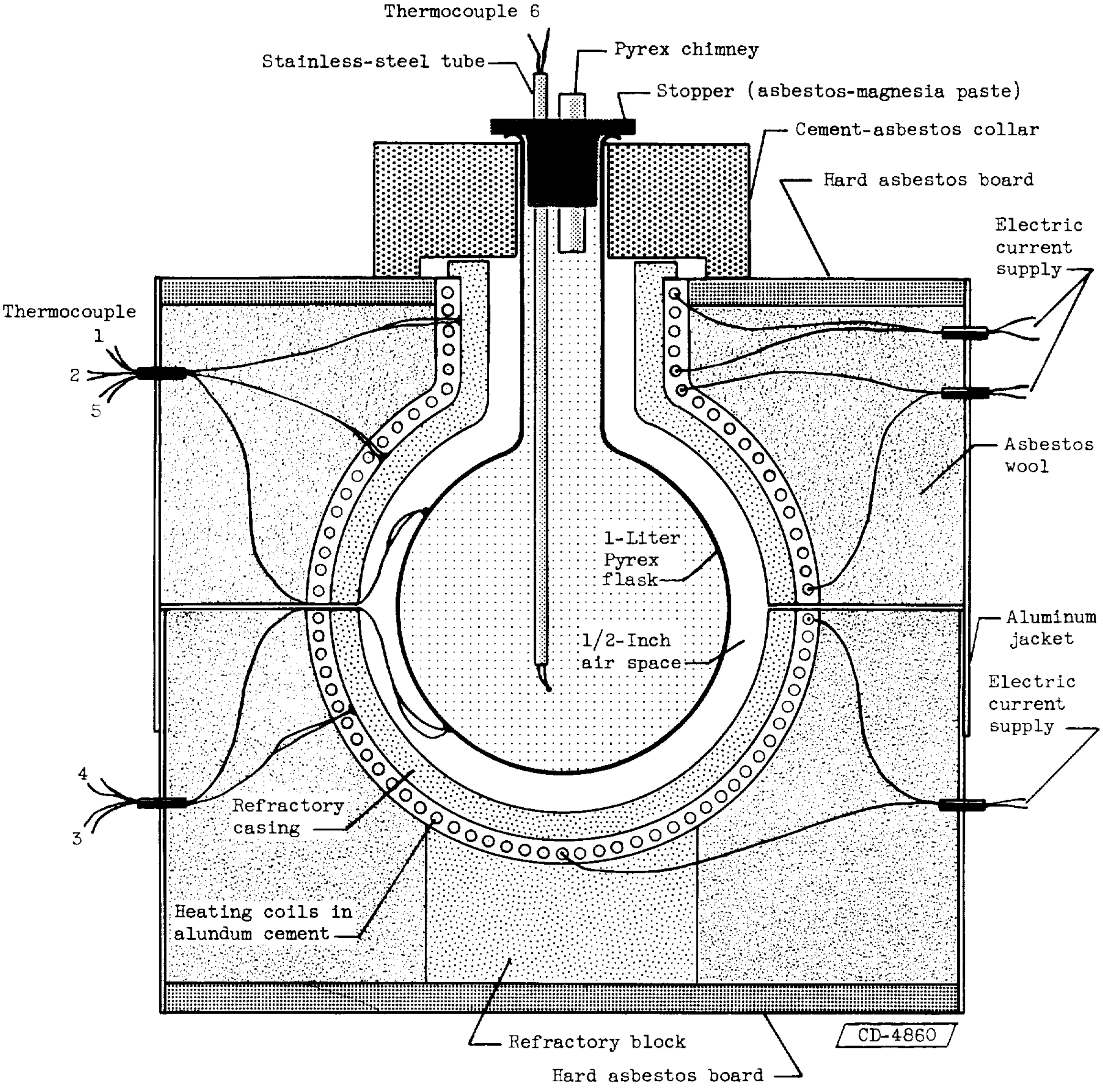


Figure 1. - Self-ignition-temperature apparatus (ref. 1).

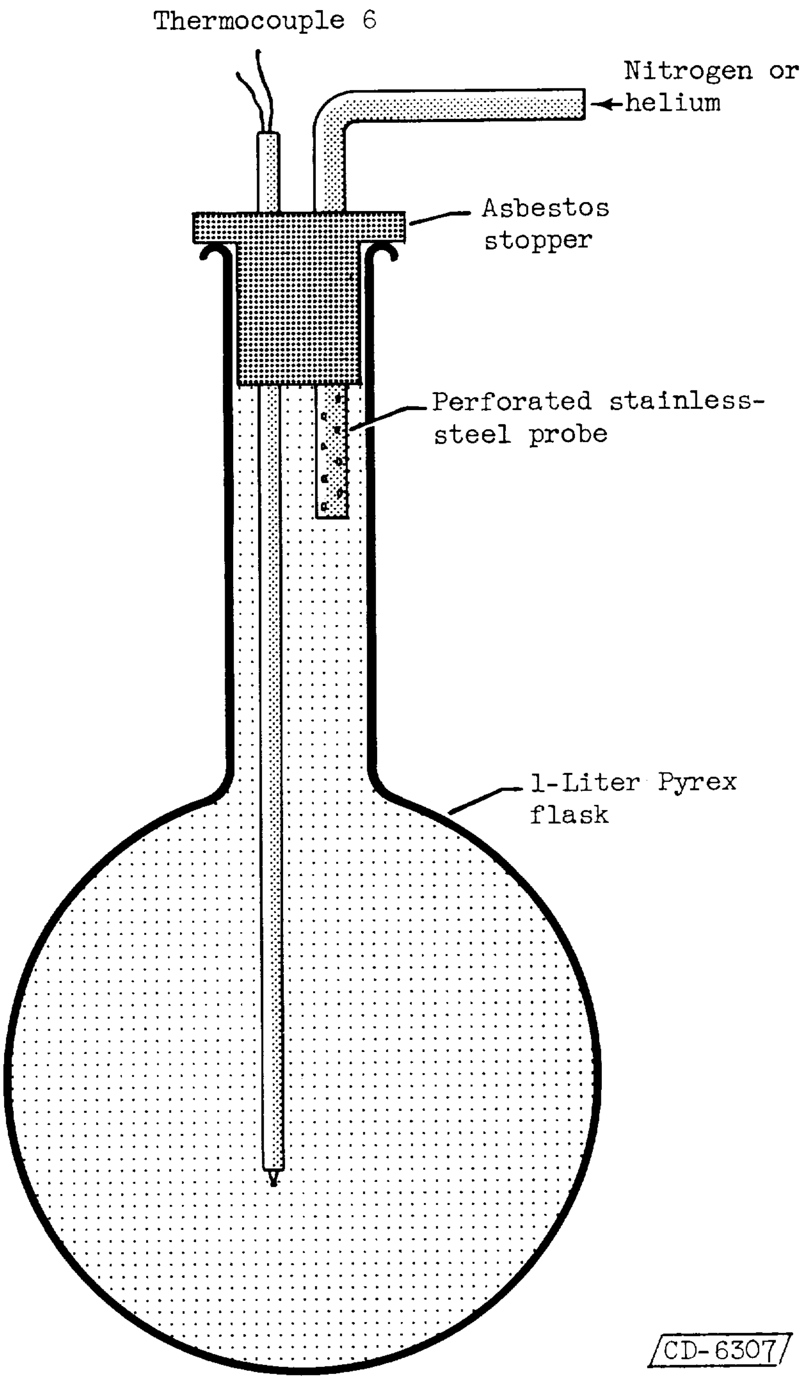
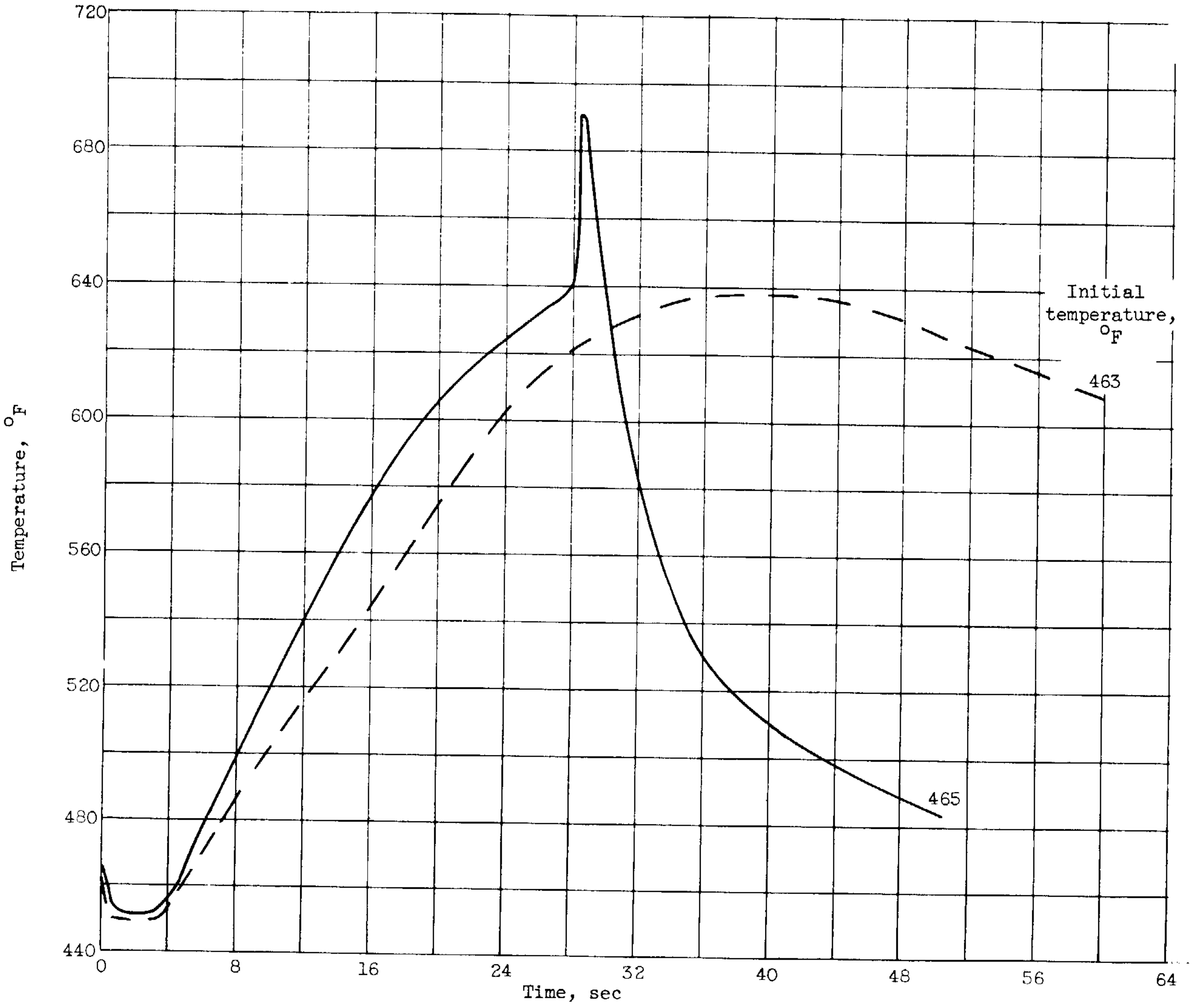
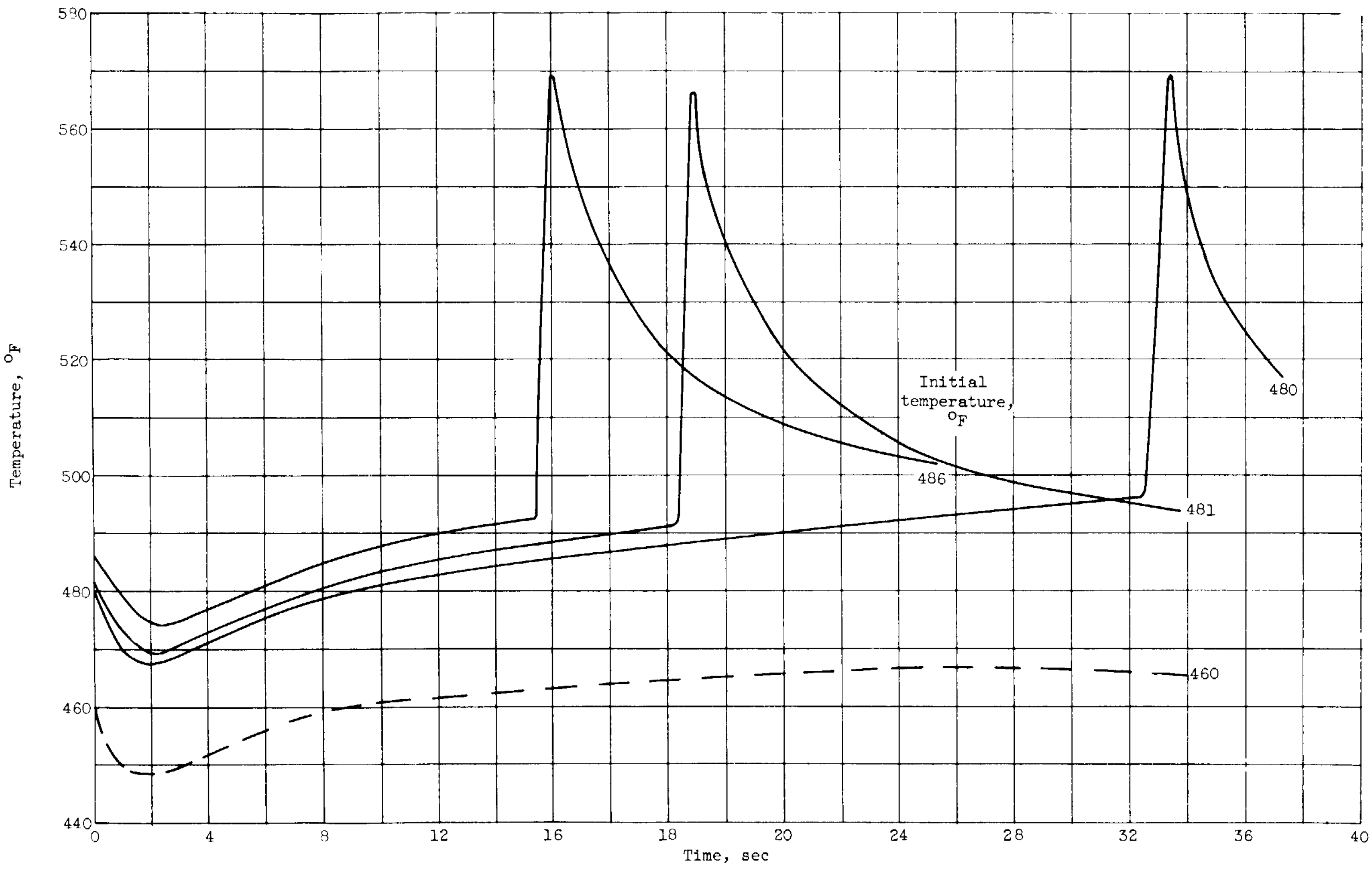


Figure 2. - Inerting system for reaction flask of self-ignition temperature apparatus.



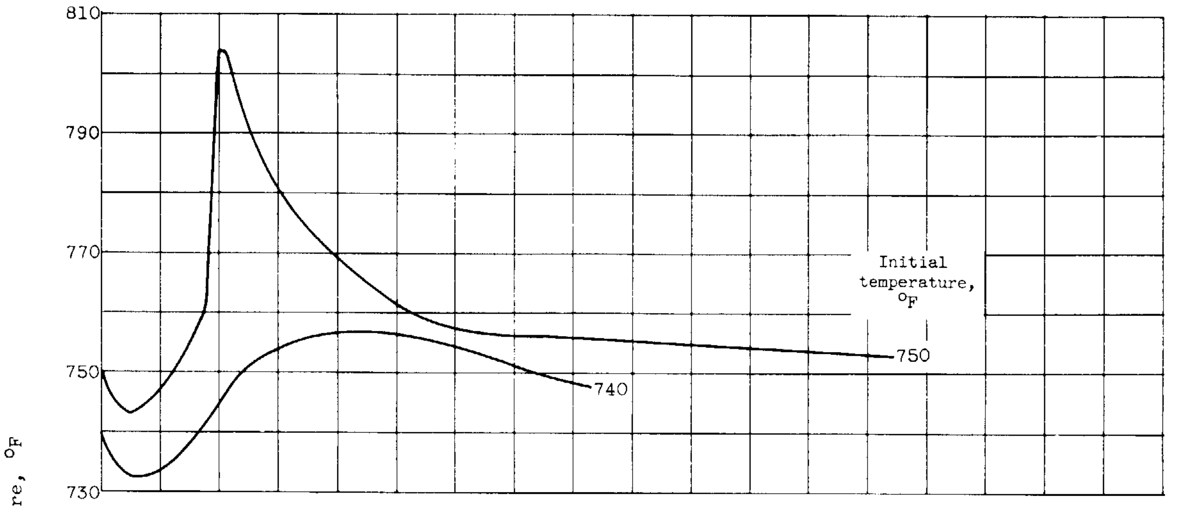
(a) Unsymmetrical dimethylhydrazine.

Figure 3. - Time-temperature plots of the self-ignition reaction.

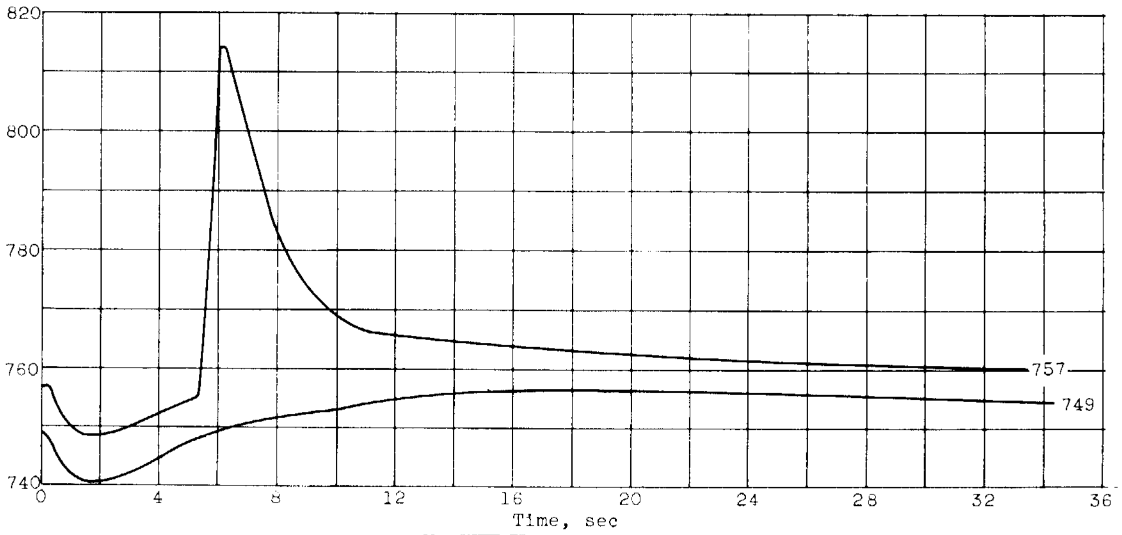


(b) 40-Percent diethylenetriamine - 60-percent unsymmetrical dimethylhydrazine.

Figure 3. - Concluded. Time-temperature plots of the self-ignition reaction.



(a) Unsymmetrical dimethylhydrazine.



(b) 40-Percent diethylenetriamine - 60-percent unsymmetrical dimethylhydrazine.

Figure 4. - Time-temperature plots of the spontaneous decomposition reactions.

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4. Combustion - Ignition of Gases (3.5.1.6)
5. Fire Hazards (7.9)

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