Limits of Flammability of Hydrazine-Hydrocarbon Vapor Mixtures

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LIMITS of flammability, as normally encountered, define the range of combustible-oxidant mixture compositions that are flammable. This range is ordinarily bound by the lower or combustible-lean limit and the upper or combustible-rich limit of flammability. However, certain combustible vapors such as hydrazine, ethylene oxide, and azomethane do not have a normal upper limit of flammability since they are flammable in the absence of an oxidant. Because these vapors in themselves create a fire or explosion hazard, there is some interest in determining the effect of stable diluents on their flammability characteristics. In this connection, the Federal Bureau of Mines in 1949 determined the effect of air, water vapor, nitrogen, helium, and *n*-heptane vapor on the flammability characteristics of hydrazine vapor (*3*). Recently there has been some interest in the use of other hydrocarbons to inhibit flame propagation in this combustible. Accordingly, the earlier work was extended to include the effects of benzene, toluene, *m*-xylene, and cumene. Specifically, the object of this project was to determine the minimum amount of each of these hydrocarbons required to prevent flame propagation through the hydrazine-hydrocarbon vapor mixtures.

APPARATUS AND PROCEDURE

The apparatus was similar to that used previously to determine the flammability of hydrazine when diluted with water vapor and *n*-heptane (*3*). The standard borosilicate glass explosion tube, 1 ¼-inch i.d., is 10 inches long and has a capacity of approximately 200 ml. Platinum electrodes form a ¼-inch gap and are placed 1 ¾ inches from the bottom of the explosion tube. A short piece of capillary tubing attached to the upper end of the tube is drawn down to aid in the final sealing. A 2-inch i.d. tube was used in addition to the standard tube to determine the effect of tube diameter on flame propagation. The larger tube is also constructed of borosilicate glass, is 18 inches long, and has a capacity of 740 ml.

A 5-gallon borosilicate glass container filled with a high flash point mineral oil was used as a constant temperature bath. The usual electric immersion type heater controlled thermostatically and a stirrer maintained the desired uniform temperature. A 15,000-volt 60 ma. luminous tube transformer was used as the ignition source.

To conduct a test, the explosion tube is evacuated and flushed with helium several times. The tube is then brought to atmospheric pressure with helium, immersed in liquid nitrogen, and again evacuated. After reaching liquid nitrogen temperature, helium is again added and the tube is disconnected from the vacuum system. The hydrazine and hydrocarbons, weighed in small hypodermic syringes, are then carefully introduced into the tube through the capillary, the syringe needle extending well into the explosion tube. The liquids drop to the bottom of the tube and are quickly frozen. The syringes are reweighed and the molar concentration is determined. The weight of the components used is sufficient to bring the pressure within the tube to approximately 1 atm. under the test conditions employed.

The explosion tube is again connected to the vacuum pump and rapidly evacuated while it is in liquid nitrogen. While the pumping continues, the capillary tube is collapsed and sealed with a torch. The tube is then removed from the cold bath and brought to room temperature, and the electrodes are connected to the luminous tube transformer. It is then submerged in an electrically heated oil bath thermostatically controlled at 125° C. After sufficient time has elapsed for vaporization and mixing of the vapors (½ hour), a spark is passed between the electrodes. A flammable mixture is taken to be one through which a visible flame passes up the explosion tube.

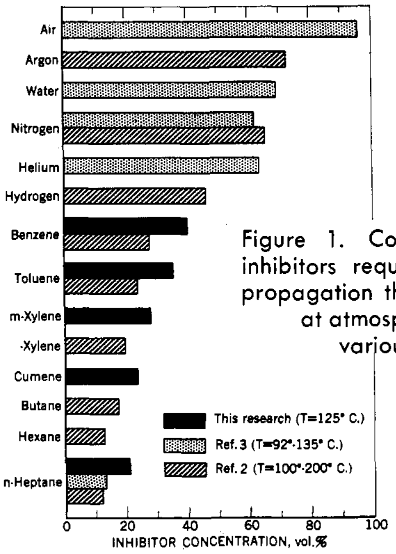

Figure 1. Concentration of various inhibitors required to suppress flame propagation through hydrazine vapor at atmospheric pressure and various temperatures

RESULTS AND DISCUSSION

Preliminary experimental results indicated that the 1 ¼- and 2-inch i.d. explosion tubes yielded comparable results; therefore, the former tube was used.

Table I lists the lower limit-of-flammability data obtained with hydrazine and the various hydrocarbons. In calculating the mixture compositions, the impurity in the hydrazine samples was assumed to be water and is reported as such. All calculations made in converting weight of sample to weight of hydrazine and water are based on the analysis of the hydrazine sample (98.46%). The conversion from weight of hydrazine to mole per cent (volume per cent) assumes no association of the hydrazine molecules (*1*). The hydrazine limits reported in Table I are the averages of the concentration values for the limit-determining tests; the spread in experimental values is given in the second column.

The results of this research, along with those obtained in the earlier Bureau of Mines investigation (*3*) and in the investigations of Pannetier and Bultingair-Laborde (*2*), are given in Table II and shown diagrammatically in Figure 1. Here the results are given in terms of the concentration of inhibitor rather than concentration of hydrazine. Further, all mixtures are treated as three-component systems in which the water concentration is a minor fraction.

A comparison of the data obtained in the earlier Bureau of Mines investigation with those obtained in this research shows that more *n*-heptane is required to suppress the flammability of hydrazine vapor than previously reported (21.0 instead of 13.2 volume %). The higher value is attributed to the more effective ignition source used in the present investigation. Hydrazine flames were suppressed

Table I. Lower Limits of Flammability of Hydrazine-Hydrocarbon Vapor Mixtures

		Mixture Composition, Vol. %		
Hydrocarbon	Spread	Hydrazine	Water	Hydrocarbon
Heptane	±0.4	76.8	2.2	21.0
Benzene	±0.2	58.5	1.7	39.8
Toluene	±0.9	63.2	1.8	35.0
m-Xylene	±0.7	70.7	2.0	27.3
Cumene	±0.2	74.1	2.1	23.8

Table II. Minimum Quantities of Various Inhibitors Required to Suppress Flame Propagation Through Hydrazine Vapor at Atmospheric Pressure and Various Temperatures

	Volume %		
Inhibitor	This research ($T = 125°$ C.)	Ref. *3* ($T = 92$-$135°$ C.)	Ref. *2* ($T = 100$-$200°$ C.)
Air	...	95.3	...
Argon	...	...	71.9
Water	...	69.1	...
Nitrogen	...	62.0	64.8
Helium	...	63.0	...
Hydrogen	...	...	45.9
Benzene	39.8	...	27.9
Toluene	35.0	...	24.0
m-Xylene	27.3	...	...
Xylene	...	...	20.0
Cumene	23.8	...	...
Butane	...	...	17.3
Hexane	...	...	12.8
n-Heptane	21.0	13.2	12.0

with 7.0% *n*-heptane vapor when an induction coil was used as the ignition source and with 9.1% when a 400 m.m.f. condenser charged to 10,000 volts was used as the ignition source (*3*). In recent years, we have found luminous tube transformers to be extremely effective ignition sources, so that such a transformer was used in the present study.

An analysis of the above data shows that the minimum quantity of a hydrocarbon diluent required to prevent flame propagation (critical volume per cent) is proportional to its heat of formation. This is illustrated in Figure 2. The data for the paraffin and the aromatic series can be represented by linear equations as follows: For the aromatic,

$$V_c = 23.5 + 0.88\ \Delta H_f - \text{(This research)}$$
$$V_c = 18.0 + 0.5\ \Delta H_f - \text{(Data from Ref. 2)}$$

paraffin compounds, $V_c = 29.5 + 0.4\ \Delta H_f$ – (Data from Ref. *2*) where V_c is the critical volume per cent and ΔH_f is the heat of formation expressed in kcal./mole. The equations derived from our research can be used to predict critical volumes of other similar hydrocarbons required to prevent flame propagation through hydrazine vapor.

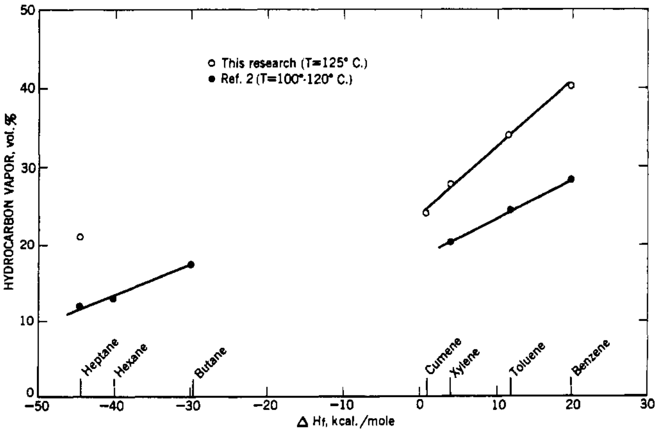

Figure 2. Effect of heat of formation (ΔH_f) on the concentration of hydrocarbon required to inhibit flame propagation through hydrazine vapor at elevated temperatures and atmospheric pressure.

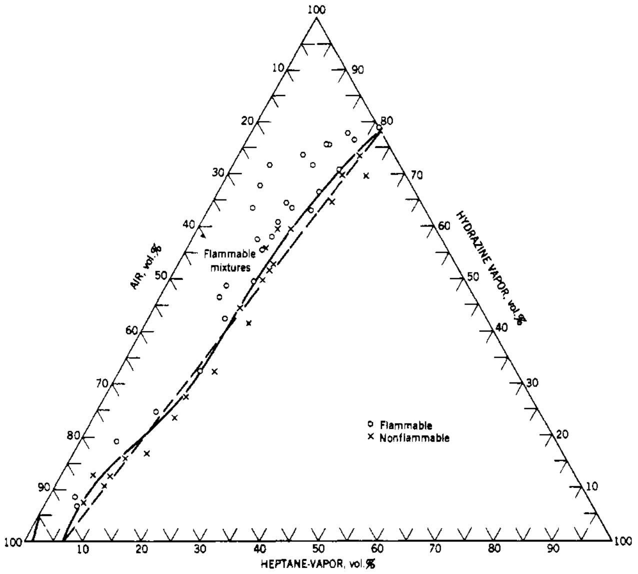

Figure 3. Flammable mixture compositions of the hydrazine-heptane-air system at 125° C. and approximately atmospheric pressure

Since a closed system containing hydrazine-hydrocarbon mixtures may become contaminated with air, we also determined the effect of adding air to a hydrazine-*n*-heptane mixture. The results are shown in Figure 3 on a water-free basis. To a first approximation, the flammable mixtures area is given by the area bound by a straight line constructed between the critical heptane volume (in the heptane-hydrazine mixture) and the upper limit of flammability of heptane in air, and one constructed between the lower limits of flammability of hydrazine and of heptane in air.

CONCLUSIONS

The minimum concentration of aromatic hydrocarbon vapor required to inhibit flame propagation through hydrazine vapor at a specified temperature and pressure is proportional to the heat of formation of the hydrocarbon. In order of increasing inhibiting ability at 125° C., those determined are: benzene, 39.8%, toluene, 35.0%, *m*-xylene, 27.3%, and cumene, 23.8%.

The flammable mixtures area of the tricomponent system hydrazine-heptane-air is defined by two lines, one between the critical heptane concentration in the hydrazine-heptane system and the upper limit of flammability of heptane in air, and the other between the lower limits of flammability of hydrazine and heptane in air.

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