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SEMI-ANNUAL REPORT - JANUARY 1947
Contract NOrd-7920
Task PRN-3

DEPARTMENT OF CHEMISTRY
PRINCETON UNIVERSITY

AD-140321

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Approved:
L. R. Hafstad, Director
Applied Physics Laboratory
The Johns Hopkins University

SEMI-ANNUAL REPORT - DECEMBER 31, 1946

Contract NOrd-7920, Princeton University

Princeton, New Jersey

Task PRN-3, Combustion Research

This Task was formally assigned to Princeton University as an Associated Contractor of the Applied Physics Laboratory, Johns Hopkins University, by letter dated June 19, 1945 from G. F. Hussey, Jr., Rear Admiral U.S.N. Chief of Bureau of Ordnance; E. N. Parker, Captain, U.S.N., by direction, in the following terms-

> "Research and development work is to be carried on in connection with rocket launched, jet-propelled, guided, anti-aircraft missiles related to Task F (Bumblebee) assigned to the Applied Physics Laboratory, The Johns Hopkins University by the Bureau of Ordnance, with special emphasis on combustion of fuels and fundamental research of chemical principles governing the operation of such devices. This work shall include experimentation and testing of such fuels and principles, and design and fabrication of supplementary equipment used in carrying out this work. It shall also include cooperation through consultation and otherwise, as may be practicable, with other agencies concerned with the development or use of devices and techniques related to this Task PRN-3."

The above has been supplemented by Problem Statement PRN-3-A - Combustion Principles, received from the Applied Physics Laboratory, The Johns Hopkins University, dated September 19, 1946. This reads as follows-

PRN-3-A - Combustion Principles -

This problem consists of basic research on chemical principles involved in the combustion of fuels in high speed air streams. It includes the following:

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A. Flame Propagation:

Determination of flame speed, flame width (ideally the space variation in percent combustion) and A/F stability limits of laminar flow to a bunsen cone as a function of pressure, temperature, flow velocity, Reynolds number, and tube diameter for hydrocarbon oxidation and for an elementary process which is well established.

Investigation of spectroscopic, photographic and sampling techniques for making these determinations. This study may be done at low pressures on a laboratory scale. The definition of the combustion zone should be accurate to 10 percent of the flame width, if possible, but definition to a few percent of the tube diameter would still be useful.

B. Reaction Kinetics:

Identification and measurement of the concentrations of intermediate ions, free radicals and molecules occurring in the oxidation of simple hydrocarbons as a function of time, temperature, pressure and A/F; and measurement of energies of the various intermediate reactions. Mass spectrometer technique should be used in making these determinations.

This portion of the project has been in active operation over the six-month period of this report under the general direction of Hugh S. Taylor, Chairman, Department of Chemistry and Dean of the Graduate School, and Robert N. Pease, Associate Professor of Chemistry. The research group has averaged six full-time research assistants and one part-time research associate.

During the period, July 1, 1946 to December 31, 1946, a total of $27443.20 has been expended, or a little less than $4600.00 per month on the average. Over the whole period from March 1, 1945 to December 31, 1946, there has been expended $71399.96 or about $3250.00 per month on the average.

[redacted]

SUMMARY OF TECHNICAL PAPERS

The results obtained in the six-month period are presented in a set of seven Technical Papers, copies of which are attached to this report.

The general aim has been to approach the problem of combustion from the standpoint of physical chemistry, rather than that of physics or of engineering. Interest therefore centers on the elementary chemical processes which are occurring in flames, and on the chemical intermediates which may be detected.

Spectroscopy affords one means of investigation. Technical Papers Nos. 19, 20 and 21 summarise preliminary studies of this sort. It is well known that hydrocarbon flames in air or oxygen emit bands due to the CC, CH, and OH radicals as well as other bands of less certain origin. Spectra of such flames have been photographed using n-butane, butene-1, butadiene-1,3, and ethylene oxide. Small amounts of added nitrous oxide (N_2O) bring out the NO, NH, and CN bands, which are not developed when air itself is the only nitrogen source.

Observations of mass-spectra should also prove useful as a means of detecting intermediates. For this purpose, a mass-spectrograph of the type used as a leak detector has been obtained, but as yet no data are available.

A serious difficulty in flame-sampling technique follows from the extreme thinness of the flame zone. This should be partially resolved by operating at low pressure. Experiments on a low-pressure burner are reported in Technical Paper No. 25. It has been found that butadiene-oxygen mixtures can be burned at as low as 5 mm. pressure at a 30 mm. port. Under these conditions the flame tends to mushroom out into a diffuse zone. Operation at still lower pressures waits on additional pumping capacity.

Flame speeds are under investigation. Technical Paper No. 23 reports the development of an electronic timer and gives some representative data on flame propagation at sub-atmospheric pressures. Analogous results based on measurements of flame-cone areas are given in Technical Paper No. 25, Table II.

[redacted]

In view of the relative difficulty of igniting hydrocarbons, experiments on the use of zinc dimethyl as a sensitiser are of interest (Technical Paper No. 24). Small amounts of zinc dimethyl cause spontaneous ignition of butane-oxygen mixtures at room temperature.

Experiments on the thermal stability of aluminum borohydride are reported in Technical Paper No. 22. The vapor begins to decompose at an appreciable rate above 150°C.

Current studies include the following:-

1. Low-pressure combustion
2. Flame sampling
3. Flame speeds
4. Piloted combustion of hydrogen-air mixtures.
5. Spontaneous ignition of boron tri-ethyl
6. Adaptation of mass spectrograph
7. Flame photography

APPROVED BY:

Hugh S. Taylor

Hugh S. Taylor
Director, Chemical Division

SIGNED

Robert N. Pease

Robert N. Pease

[redacted]

EMISSION SPECTRA FROM THE COMBUSTION OF C_4 HYDROCARBONS

By P. Strubing Blatz and Elmer J. Badin

(Transmitted by Robert N. Pease)

Department of Chemistry, Princeton University

Princeton, New Jersey

Contract NOrd-7920, Task PRN-3

Technical Paper No. 19

February 1, 1947

SUMMARY

Emission spectra of air flames of n-butane, butene-1 and butadiene-1,3 have been obtained for a variation in each case from lean through stoichiometric to rich mixtures for the visible and near ultra-violet regions. The purpose of the investigation has been to determine the variation in intensities of the emitters C_2, CH, OH and "hydrocarbon flame bands" with increase in hydrocarbon concentration and to obtain data which will serve as a basis for subsequent spectroscopic studies. For the C_2 bands it has been found that the (n,n) bands and (n,n+1) bands are most prominent; next in order are the (n,n-2) and (n,n-1) bands.

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INTRODUCTION

The study of flame spectra is obviously one of several important approaches to the study of combustion. Many earlier investigations have identified bands due to C_2, CH, OH, "HCO" and an unknown system (Raffety bands) in hydrocarbon flames Not much information, however, is available as to relative (or absolute) intensities and the way these change with experimental conditions especially concentration of the reactants. The data obtained here represent an experimental survey of emission spectra for the hydrocarbon-air flames of n-butane, butene-1, and butadiene-1,3 at atmospheric pressure.

APPARATUS AND METHOD

Combustion of n-butane, butene-1, and butadiene-1,3 were carried out using a flow and metering system essentially similar to that shown in Figure I, Technical Paper No. 4.(1) Flowmeters were calibrated for each gas used and during exposures a constant flow was maintained. The burner consisted of a 6.2 mm. I.D. quartz tube with a 25 mm. I.D. pyrex mantle. The mantle had a short extension side tube of 24 mm. I.D. to the end of which a plate of optically clear quartz was cemented. A copper cooling coil around the extension near the seal prevented overheating of the sealed joint. All combustions were carried out at atmospheric pressure.

Emission spectra were taken using a medium type Hilger spectrograph having a 60 cm. focal length with a quartz prism, and holding a 4 by 10 inch plate. Plates were Eastman Kodak plates sensitized for the region 2500Å to 6000Å (type IV-G). The center portion of the inner cone (the outer cone was eliminated by the mantle) was focused through a water filled spherical quartz lens onto the spectroscope slit

As a comparison and calibration spectrum, a copper arc was photographed before each flame exposure on the same plate directly adjacent to the flame spectrum. The current in the arc circuit was kept at approximately 4 amperes and an exposure time of from 1/10 to 1/4 of a second was used when the arc was at a distance of 10 centimeters.

[redacted]

For each of the three gases studied (n-butane, butene-1, butadiene-1,3) eight exposures on a single plate were made. The limits under the particular conditions used were 3.0 to 4 1% for n-butane, 3.0 to 4.7% for butene-1 and 3.0 to 5.4% for butadiene-1,3. Four different points in the burning range of the gases in air were taken for exposure: a point near the lower burning limit; a point at the stoichiometric point of the air-gas mixture; an intermediate point between the stoichiometric point and the upper burning limit; and a point near the upper burning limit. It was not practical to regulate the flow of gas as close as possible to the upper and lower burning limits while making the exposures because only a slight change in the gas rate would either cause the flame to go out altogether when at the lower limit or cause the inner flame to jump up to the top of the mantle when at the upper limit. The points were taken, consequently, as close to the limits as was practical without such interferences. The stoichiometric point was obtained very accurately, while the intermediate point between the stoichiometric point and the upper burning limit was arbitrarily chosen at a specific spot about half-way between the two. At each of the four points two exposures were made; one of 20.0 minutes and one of 90.0 minutes with a fine slit adjustment, the burner window being 42 cm. from the slit with the focusing lens at 11 cm. from the slit.

In order to insure uniformity all spectra which were to be compared were taken on the same plate; a standardized development and printing procedure were used. Prints were made using high contrast paper.

Standardization of wave lengths and calibration of plates were carried out using the standard tables(2) and a travelling calibrator microscope.

RESULTS AND DISCUSSION

For each of the three hydrocarbons, n-butane, butene-1, and butadiene-1,3, whose emission spectra were obtained, exposures were made at constant air flow (2.71 liters/min.), at atmospheric pressure and the following compositions:

(1) A point just above the lower limit with an excess of air,

(2) A point near the stoichiometric composition calculated for complete combustion to CO_2 and H_2O (this corresponded to 3.12% for n-butane, 3.38% for butene-1 and 3.68% for butadiene-1,3),

[redacted]

(3) A point mid-way between the stoichiometric composition and the upper limit (excess of hydrocarbon), and

(4) A point just below the upper limit (larger excess of hydrocarbon).

On the basis of the variation of spectra from hydrocarbon to hydrocarbon and from a "lean" mixture to a "rich" mixture in each case it was hoped to understand more fully hydrocarbon combustion. Observations in each case have been made on the center of the inner cone (mantled burner). Data for visual estimates (scale 1 to 10) of the intensities of the emitters for combustion of the three hydrocarbons in air are contained in Tables I, II and III. Typical spectra of butadiene-1,3 air flames are contained in Plate I.

The variation in intensities of the band systems with increase in unsaturation is shown in Plate II where the spectra for n-butane, butene-1 and butadiene-1,3 flames at constant air flow, constant exposure time and stoichiometric composition are shown. In each case a band becomes more intense with increasing unsaturation. This might be expected for the C-containing emitters, since with increasing unsaturation the relative amount of carbon present increases, but is not to be expected for OH since on the same basis the amount of hydrogen decreases. Another explanation which presents itself is that the flame temperature increases from n-butane to butadiene-1,3 with butadiene-1,3 flames having the highest temperatures hence greatest excitation and emission of radiation. Calculation* of the equilibrium theoretical flame temperatures for the mixtures shown in Plate II leads to values of 2275 °K for n-butane, 2315 °K for butene-1 and 2267 °K for butadiene-1,3 flames. This is again not in agreement with the observed intensities. A chemical explanation,

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(*) Equilibrium calculation of the theoretical flame temperature assuming complete combustion to CO_2 and H_2O with dissociation to H_2, O_2, CO and OH.

[redacted]

therefore, is indicated, namely, that reactivities of the three hydrocarbons with air are in the order

butadiene-1,3 > butene-1 > n-butane

with the conclusion that butadiene-1,3 is capable of forming excited molecules, e g., OH, more readily than the other two hydrocarbons.

The variation in intensity of each of the band systems will be considered separately for each system. C₂ (Swan bands). For the C_2 bands (degraded to the violet) the intensity in each case (Tables I, II, III, and Plate I) increased with increasing richness of the mixture. The first C_2 band to appear (Plate Ia) is at 5165.2Å and is the (0,0) band corresponding to vibrational quantum number change +0, the easiest transition. At the stoichiometric composition (Plate Ib) the system headed by the (0,0) band at 5165.2Å increases in intensity with the appearance of the (1,1), and (2,2) bands The next likely transition (vibrational quantum number change +1) with the (0,1) band at the head 5635.5Å also appears together with the (1,2), (2,3), (3,4) and (4,5) bands at 5585.5Å, 5540.7Å, 5501.9Å and 5470.3Å. In Plate Ic at the composition mid-way between the stoichiometric point and the upper limit the (1,0), (2,1), (3,2), (4,3) bands with their head at 4737.1Å and corresponding to vibrational quantum number change, -1, first appear. One anomaly, however, can be noted in the system with head at 4382.5Å corresponding to the vibrational quantum number change, -2. It would be thought that this would not appear until after the composition causing the appearance of the bands at 4737.1Å had been exceeded. Actually they first appear at the stoichiometric composition and become more intense with richness of the mixture. Furthermore, the intensity falls off at the upper limit as noted in Tables I, II, III and in Plate I. No ready explanation for this is obvious.

The absence of C_2 bands in mixtures rich in oxygen for ethylene combustion has been accounted for by Smith(3) by pointing out that the $^3\Pi C_2$ molecules can react readily with molecular oxygen in the ground state ($^3\Sigma$).

[redacted]

TABLE I

VARIATION OF EMITTER INTENSITY WITH COMPOSITION.

N-BUTANE-AIR INNER CONE.

BAND SYSTEM		COMPOSITION--VOL.% n-C_4H_{10} IN AIR		
Emitter	Wave length (angstroms)	3.02	3.65	4.14
		Relative Intensities		
C_2	5635.5	0	3	8
	5585.5	0	3	8
	5540.7	0	1	7
	5501.9	0	0	4
	5470.3	0	0	3
	5165.2	1	6	10
	5129.3	0	5	9
	5097.7	0	4	7
	4737.1	0	1	2
	4715.2	0	1	2
	4697.6	0	1	2
	4684.8	0	0	2
	4678.6	0	0	1
	4382.5	1	3	2
	4371.4	2	4	3
	4365.2	2	6	4
Unknown*	4942.0) 4937.5)	0	[1]	0
	4890.0	0	[1]	0
	4855.0 (?)	0	[1/2]	0
CH	4315.0) 4312.5)	6	9	7
	3889.0	5	6	4
	3872.0	5	6	4
	3144.9) 3144.1) 3147.4)	1	3	4
Hydro-carbon Flame Bands	3730.5	3	2	1
	3588.6	3	2	1
	3502.7	3	2	1
	3377.4	3	2	1
	3299.2	3	2	1
CH	3089.0	7	6	5
	3078.0	5	4	3

Unknown*	4942.0) 4937.5)	0	[1]	0
	4890.0	0	[1]	0
	4855.0 (?)	0	[1/2]	0
CH	4315.0) 4312.5)	6	9	7
	3889.0	5	6	4
	3872.0	5	6	4
	3144.9) 3144.1) 3147.4)	1	3	4
Hydrocarbon Flame Bands	3730.5	3	2	1
	3588.6	3	2	1
	3502.7	3	2	1
	3377.4	3	2	1
	3299.2	3	2	1
OH	3089.0	7	6	5
	3078.0	5	4	3
	3067.2	7	6	5
	3063.6	7	6	5
	2816.0	3	2	1
	2811.3	3	2	1

* See Raffety(e)
Brackets indicate 90 min. exposures.

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[redacted]

TABLE II

VARIATION OF EMITTER INTENSITY WITH COMPOSITION.

BUTENE-1 AIR INNER CONE.

BAND SYSTEM		COMPOSITION--VOL. % C_4H_8 IN AIR			
Emitter	Wave length (angstroms)	2.90	3.27	3.94	4.69
		Relative Intensities			
C_2	5635.5	0	3	6	9
	5585.5	0	3	6	9
	5540.7	0	2	6	8
	5501.9	0	1	5	7
	5470.3	0	0	4	6
	5165.2	1	6	8	10
	5129.3	1/2	5	8	9
	5097.7	0	3	6	8
	4737.1	0	1	3	5
	4715.2	0	1	3	5
	4697.6	0	1	3	5
	4684.8	0	0	2	5
	4678.6	0	0	2	3
	4382.5	0	1	3	1
	4371.4	1	3	5	3
	4365.2	2	5	7	5
Unknown*	4942.0) 4937.5)	0	[1]	[2]	0
	4890.0	0	[1]	[2]	0
	4855.0 (?)	0	[1]	[2]	0
CH	4315.0) 4312.5)	6	8	9	7
	3889.0	5	6	7	5
	3872.0	5	6	7	5
	3144.9) 3144.1) 3143.4)	1	3	5	6
Hydro-carbon Flame Bands	3730.5	5	6	4	2
	3588.6	5	6	4	2
	3502.7	5	6	4	2
	3377.4	5	6	4	2
	3299.2	4	5	3	1
	3015.0	5	6	4	2
OH	3089.0	7	6	5	4

Unknown*	4942.0) 4937.5)	0	[1]	[2]	0
	4890.0	0	[1]	[2]	0
	4855.0 (?)	0	[1]	[2]	0
CH	4315.0) 4312.5)	6	8	9	7
	3889.0	5	6	7	5
	3872.0	5	6	7	5
	3144.9) 3144.1) 3143.4)	1	3	5	6
Hydrocarbon Flame Bands	3730.5	5	6	4	2
	3588.6	5	6	4	2
	3502.7	5	6	4	2
	3377.4	5	6	4	2
	3299.2	4	5	3	1
	3015.0	5	6	4	2
OH	3089.0	7	6	5	4
	3078.0	6	5	4	3
	3067.2	7	6	5	4
	3063.6	7	6	5	4
	2816.0	3	3	2	1
	2811.3	3	3	2	1

* See Raffety (4)
Brackets indicate 90 min. exposure used.

TABLE III

VARIATION OF EMITTER INTENSITY WITH COMPOSITION.

BUTADIENE-1,3-AIR INNER CONE.

BAND SYSTEM		COMPOSITION--VOL. % C_4H_6 IN AIR			
Emitter	Wave length (angstroms)	3.07	3.66	4.27	5.30
		Relative Intensities			
C_2	5635.5	0	2	5	9
	5585.5	0	2	5	9
	5540.7	0	1	4	8
	5501.9	0	0	3	6
	5470.3	0	0	1	3
	5165.2	1	3	8	10
	5129.3	0	1	6	8
	5097.7	0	0	3	5
	4737.1	0	0	2	4
	4715.2	0	0	2	4
	4697.6	0	0	2	4
	4684.8	0	0	2	4
	4678.6	0	0	0	[1]
	4382.5	0	0	1	1/2
	4371.4	0	1	3	2
	4365.2	0	1	3	2
Unknown*	4942.0) 4937.5)	0	[1/2]	[1]	0
	4890.0	0	[1/2]	[1]	0
	4855.0 (?)	0	0	[1/2]	0
CH	4315.0) 4312.5)	5	8	9	2
	3889.0	2	4	5	3
	3872.0	2	4	5	3
	3144.9) 3144.1) 3143.4)	1	3	5	6
Hydrocarbon Flame Bands	3730.5	2	3	1	0
	3588.6	2	3	1	0
	3502.7	2	3	1	0
	3377.4	2	3	1/2	0
	3299.2	1	2	0	0
	3015.0	2	3	1	0
OH	3089.0	6	5	4	3
	3078.0	5	4	3	2
	3067.2	6	5	4	3
	3063.6	6	5	4	3
	2816.0	2	2	1	0
	2811.3	2	2	1	0

Unknown*	4942.0) 4937.5)	0	[1/2]	[1]	0
	4890.0	0	[1/2]	[1]	0
	4855.0 (?)	0	0	[1/2]	0
CH	4315.0) 4312.5)	5	8	9	2
	3889.0	2	4	5	3
	3872.0	2	4	5	3
	3144.9) 3144.1) 3143.4)	1	3	5	6
Hydrocarbon Flame Bands	3730.5	2	3	1	0
	3588.6	2	3	1	0
	3502.7	2	3	1	0
	3377.4	2	3	1/2	0
	3299.2	1	2	0	0
	3015.0	2	3	1	0
OH	3089.0	6	5	4	3
	3078.0	5	4	3	2
	3067.2	6	5	4	3
	3063.6	6	5	4	3
	2816.0	2	2	1	0
	2811.3	2	2	1	0

* See Raffety(4)
Brackets indicate 90 min. exposure used.

[redacted]

CH Bands The CH bands divided into three systems, the 4315 0Å system ($^2\Delta$ to $^2\Pi$ transition) the 3899.0 system ($^2\Sigma$ to $^2\Pi$ transition), and the 3144.1Å system ($^2\Sigma$ to $^2\Pi$ transition), increase in intensity to a maximum at a point intermediate between the stoichiometric point and the upper limit except for the 3144.1Å band. The band at 3144 1Å resembling a broad atomic line appears most intense at the mixture richest in hydrocarbon.

The Hydrocarbon Flame Bands. For all three hydrocarbons the hydrocarbon flame bands are most intense at the stoichiometric composition shading off in intensity for mixtures both lean and rich in hydrocarbon (Tables I, II and III and Plate I). These bands were originally observed for ethylene by Vaidya(4) who postulated HCO as the emitter. Association of the band system with the formation of alkyl peroxides has led Gaydon(5) to the conclusion that HCO was also the emitter. Smith(3) proposed HC-OH, as isomeric form of formaldehyde, on the basis of persistence of these bands mainly in mixtures rich in oxygen. Since they definitely appear to be most intense at the stoichiometric composition (e.g. Plate Ib) they doubtless contain oxygen but their exact nature is unknown. Of the probable reactions that might occur,

$$CH + O_2 \rightleftharpoons [CH.O_2] \rightleftharpoons CHO + O \qquad (1)$$

$$CH_2 + O_2 \rightleftharpoons [CH_2.O_2] \rightleftharpoons CHO + OH \qquad (2)$$

$$CH_3 + O_2 \rightleftharpoons [CH_3.O_2] \rightleftharpoons CHOH + OH \qquad (3)$$

(1) is ruled out because CH bands, as noted previously persist throughout the entire range and the CH molecule in a $^2\Pi$ state will not readily react with O_2 molecules in the lowest $^3\Sigma$ state. It might very well be that the hydrocarbon flame bands are due to both CHO and CH-OH formed by reactions of types (2) and (3)

OH Bands. The OH bands, two heads of which, 2811Å and 3063Å, are shown in Plate I are degraded to the red and for all three hydrocarbons (Tables I, II and III) decreased in intensity with increasing richness of the hydrocarbon-air mixture. The relative stability and abundance of the OH molecule indicates it to be of importance in combustion mechanisms.

[redacted]

Unknown Flame Bands. On longer exposure (Tables I, II and III) a series of bands of unknown origin at 4942.0Å, which have been termed the Raffety bands(8), appears at stoichiometric and intermediate composition but is absent in lean and very rich mixtures. They are degraded to the violet.

It should be emphasized that the emission spectra obtained contain no information about the absolute concentration of the radicals noted. Calculations(7) of the equilibrium concentrations of OH and C_2 and CH indicate that, although relatively high concentrations of OH are present, extremely small amounts of C_2 and CH are present in hydrocarbon combustion. Since one can observe (green color) C_2 and CH in a very narrow layer beyond the inner cone of a Bunsen burner(8) and since extremely intense C_2 and CH lines are seen even on short exposure these radicals must be non-equilibrium. Further, as pointed out in Technical Paper (3)(7) the C_2 and CH molecules are undoubtedly formed in an excited state at large concentrations, survive many collisions and then radiate the observed emission bands in going to the ground state where they quickly disappear.

[redacted]

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(6) Raffety, Phil.Mag., 32, 546 (1916).

(7) Technical Paper No. 3, "Atoms and Radicals in Flames. Estimates of Equilibrium Concentrations in the Combustion of n-heptane," March 1, 1946.

(8) Lewis and von Elbe, J. Chem. Phys., 11, 75 (1943).

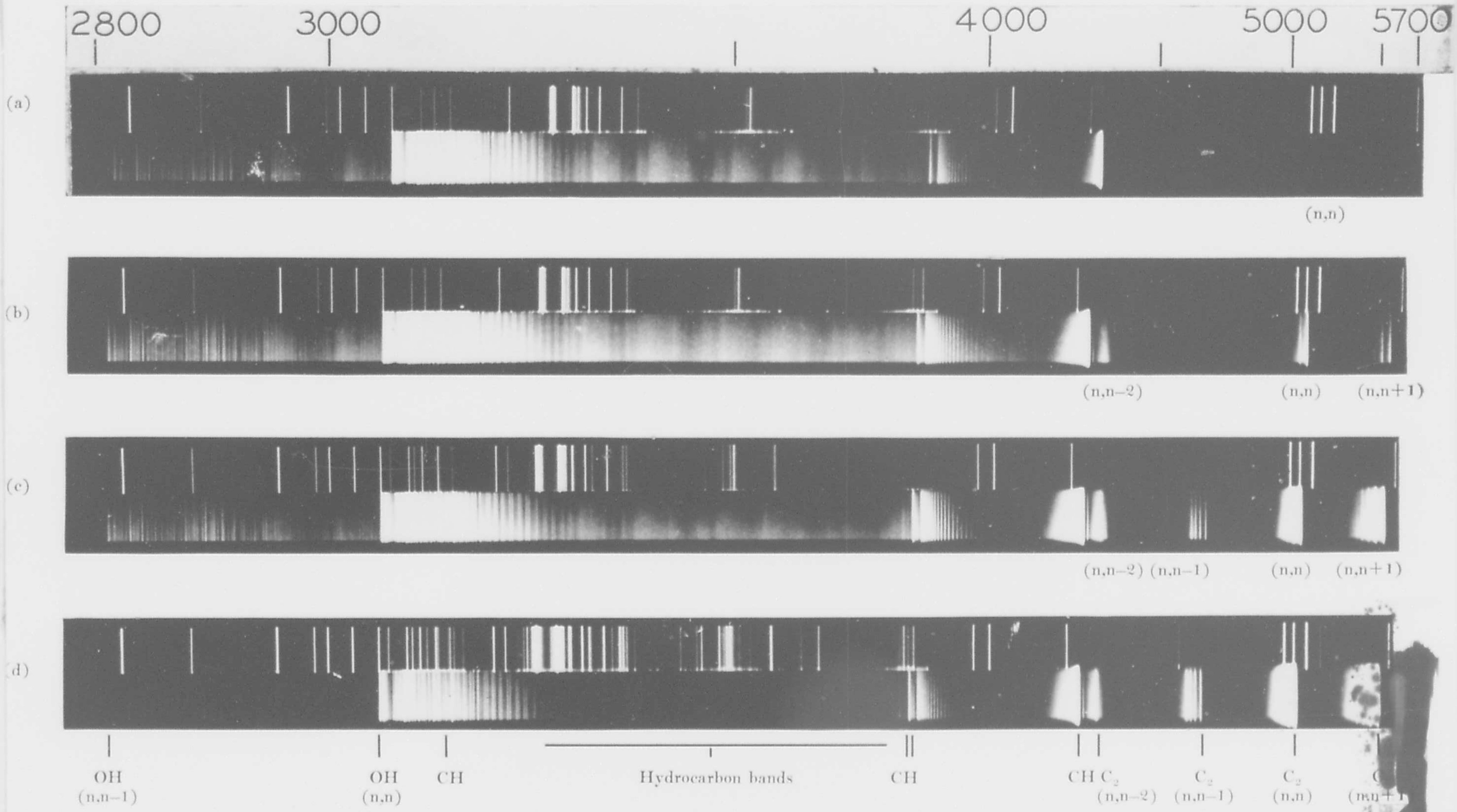

PLATE I. Emission Spectra of Butadiene-1,3 Air Flames.
(Copper comparison, 20.0 min. exposure, Air rate 2.71 liters/min.)

(a) 3.08 volume per cent butadiene-1,3 in air.
(b) 3.69 volume per cent butadiene-1,3 in air (stoichiometric point).
(c) 4.63 volume per cent butadiene-1,3 in air.
(d) 5.28 volume per cent butadiene-1,3 in air.

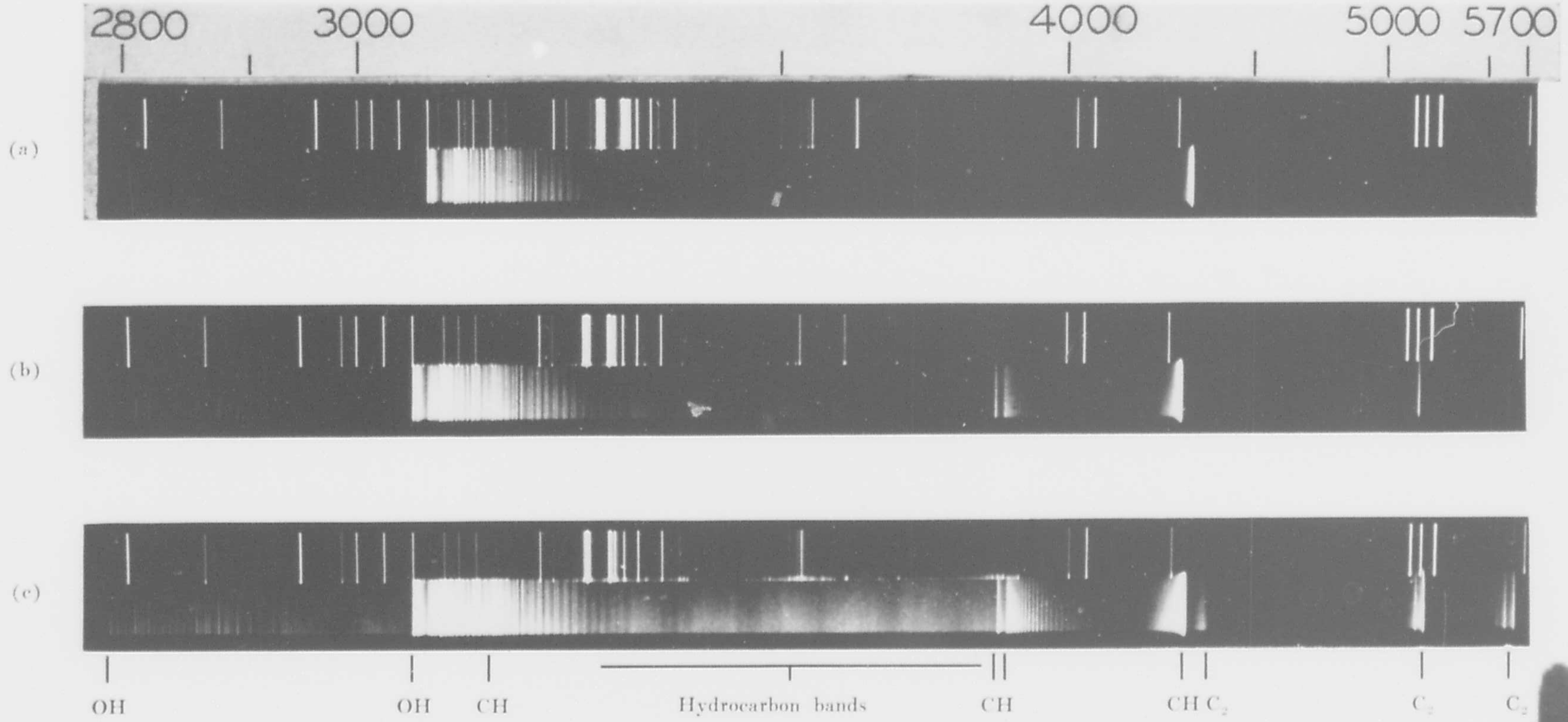

PLATE II. Emission Spectra for Combustion of C_4 Hydrocarbons.
(Copper comparison, 15.0 minute exposure, air rate 3.00 liters per minute)

(a) 3.12 volume per cent n–butane in air (Stoichiometric).
(b) 3.38 volume per cent butene–1 in air (Stoichiometric).
(c) 3.68 volume per cent butadiene–1,3 in air (Stoichiometric).

[redacted]

[redacted]

EMISSION SPECTRA OF HYDROCARBON COMBUSTION.
THE EFFECT OF ADDED NITROUS OXIDE

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(Transmitted by Robert N. Pease)

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Contract NOrd-7920, Task PRN-3

Technical Paper No. 20

February 1, 1947

SUMMARY

Hydrocarbon-air flames have been re-examined for the presence of NO bands. It was concluded that little or no NO is present in ordinary hydrocarbon-air flames.

Small added amounts of nitrous oxide led to formation of NO (γ-group), NH and CN bands in addition to CH, C_2, OH and "hydrocarbon bands." For a small controlled concentration of N_2O in air, intensities of NH and CN bands increased with increase of n-butane concentration. Furthermore, with increase of N_2O concentration, intensities of the CH bands seemed to increase. Combustion limits were broadened by the addition of small amounts of N_2O.

[redacted]

INTRODUCTION

In a previous paper(1) the variation of the various emitters in C_4 hydrocarbon combustion was observed for a traverse from the lower limit to the upper limit of combustion. It has been suggested that, if oxides of nitrogen, formed from oxygen and nitrogen in the air, are present in appreciable amounts they should be considered in mechanisms for combustion.

It has been observed by Strutt(2) that, with coal gas and air, neither the α nor the β groups of NO bands were present. If NO were present at any concentration near the equilibrium amount, the properties of a combustion zone usually attributed to an ion concentration (e.g., electrical conductivity, deflection by a d.c. field) could be accounted for on the basis of ionized NO alone, NO having a lower ionization potential (~9 e.v.) than any of the other species present.

Emission spectra here comprise a re-examination of hydrocarbon-air flames for NO bands, addition of varying amounts of nitrous oxide to the hydrocarbon and substitution of helium for nitrogen in the air.

APPARATUS AND METHOD

The apparatus and method used were identical with those employed in Technical Paper No. 19(1). Plates sensitized for the region 2000-5000 Å (Eastman type III-O) were used with a medium type Hilger quartz spectrograph.

Three flowmeters calibrated for the proper ranges were used; one for metering air, one for the hydrocarbon and one for nitrous oxide. Photographs were taken of a "mantled flame" through a quartz window, the light being focused by means of a spherical water-filled quartz lens onto the spectroscope slit. All spectrograms which were to be compared were taken on the same plate with standardized developing and printing times.

To determine the effect of nitrous oxide, three sets of exposures were made, each set including a composition just above the lower limit, the stoichiometric point, and a point just below the upper limit.

(1) n-butane-air:

(a) 2.95% n-butane
(b) 3.12% n-butane
(c) 4.16% n-butane

(2) n-butane-air (containing 2.00% N_2O):

(a) 2.91% n-butane
(b) 3.11% n-butane
(c) 4.36% n-butane

(3) n-butane-air (containing 5.03% N_2O):

(a) 2.88% n-butane
(b) 3.14% n-butane
(c) 4.50% n-butane

These spectrograms are shown in Plates I and II. The combustion limits (mantled 6.2 mm. I.D. quartz burner) for the three cases were 2.89 to 4.16%, 2.81-4.36%, and 2.81 to 4.53% by volume respectively.

RESULTS AND DISCUSSION

For additions of nitrous oxide to n-butane-air combustion two sets of exposures were obtained, one at short exposure time (10. min.) for the region 3000-4500Å and one of longer time (2 hrs.) for the region 2400-3000Å. In each case spectra were obtained at just above the lower limit, at a stoichiometric point and just below the upper limit as shown in Plates I and II.

For the region 3000-4500Å (Plate I) in addition to OH, CH and C_2 normally observed without N_2O addition, the NH bands (3360Å system, ${}^3\Pi \rightarrow {}^3\Sigma$ transition)

3360Å (0,0)
3370Å (1,1)

were observed. These bands were noted to increase in intensity with increase of N_2O concentration and with increase of n-butane concentration.

In addition the CN bands (violet system, ${}^2\Sigma \rightarrow {}^2\Sigma$ transition) with heads at 4216.0, 3883.4, and 3590.4Å were obtained. These include

4216.0	(0,1)
4197.2	(1,2)
4181.0	(2,3)
4167.8	(3,4)
4158.1	(4,5)
4152.4	(5,6)

[redacted]

3883.4	(0,0)
3871.4	(1,1)
3861.9	(2,2)
3854.7	(3,3)
3851.	(4,4)

3590.4	(1,0)
3585.9	(2,1)
3583.9	(3,2)

The last two bands in each case merged due to their close proximity. Further the (0,0) and (1,1) were masked by the CH bands at 3872 and 3889Å. The CN bands also increased in intensity with N_2O concentration and with n-butane concentration.

For the region 2400-3000Å (Plate II) the only emitter present in addition to OH was the γ-group of NO bands (Deslandres' third positive nitrogen group, transition $^2\Sigma \rightarrow {}^2\Pi$). These were double headed at

2478.7	(0,2)
2471.1	
2558.6	(1,4)
2551	
2595.7	(0,3)
2587.5	
2680	(1,5)
2671	
2722.2	(0,4)
2713.2	

Two other bands of the same system with heads at 2859.5 and 2849.8Å and 3008.8 and 2997.6Å were masked by the OH bands. Examination of Plate II (1), n-butane-air containing no N_2O, shows a diffuse band system corresponding roughly to the NO band system at 2558Å. The diffuse system is not OH (lowest recorded value 2608.5Å) nor is it a "hydrocarbon flame band" (lowest recorded value 2585.5Å, degraded to the red). The "hydrocarbon flame band" is further ruled out because the diffuse system persists in mixtures rich in n-butane. Substitution of helium for nitrogen yielded the same system but much fainter. The same band also appeared with a butadiene-1,3 air flame The conclusion, therefore, is that it is not

[redacted]

due to NO or, if it is NO, NO is present to a very small extent in the hydrocarbon air flame.

Bands due to NO, NH and CN have been observed faintly in hot flames such as acetylene-air. Strutt(2) has observed the γ-group of NO bands in gas-N_2O flames without observing it in coal gas-air flames. Vaidya(4) has observed CN bands in flames of nitrobenzene, piperidene and aniline and Gaydon(5) has observed both CN and NH in flames containing ethyl nitrate. Barratt(6) also observed CN bands in coal gas-nitrous oxide flames.

An interesting observation is that although the NO bands remain at about the same intensity for lean, stoichiometric and rich mixtures of n-butane in air (containing N_2O), the intensities of the NH and CN bands increase with hydrocarbon concentration. This, coupled with the broadening of limits produced by small N_2O additions* indicates that these radicals and N_2O are of importance in the primary reaction and are not produced simply in a secondary way after combustion is essentially complete. This could lead to excited N_2 molecules as carriers as postulated by Kondratjew et al(7) and Bone and Newitt(8) on the effect of N_2 on the CO-oxygen flame. In this reaction it is likely that N_2 is activated by collision with excited CO_2 and can then react with O_2 to yield NO. For the presence of N_2O in butane-air

$$N_2O \longrightarrow N_2^* + O \qquad (1)$$

and

$$N_2^* \longrightarrow N + N$$

Then

$$CH_3 + N_2^* \longrightarrow NH + NH + CH \qquad (2)$$

or

$$CH_2 + N \longrightarrow CH + NH$$

Similarly

$$CH + N_2^* \longrightarrow CN + NH \qquad (3)$$

This type of reaction could lead, not only to CN and NH, but would tend to increase CH band intensities. This is actually observed (Plate I) with increase of N_2O concentration.

(*) n-butane air limits: 2.89-4.16%
n-butane-air (containing 2.00% N_2O) limits: 2.81-4.36%
n-butane-air (containing 5.03% N_2O) limits: 2.81-4.53%

[redacted]

It was observed in the combustion studied with N_2O added that a yellow-green color was imparted to the flames. It has been concluded by Spealman and Rodebush(9) that the air after-glow (discharge passed through air) was due to

$$NO + O \longrightarrow NO_2 + h\nu$$

Gaydon(10) also found that a continuous emission with its maximum in the yellow-green was due to reaction between atomic oxygen and NO and concluded(11) that this was a possible test for atomic oxygen in flames; the presence of atomic oxygen being visually apparent by the yellow-green color of NO_2. In the present study this color was noted to be very pronounced in the outer (mantled) cone verifying the observations of Gaydon on hydrocarbon flames.

[redacted]

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(1) Technical Paper No. 19, "Emission Spectra from the Combustion of C_4 Hydrocarbons", February 1, 1947.

(2) Strutt, Proc. Roy. Soc., 93, 254 (1917)

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(8) Bone and Newitt, Proc. Roy. Soc., A115, 41 (1927).

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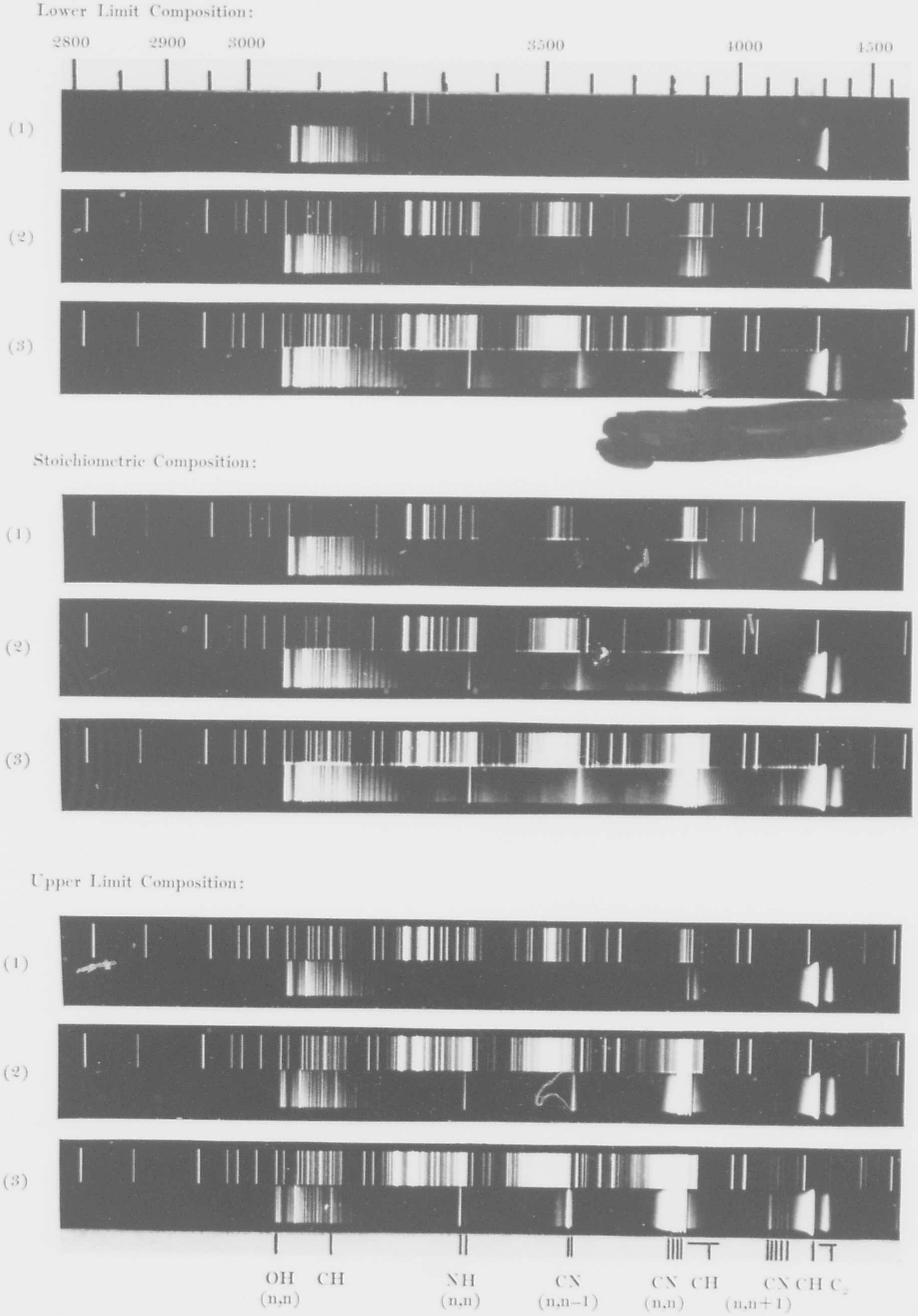

PLATE I. Emission Spectra of n–Butane–Air Flames containing N_2O (Cu comparison, 10.0 min. exposure).

(1) n–Butane–Air.

(2) n–Butane–Air (containing 2.00 % N_2O).

(3) n–Butane–Air (containing 5.03 % N_2O).

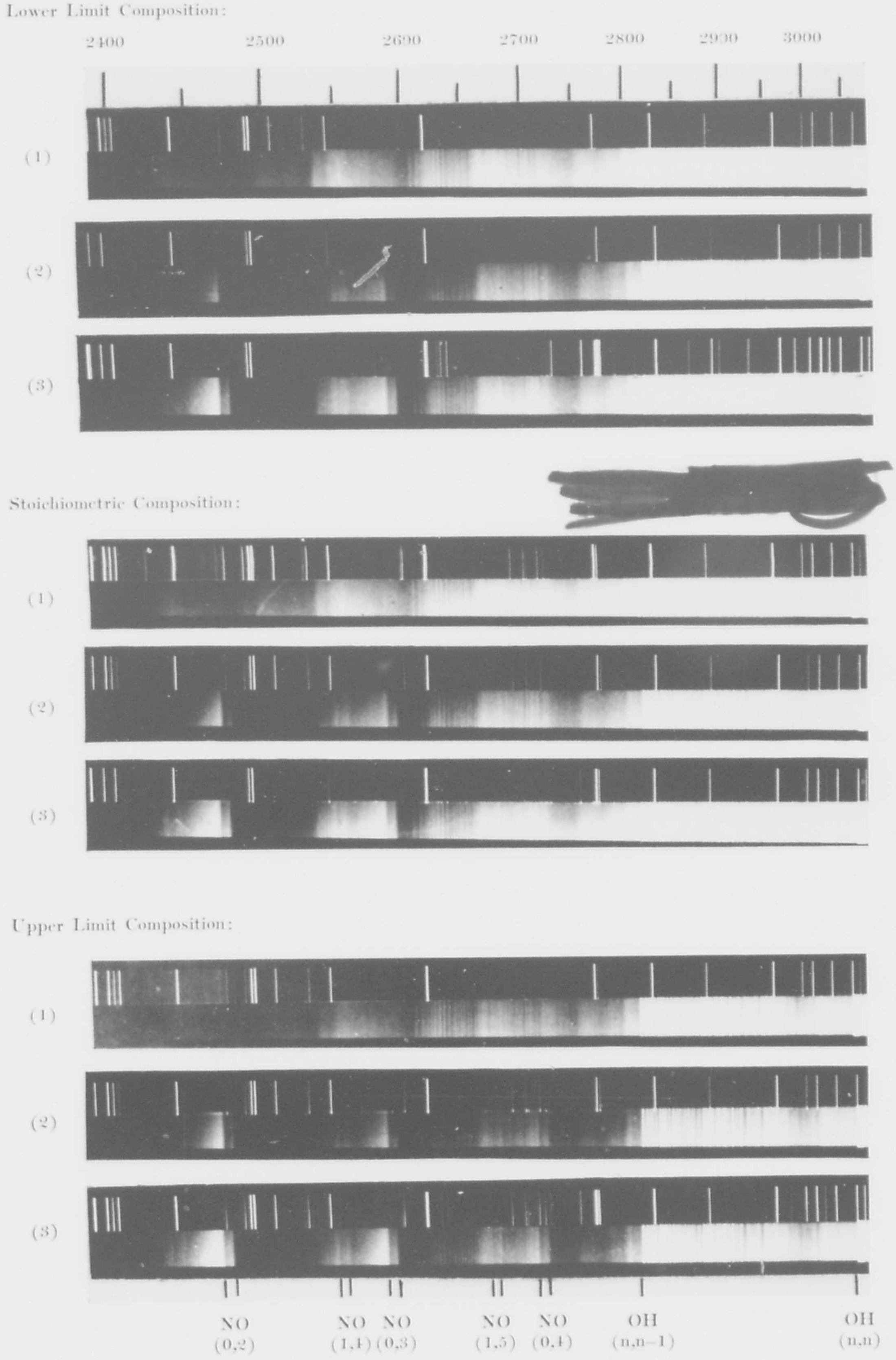

PLATE II. Emission Spectra of n–Butane–Air Flames containing N_2O (Cu Comparison, 120. min. exposure).

(1) n–Butane–Air.

(2) n–Butane–Air (containing 2.00 % N_2O).

(3) n–Butane–Air (containing 5.03 % N_2O).

[redacted]

COMBUSTION OF ETHYLENE OXIDE IN AIR.

EMISSION SPECTRA STUDY.

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Contract NOrd-7920, Task PRN-3

Technical Paper No. 21

February 1, 1947

SUMMARY

Emission spectra for ethylene oxide-air flames have been obtained for variation in composition of ethylene oxide and air. From the variation in the relative intensities of C_2, CH, OH and "hydrocarbon bands" it has been concluded that mixtures "rich" in ethylene oxide exhibit "weaker" flames or "cool flame" characteristics. The outer cone of ethylene oxide air flames contains predominantly OH and the CO bands.

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INTRODUCTION

Ethylene oxide-air mixtures are combustible over a very much larger range than ordinary compounds. In addition it has been observed(1) that, for the low pressure limits in ignition experiments for upward flame propagation in a pyrex tube, a very broad "cool flame" region existed. The area of this cool flame region and the slowness of flame propagation indicated that mixtures rich in ethylene oxide underwent a type of combustion differing from the normal.

The ethylene oxide-air flame has been examined spectroscopically for

(1) a variation in relative emitter intensities from lean to rich, and

(2) emission spectra of the inner and outer cones of a "rich" flame

The results are reported in this paper.

APPARATUS AND METHOD

The apparatus and method used were essentially similar to that described previously.(2)

A 6.2 mm. I.D. quartz burner was used in all experiments. Gases from the metering system were premixed and ignited at the burner port. Light was focused through a spherical quartz lens onto the spectroscope slit. In making exposures of a particular flame zone, stray light from the rest of the flame was partially eliminated by sectioning it off with black metal sheets.

A 25 mm. I.D. quartz mantle with side viewing tube to which a plane section of quartz was cemented was used for viewing the mantled flames. The mantle was removed for making exposures of the outer diffusion cone.

The ethylene oxide was obtained from the Mathesm Co.

RESULTS AND DISCUSSION

In Table I data are contained for variation of emitter intensity with composition for ethylene oxide-air combustion Intensities have been rated on a scale 0 to 10 from exposures taken on the same plate (not shown). In plate I spectra for variation of ethylene oxide composition are shown to indicate the same relative changes in intensities.

From Table I the spectra of ethylene oxide-air flames can be seen to differ from hydrocarbon-air flames (previously reported[(2)]) in the following respects.

(1) C_2 (4382.5A) increases to a maximum intensity at stoichiometric and then decreases.

(2) CH (4315, 3889.0, 3872A) increases to maximum intensity at stoichiometric then decreases.

(3) OH (3089, 3063.6, 2811.3A) decreases in intensity from lean to rich. (i.e. lean and rich in ethylene oxide).

From these observations it would seem that, in general, maximum intensities of all emitters occur either in lean or stoichiometric mixtures and never in mixtures rich in fuel as sometimes noticed in hydrocarbon combustion. This may be interpreted as indicating that in "rich" mixtures of ethylene oxide a "weaker" type of combustion is obtained. This is in agreement with the observations that very high upper limits for ethylene oxide combustion are obtained and that "cool flame characteristics" occur in rich mixtures.

When ethylene oxide was burned in a mantled burner (Smitthels flame separator), three distinct zones of combustion were observed. These are diagrammed in Figure I. Spectra for the inner cone and the outer separated cone were photographed, the outer cone showing only OH bands. The middle (red-violet) cone (Figure I) was also photographed and showed a very slight intensity of OH only. This cone was very faint and was only visible in a darkened room. When the flame was allowed to burn without a mantle OH and CO bands were observed in the outer diffusion cone. The spectrum of the outer cone of the Bunsen flame has been shown to contain OH and the CO spectrum(3) as has been observed here for ethylene oxide.

[redacted]

TABLE I

VARIATION OF EMITTER INTENSITY WITH COMPOSITION.

ETHYLENE OXIDE-AIR INNER CONE.

BAND SYSTEM		INTENSITIES [1]			
Emitter	Wave length (Angstroms)	4.31% C_2H_4O in air	7.75% [2] C_2H_4O in air	8.75% C_2H_4O in air	9.67% C_2H_4O in air
C_2	5635.5	0	5	7	9
	5165.2	0	6	8	10
	4737.1	0	2	3	3
	4382.5	1	5	3	2
CH	4315.	3	10	8	6
	3889.0	6	8	5	2
	3872.	6	8	5	2
"Hydro-carbon Bands"	3588.6	6	5	1	0
	3502.7	6	5	1	0
	3377.4	6	5	2	1
	3299.2	6	5	2	1
OH	3089.	9	7	5	3
	3063.6	9	7	5	3
	2811.3	3	2	1	0

[1] Visual estimates, arbitrary scale 0 to 10.

[2] Stoichiometric composition. Combustion to CO_2 and H_2O.

[redacted]

REFERENCES

(1) Technical Paper 6, "Low Pressure Ignition Limits (Spark) of 16 Organic Vapors in Air", Figure VIII, April 10, 1946.

(2) Technical Paper No. 19, "Emission Spectra of C_4 Hydrocarbon Flames", February 1, 1947.

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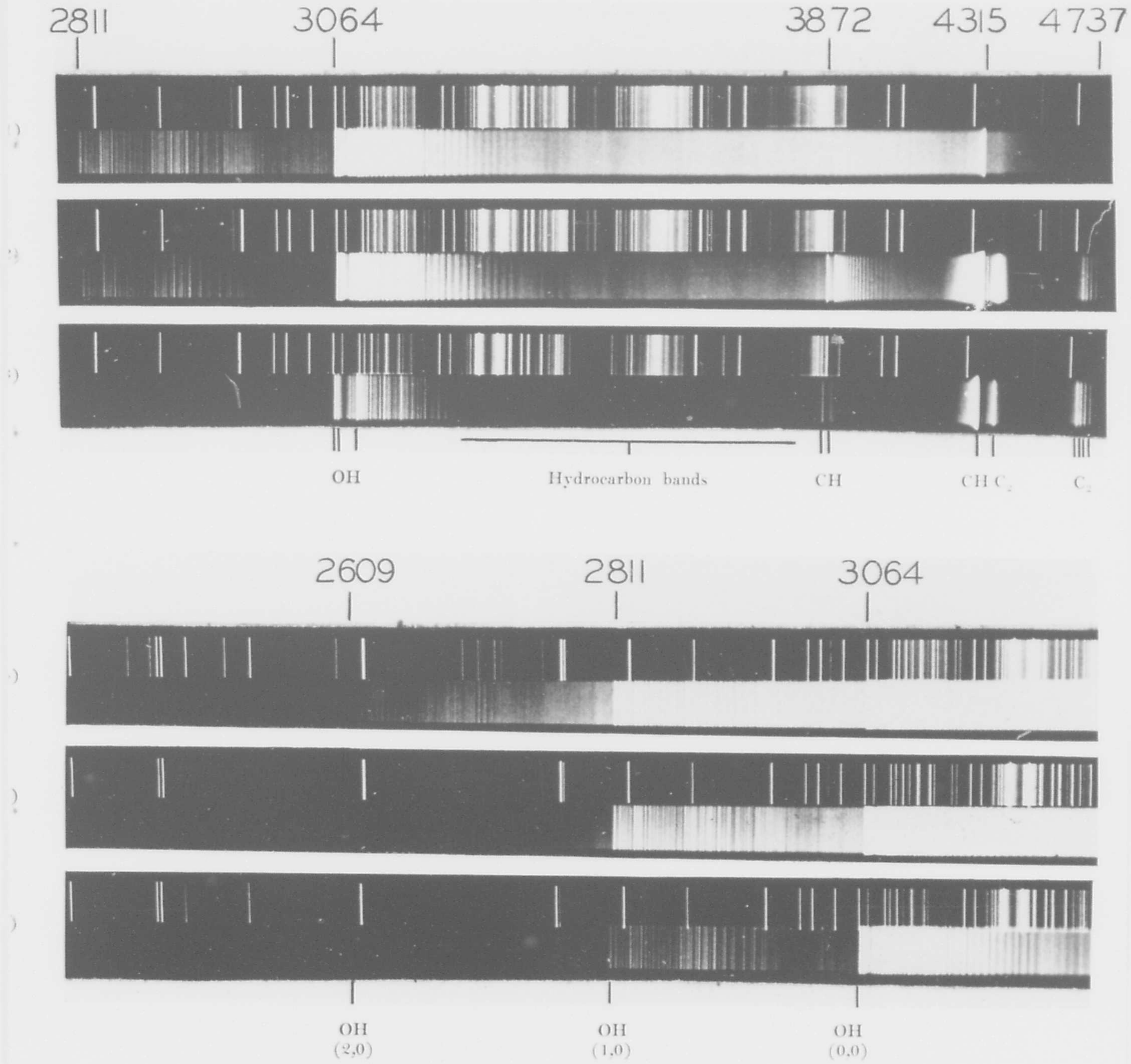

PLATE I. Emission Spectra for Ethylene Oxide–Air Combustion (Cu comparison).

(1) 4.67 volume % ethylene oxide in air (10 min. exposure).
(2) 8.09 volume % ethylene oxide in air (10 min. exposure).
(3) 9.67 volume % ethylene oxide in air (10 min. exposure).
(4) Same as (1) (60 min. exposure).
(5) Same as (2) (60 min. exposure).
(6) Same as (3) (60 min. exposure).

[redacted]

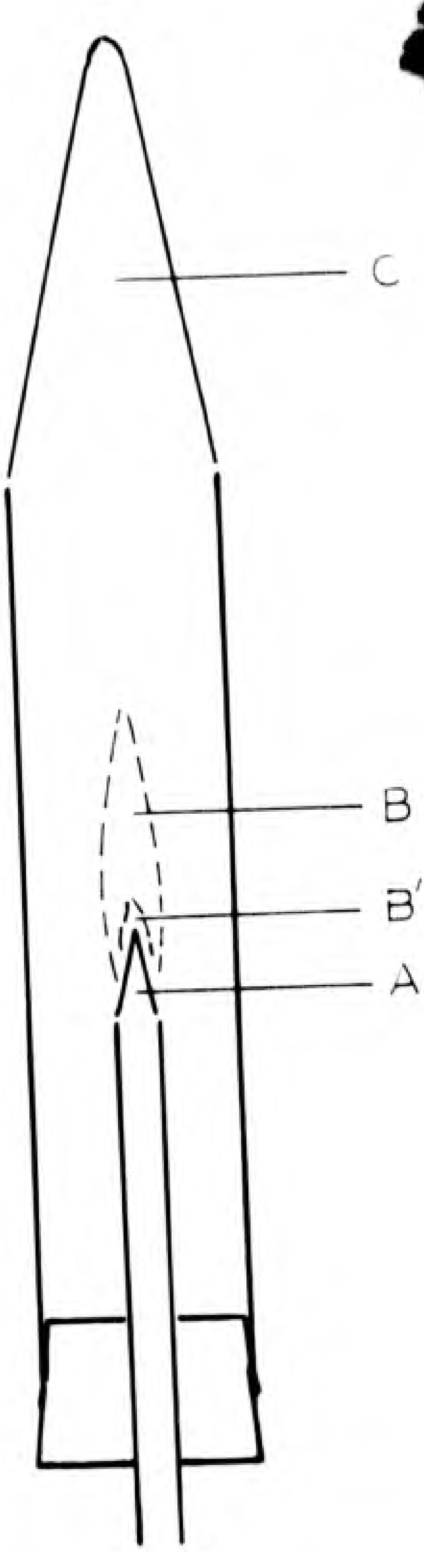

FIGURE 1

DIAGRAM OF ETHYLENE OXIDE - AIR FLAME (MANTLED)
(8.6 % ETHYLENE OXIDE IN AIR)

A	Primary (inner) cone. Green-blue.
B,B′	Violet red cone (visible only in darkened room).
C	Large outer cone. Pale violet blue.

[redacted]

THERMAL DECOMPOSITION OF ALUMINUM BOROHYDRIDE

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Contract NOrd-7920, Task PRN-3

Technical Paper No. 22

February 1, 1947

SUMMARY

A study of the vapor phase thermal decomposition of aluminum borohydride vapor has been made for the temperature range 150°-200°. The principal products of decomposition were hydrogen and a polymeric inhomogeneous solid residue. The latter evolved hydrogen on addition of water. Water vapor was found to inhibit the rate of decomposition; further, the amount of hydrolysis of aluminum borohydride vapor with liquid water, as measured by the amount of gas evolution, decreased with increase of temperature.

[redacted]

INTRODUCTION

In studying the combustion of aluminum borohydride(1) it was found that spontaneous explosive oxidation of aluminum borohydride vapor with dry oxygen occurred readily at 110°. Further, water vapor catalyzed the combustion to such an extent that moist oxygen would cause spontaneous reaction at 20°. This has prompted an investigation of the vapor phase thermal decomposition of aluminum borohydride at reduced pressures to determine primarily,

(a) the temperatures at which decomposition was appreciable.

(b) the products of thermal decomposition as being of importance for the initiation of the combustion reaction with oxygen.

In addition, since water vapor had such a profound effect on the explosive oxidation limit, the effect of water vapor on the thermal decomposition has been noted.

APPARATUS AND METHOD

The apparatus used is diagrammed in figure I. The spherical reaction bulb B (diameter 6.8 cm., pyrex) was equipped with a capillary side arm as shown in figure I, and was sealed directly to the apparatus or to a bulb of the same size fastened to the apparatus by means of a glass joint. Reaction flasks were cleaned with boiling nitric acid and distilled water and dried at 135°C.

The aluminum borohydride was obtained from the Naval Research Laboratory and the Ethyl Corporation and contained in vial A fitted with a glass enclosed iron core which could be lowered magnetically to break the seal. The aluminum borohydride was kept frozen when not in use. A thin film of Apiezon stopcock grease was used on all stopcocks. Use of an all metal valve X was not as satisfactory as an ordinary stopcock. Contamination from stopcock grease was negligible since all experiments were of such short duration.

Aluminum borohydride vapor was metered into the thermostated reaction bulb and the pressure changes followed on a mercury manometer. The connecting tubing to the manometer was lightly wound with electrically heated wire. At the higher temperatures where decomposition was very fast, the aluminum borohydride was metered at room temperature and the thermostat applied.

[redacted]

Tube C was a Töpler pump used to obtain gas samples while D was a graduated burette connected to a manometer so that a given quantity of gas could be obtained. Initially gaseous products of combustion were tested for volatile boron hydrides in D by adding water through the capillary side arm The volatile boron hydrides B_2H_6 and B_4H_{10} were shown to be absent since no hydrogen was evolved even after 24 hours. Side arm E was used to admit water to the reaction bulb B.

Gases were analyzed for hydrogen by CuO combustion at 310°. Analyses for aluminum were made using 8-hydroxy quinoline.

RESULTS AND DISCUSSION

THERMAL DECOMPOSITION

The thermal decomposition of aluminum borohydride was measurable at 150° and higher temperatures. A set of data for various initial pressures at 200° is shown in figure I. The initial or maximum rate, $\frac{d(\Delta P)}{dt}$, has been determined from the slopes of the decomposition curves and is shown in table I.

A plot of the rate versus the initial pressure of aluminum borohydride (figure II) was essentially linear indicating that initially the rate = k $[Al(BH_4)_3]$. However, the rate of decomposition at a given temperature decreased rapidly indicating the reaction to be inhibited by the products formed as can be seen in figure I.

If the formula for aluminum borohydride be examined, it will be seen that six hydrogen atoms on the average are unsatisfied electronically with resonance stabilizing the molecule. Easy loss of hydrogen is thus explained. Schlesinger and coworkers(2) have shown that aluminum borohydride at room temperature loses 0.5 to 1% of its hydrogen over a course of 20-30 days, the decomposition at room temperature being entirely in the liquid phase. They have also shown that extensive decomposition yields hydrogen and a polymeric residue which is not homogeneous and has the average composition AlB_3H_8.

[redacted]

TABLE I

THERMAL DECOMPOSITION OF ALUMINUM BOROHYDRIDE

(Vapor Phase, 6.8 cm. diameter bulb)

Temperature (°C)	Initial pressure $Al(BH_4)_3$ at the reaction temperature, (mm. Hg.)	Initial rate $\frac{d(\Delta P)}{dt}$ (mm./sec x 10^2)
150°	50	0.74
	100	0.98
	200	1.6
175°	50	5.0
200°	25	2.7
	50	7.5
	100	13.
	150	24.
225°	25	17.
250°	50	380.

[redacted]

Vapor phase thermal decomposition in the present study was carried out using spherical pyrex bulbs of 6.8 cm. diameter. The bulbs were uniformly cleaned and dried at 135°C to insure "dry" surfaces. Under these conditions no precipitate was noticed as forming at 150° and 175° although hydrogen was evolved. At 200° amber irridescence formed on the walls while at 225° and 250° a denser brown precipitate formed. These results seemed to indicate inhomogeneity of the deposit. In table II data are shown for decompositions at several temperatures; the extent of each decomposition was determined by weighing a 150 ml. sample of the gaseous products at a known temperature (20°) at the end of 2500 seconds. Since volatile boron hydrides (e.g. B_2H_6, B_4H_{10}) other than aluminum borohydride were shown to be absent, (see above) this sample was a mixture of hydrogen and undecomposed aluminum borohydrid The percentage of each present has been calculated from the molecular weight obtained.

Taking the reaction

$$AlB_3H_{12} \longrightarrow AlB_3H_x + (\frac{12-x}{2})\ H_2$$

as one reaction which probably predominates and with x equal to about 8, two molecules of hydrogen should be evolved for every aluminum borohydride molecule. The pressure changes shown in table II and analysis of residues are in agreement with this. However, it seems that at higher temperatures (e.g. 250°) more than $2H_2$ for every $Al(BH_4)_3$ can be evolved. In the temperature range to 200° it seems that hydrogen is evolved with formation of a polymeric inhomogeneous residue of empirical formula AlB_3H_8 in agreement with the observations of Schlesinger and coworkers(2). When consecutive experiments were made in the same bulb it was found that a slightly slower decomposition rate took place with a vessel coated with the brown residue. This was also observed by Schlesinger(2) who stated that the brown coating formed at 200° seemed to inhibit the decomposition. The effect of added hydrogen seemed to be one of inhibition also. Thus, decomposition of 50 mm. initial pressure of $Al(BH_4)_3$ at 200° had an initial rate of 7.5×10^{-2} mm./sec. while 50 mm. $Al(BH_4)_3$ and 10 mm. hydrogen gas initial had the rate 5.3×10^{-2} mm./sec.

A further study of the residue was made by subjecting it to hydrolysis. At the end of a decomposition the gas evolved was pumped off, the reaction bulb evacuated and cooled and liquid water added through the side capillary tube. Hydrogen was steadily evolved at a rate which had levelled off at the end of 2500 seconds. However, in no case was all the hydrogen contained in the residue evolved. For example,

[redacted]

TABLE II

THERMAL DECOMPOSITION OF ALUMINUM BOROHYDRIDE

(6.8 cm. diameter bulb, reaction time 2500 sec.)

Decomposition Temperature °C	Initial Pressure $Al(BH_4)_3$ at the reaction temperature (mm.)	FINAL MIXTURE			
		Pressure at the reaction temperature (mm.)	Mean Molecular Weight (approx.)	Composition (calc'd. from mol. wt.)	
				% H_2	% $Al(BH_4)_3$
175°	160	201	23	70	30
200°	160	326			
200°(1)	160	347	5	96	4
200°	160	318	4	96	4
250°	160	445	6	95	5

---

[1] Deposit formed contained 39.4% Al. For $Al(BH_4)_3$, 37.7% Al. For AlB_3H_8, 40.0% Al.

a thermal decomposition with 160 mm. initial pressure $Al(BH_4)_3$ at 200° was carried out to 2500 seconds. At the end of this time the hydrogen evolution had substantially levelled off and the hydrogen evolved corresponded approximately to the equation

$$AlB_3H_{12} \longrightarrow "AlB_3H_8" + 2H_2$$

The residue (0.2930 g.) analyzed for 39.4% Al. The experiment was repeated and the gases evolved at the end of 2500 seconds were pumped off. The residue was cooled and liquid water added through the side capillary tube and the residue hydrolyzed at 66°. After 2500 seconds when substantially no more hydrogen was evolved, the pressure of the gas (quantitatively combustible over CuO at 310°C, density corresponding to molecular weight 2) was 448 mm. (corrected for water vapor pressure). This corresponded to 82. ml. H_2 at S.T.P. The amount of hydrogen expected on the basis of the equation

$$"AlB_3H_8" + 12H_2O \longrightarrow 3B(OH)_3 + Al(OH)_3 + 10H_2$$

would be 972. ml. H_2 at S.T.P. assuming that the same amount of residue (i.e. 0.2930g.) was formed in the second experiment

[redacted]

as in the first. The residue before reaction with water was brown; after reaction, white.

We may, therefore, conclude that during thermal decomposition in the temperature range 200° hydrogen is evolved yielding about $2H_2$ for every AlB_3H_{12} molecule. The solid residue formed can also yield a further small quantity of hydrogen with the final hydrolyzed residue retaining hydrogen and probably coordinated water in a polymerized molecule.

EFFECT OF WATER ON THE THERMAL DECOMPOSITION

In table III data are shown for the effect of water vapor on the thermal decomposition of $Al(BH_4)_3$ vapor. When the $Al(BH_4)_3$ was added to the initial amount of water vapor, a dense white cloud formed immediately followed in each case by a pressure rise of 4 mm. The decomposition then followed a course as without the presence of water vapor. In calculation of the rates in table III the first initial increase of 4 mm. has been discounted. From the data it can be seen that water vapor has an inhibiting effect on the decomposition

In the same connection it has been found of interest to study the hydrolysis of aluminum borohydride vapor itself by adding liquid water to the initial pressure of $Al(BH_4)_3$ vapor at a definite temperature and determine the amount of hydrogen evolved. Data are contained in table IV. Hydrolyses were carried out to 2500 sec. at which time hydrogen evolution had substantially ceased and analysis showed the gas present to be hydrogen only. Data have been expressed as a ratio $P_{H_2}/P_0Al(BH_4)_3$ where P_{H_2} is the final gas pressure corrected for the vapor pressure of water and $P_0Al(BH_4)_3$ is the initial pressure of aluminum borohydride vapor. For quantitative hydrogen evolution according to

$$AlB_3H_{12} + 12H_2O \longrightarrow Al(OH)_3 + 3B(OH)_3 + 12H_2$$

one would expect the ratio to have a value of 12. Actually the ratio decreases with increase of temperature and at 60° formed a brown residue. It thus seems that hydrogen in each case is still retained in the solid residue and that the higher temperature inhibits the evolution of hydrogen. The data are in agreement with results in table III which show inhibition by water vapor during thermal decomposition.

It is believed that the "combustion" of aluminum borohydride and water vapor will take place. This reaction of aluminum borohydride with water has been reserved for future study.

[redacted]

TABLE III

EFFECT OF WATER VAPOR ON THE THERMAL DECOMPOSITION OF ALUMINUM BOROHYDRIDE

Temperature °C	Initial Pressure $Al(BH_4)_3$ (mm.)	Initial Pressure H_2O (mm.)	Initial Rate $\frac{d(\Delta P)}{dt}$ (mm./sec. x 10^2)
175°	25	0	0.58
	25	10	0.46
200°	25	0	2.8
	25	10	1.5
225°	25	0	17
	25	10	4.6

[redacted]

TABLE IV

HYDROLYSIS OF ALUMINUM BOROHYDRIDE VAPOR WITH LIQUID WATER

Temperature °C	Initial Pressure Aluminum borohydride $P_oAl(BH_4)_3$ (mm at reaction temperature)	$\frac{P_{H_2}}{P_oAl(BH_4)_3}$ (at 2500 sec.)	Residue
0	40.7	8.3	White
0	40.9	8.4	White
20	20.0	8.5	White
20	20.2	8.5	White
20	37.3	8.4	White
40	42.6	7.6	Brown-White
40	40.2	7.6	Brown-White
60	41.3	7.0	Brown
60	39.1	6.9	Brown

[redacted]

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(1) Technical Paper No. 13. "Preliminary Report on Combustion of Aluminum Borohydride", July 8, 1946.

(2) Schlesinger, "Boron Hydrides", Final Report July, 1946, Naval Research Laboratory, N.R.L. Report P 2964.

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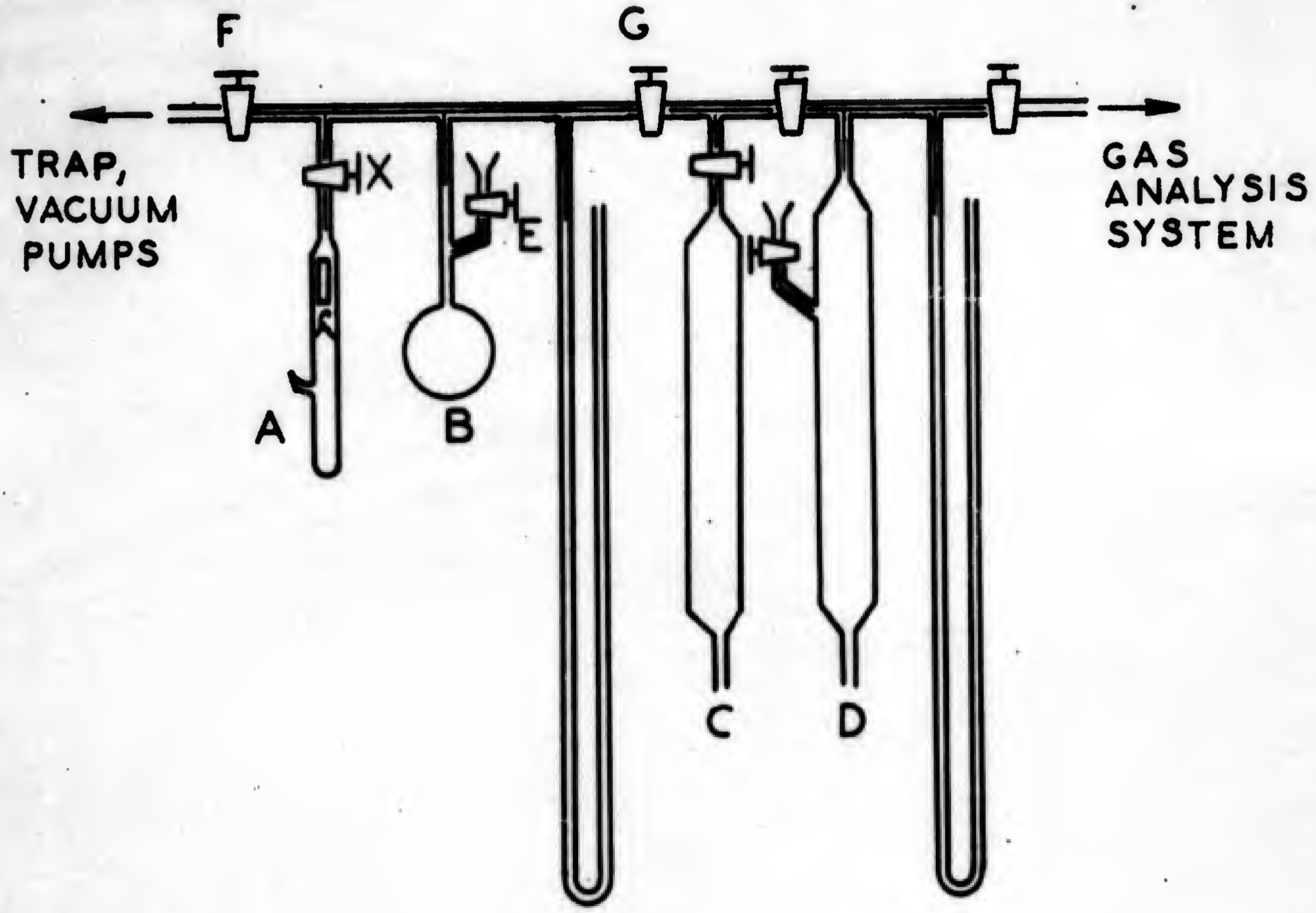

FIGURE 1

APPARATUS

[redacted]

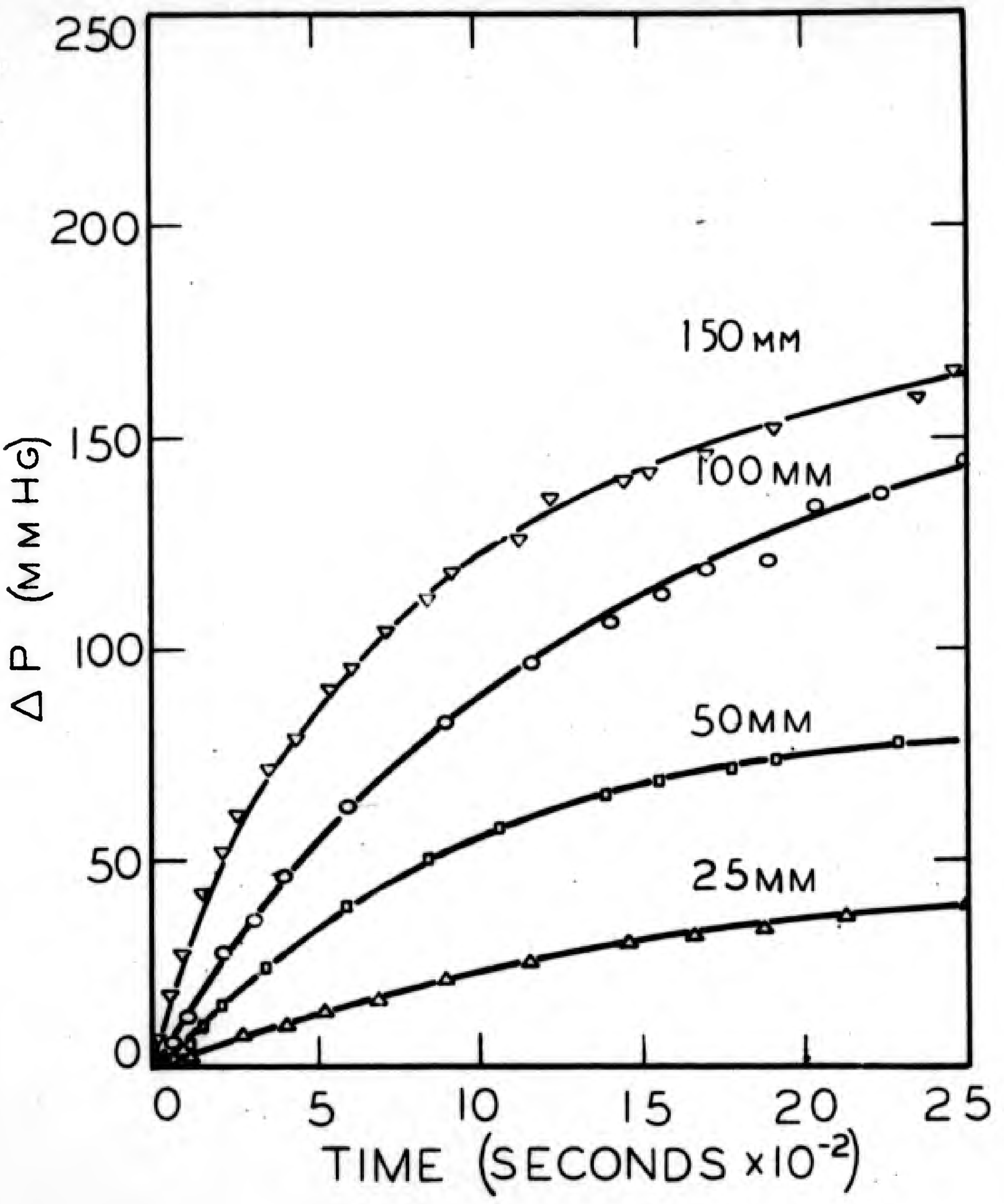

FIGURE 11 THERMAL DECOMPOSITION OF ALUMINUM BOROHYDRIDE AT 200° AND VARIOUS INITIAL PRESSURES.

(ALL PRESSURES AT 200°)

[redacted]

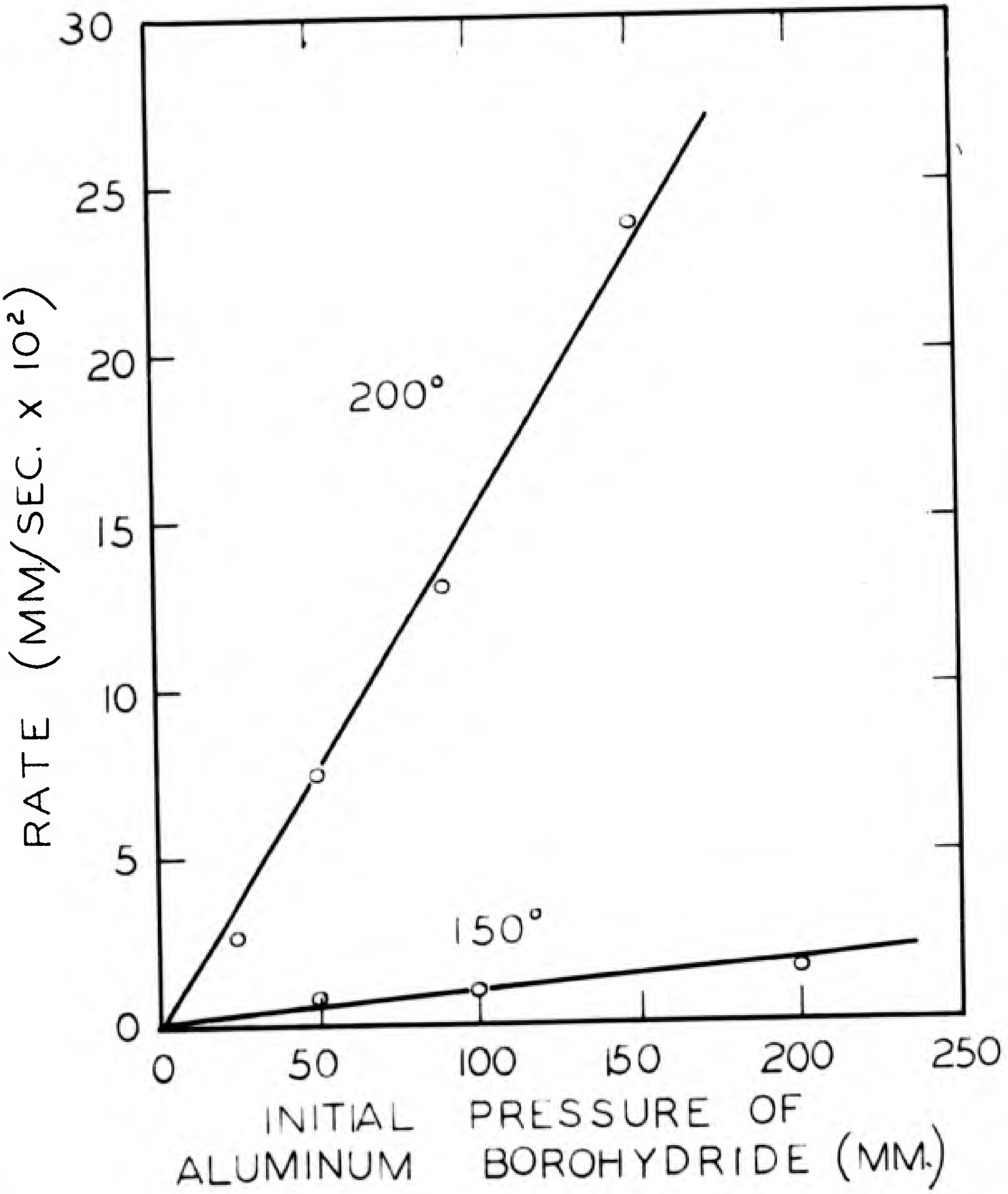

FIGURE III

THERMAL DECOMPOSITION OF ALUMINUM BOROHYDRIDE. VARIATION OF RATE WITH INITIAL PRESSURE.

[redacted]

ELECTRONIC CHRONOSCOPE FOR MEASUREMENT OF FLAME SPEEDS

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Contract NOrd-7920, Task PRN-3

Technical Paper No. 23

February 1, 1947

SUMMARY

An electronic chronoscope has been designed and constructed with eleven available ranges, the full scale reading varying from $4X10^{-3}$ seconds to 14 seconds. The instrument has been calibrated by means of a one-shot multivibrator, which is described herein, against an electric stop watch and an audio oscillator.

By utilizing the flame conductivity, flame speeds have been measured from 35 mm. of Hg up to atmospheric pressure. The flame speeds measured have covered the range from 26 cm. per sec. to 5700 cm. per sec., corresponding to time intervals of 0.76 seconds to $3.6X10^{-3}$ sec. respectively.

[redacted]

INTRODUCTION

The measurement of flame speeds may be achieved by a variety of methods, the majority of which require the use of a camera. Since it is desirable to have a simple method in which the velocity can be read directly on a meter, avoiding the time delay incurred in developing film, an electronic chronoscope has been designed and constructed for this purpose.

As the flame passes a given point in the reaction tube a condenser is started discharging through a resistance, and the discharging is stopped when the flame passes a second point. The charge on the condenser is then indicated by an electrometer voltmeter, the instrument having been previously calibrated by the introduction of two pulses separated by a known interval of time. The pulses used to start and stop the discharge in an actual determination might be obtained from the flame luminosity by using photocells, from the flame conductivity by introducing a probe into the tube or from the flame temperature by allowing it to melt fine wires. The flame conductivity has been used with this instrument.

DESCRIPTION OF INSTRUMENT

The instrument as shown in the block diagram of fig. 1 consists of a cathode follower input to match the high impedance of the flame to the circuit. One half of a 6SN7 double triode serves as the input tube for the "starting pulse", the other half being used for the "stopping pulse" input tube. The outputs of these two cathode followers are fed to a common 6SJ7 pentode amplifier and then to the grid of an 884 gas triode. The purpose of the last tube is twofold, it serves to generate a uniform pulse of steep wave front for the following stage and it discriminates between several pulses which may be generated by the flame at either of the two pick-up points.

The output pulse from the 884 tube triggers the Eccles Jordan trigger circuit to a new stable position so that the D.C. plate voltage of the previously "on" triode turns "on" the 6SJ7 electronic key which was originally biased beyond cut-off. The condenser in the RC timing circuit is thus allowed to discharge through the 6SJ7 electronic key until the "stopping pulse" arrives, throwing the Eccles Jordan circuit back to its original position, biasing the 6SJ7 again beyond cut-off. The amount that the condenser has discharged is then determined by the reading of the 6J5 electrometer voltmeter. The original charge on the condenser is fixed by maintaining the switch across it closed until just preceding the measurement.

The power for the circuit is obtained from a 6X5 vacuum tube rectifier and transformer except for the plates of the electronic key and voltmeter tubes which are obtained from a single center tapped 45 volt "B" battery.

The entire circuit is contained in a wooden box 19X15X11 inches with the meter and controls mounted on the front. The inside of the box is lined with tin which is grounded to shield the circuit from any stray fields.

DESCRIPTION OF CIRCUIT OPERATION

To facilitate an understanding of the circuit a simplified circuit diagram is shown in fig. 2. V_1 is the rectifier tube connected in a conventional full wave rectifier circuit, the A.C. being supplied from the 110 volt line through the transformer T_1. The condensers C_6 and C_7, and the choke L form the filter circuit. The low side of the output is not grounded as usual, for reasons which will be discussed later. V_2 and V_3 are the two halves of a 6SN7 double triode connected in a conventional cathode follower circuit having a high input impedance. Cathode bias is furnished by the voltage drop across R_4. The voltage gain of this stage is less than one. The voltage drop across R_5 is coupled by condenser C_3 to the grid of V_4, a 6SJ7 pentode, through a common grid resistance, R_6. V_4 is connected in a conventional voltage amplifier circuit, cathode bias being furnished by the D.C. drop across R_7. The output is taken from the plate of V_4 and coupled through an RC coupling circuit R_8C_4 to the grid of V_5, an 884 thyratron.

This tube is biased by the potentiometer P_1 and the cathode resistance R_3 just below the firing potential so that a small positive potential on the grid will cause the tube to breakdown, discharging C_2 through the cathode resistance R_3. Since the discharge time of C_2 through V_3 is smaller than the charging time through R_1 the plate of V_5 will very quickly drop to the cut-off point and the tube will cease to conduct. This action will give a sharp pulse across the cathode resistance R_3 which is coupled to the grids of the succeeding tubes V_6 and V_7 through the two condensers C_5. The sensitivity of V_5 may be controlled by varying the bias with P_1. Discriminating action between pulses on the grid of V_5 which are very close together is obtained by controlling the charging time of C_2 with the variable resistance R_1 so that the plate voltage is insufficient to permit the tube to fire when the unwanted pulse arrives at the grid of V_5.

V_6 and V_7 are connected in an Eccles Jordan trigger circuit. The bias is obtained from the potentiometer P_4, which is part of the potential divider across the power supply. The normal condition of the circuit is with V_6 "on" and V_7 "off". This condition is assured by closing the momentary push button switch S_1, which momentarily cuts V_7 "off", assuring it to have been previously "on". The decrease in current through V_7 causes its plate voltage to increase since the current through R_{10} is decreased. This voltage increase is coupled to the grid of V_6 by C_6 and R_{11}, so that V_6 is made to conduct giving a voltage drop across R_9. This drop is coupled to the grid of V_7 through C_7 and R_{12} helping to drive the grid of V_7 beyond cut-off. When a positive pulse from R_3 is coupled to the grids of V_6 and V_7 in the normal condition the triggering action, as above, throws V_6 "off" and V_7 "on". This switching action takes place almost instantaneously. The next pulse triggers the circuit back to its normal position with V_6 "on" and V_7 "off".

The circuit values are so chosen that the voltage drop across R_9 is sufficient in the normal "on" condition of V_6 to maintain the grid of V_8, the electronic switch, below cut-off so that it does not allow current to pass. When V_6 is "cut-off" its plate voltage rises so that V_8 is turned "on". The resistance R_{13} is necessary to limit the grid current since the grid of V_8 would be driven positive by the plate voltage of V_6. With the next pulse turning V_6 "on" the grid of V_8 is again driven beyond cut-off and the tube ceases to conduct.

When V_8 is keyed "on" the condenser C_1 is allowed to discharge through the variable resistance R_2, the time of discharge being determined by the time V_8 is keyed "on". The amount that the condenser can discharge in this time is determined by the resistance R_2 in the circuit, which by its variability makes possible several ranges. The original charge on the condenser is determined by closing S_2 which connects the floating side of the condenser to the potential divider P_2.

V_9 in the voltmeter circuit is an ordinary triode connected to operate as an electrometer tube in lieu of a regular electrometer tube. Grid current is prevented from flowing by several precautions: 1. the plate voltage is kept low, 2. the heater voltage is greatly reduced, from normally 6.3 volts to 3.7 volts, 3. the heater is made 6 volts positive relative to the cathode, 4. the grid of the tube is always operated far below the cathode potential by means of P_2 and the large amount of negative feedback introduced by R_{15} and the resistance of the microammeter M in the cathode circuit.

In addition, to prevent the condenser C_1 from changing its charge, V_8, V_9 and the RC timing circuit are mounted on bakelite. However bakelite has an appreciable surface conductivity so that if the circuit were grounded in the conventional manner, placing the condenser voltage more than 100 volts above the chassis voltage the condenser C_1 would discharge to the chassis, causing the meter reading to decay.

To avoid this and any other charge accumulation or loss by the condenser, the condenser leakage is balanced by making the chassis potential variable with respect to the negative side of the power supply. It is thus possible by setting P_3 once or twice a day to avoid all meter decay. In order to prevent stray electrons from striking the plate of V_8 and charging the condenser C_1, the operating voltages of V_8 are kept low and the heater operated at 5 volts instead of the normal 6.3 volts.

OPERATING PROCEDURE

The detailed operating procedure for using the electronic chronoscope is given below in outline form. It is assumed that the instrument has been properly connected to the 110 volt line, is correctly grounded and that the 45 volt battery is properly connected to the circuit. It is further assumed that the source of pulse input has been connected to the chronoscope and is turned on ready to operate.

1. Turn meter on: (Refer to fig. 3)

    A. Throw S_3 to ON and wait until meter gives an indication.

    B. Make sure S_2 is in DOWN position (closed).

    C. Throw S_5 to ON.

    D. Throw S_4 to ON.
    S_5 and S_4 must be thrown in this order or the meter will read off scale.

    E. Let the instrument warm up for approximately ten minutes.

2. Adjust the meter preliminary to taking measurements:

    A. While S_2 is in the DOWN position (closed), with P_2 adjust the meter reading to full scale.

    B. Throw S_2 in UP position (open) and adjust P_3 for zero meter drift i.e. until the scale reading remains constant at 200.

        (a) If the meter decays rapidly, S_2 should be placed in the DOWN position and S_1 momentarily pressed. S_2 may now be thrown to the UP position and the P_3 adjustment made.

        (b) If the meter persists in decaying rapidly or spontaneously decays, the sensitivity should be decreased by turning P_1 to the left.

[redacted]

C. The sensitivity may be set to a maximum by setting the range selector switch R_2 to 11 and turning P_1 slowly clockwise until the meter starts to decay in jumps. P_1 should then be turned slightly counter-clockwise until the jumping ceases. It is seldom necessary to operate at full sensitivity. (See table 1)

(a) To return the meter to full scale during this adjustment place S_2 in the DOWN position and momentarily press S_1.

D. The position of the pulse discriminater switch R_1 will vary with the triggering pulse form and the time interval to be measured as well as with the sensitivity adjustment. It must thus be determined by experience. R_1 will be higher for longer time intervals and vice versa. (See table 1)

E. Set the range selector switch R_2 to the scale to be used.

F. Always leave S_2 in the DOWN position when not actually making a measurement.

3. Determine time interval:

A. Momentarily press S_1.

B. Throw S_2 in the UP position.

C. Carry out operation to be measured.

D. Record meter reading and obtain the time interval from a calibration chart.

E. Promptly throw S_2 to the DOWN position.
The meter is now ready for the determination of another time interval. Repeat 3.

4. Turn meter off:

A. Place S_2 in DOWN position.

B. Set S_4 to OFF.

C. Set S_5 to OFF.

D. Set S_3 to OFF.

B, C and D must be done in that order.

[redacted]

SUGGESTED IMPROVEMENTS IN CIRCUIT

To avoid the necessity of operation 2-D it is suggested that the circuits preceding the Eccles Jordan trigger circuit (fig. 1) be replaced by an individual amplifier and pulse generating circuit for each pulse, i.e. the "starting pulse" and the "stopping pulse". These circuits should be of such a design that each will pass only one pulse until it is manually returned to an unstable condition. This could be achieved by duplicating the 6SJ7 amplifier and the addition of another 884 thyratron tube, using a sufficiently small plate resistance for each tube so that it will continue to fire until the plate circuit is opened.

The use of two gas tetrodes (2050 or 2051) with the elimination of the 6SJ7 amplifier, and possible elimination of the cathode followers should also be considered.

CALIBRATION OF CHRONOSCOPE

The chronoscope has been calibrated against two standards; an electric stop watch and an electronic audio oscillator, and the two calibrations checked against each other to within 2%.

The electric stop watch was a "Time It" made by the Precision Scientific Co., Chicago, Illinois, readable to 0.1 sec. Its time is based upon the 60 cycle line by the operation of a synchronous motor. Scale 10 to 11 only were calibrated directly by this means; their full scale readings are 7 and 14 sec. respectively. A six inch piece of bare wire was connected to one input lead of the chronoscope to act as an antenna which picked up the pulses when the stop watch was started and stopped.

By using these two calibrated scales of the chronoscope as a secondary standard the various scales of the one shot multivibrator shown in fig. 5 can be calibrated. The two output leads of the multivibrator are connected to the input leads of the chronoscope and the momentary push button switch Sw is pushed a known number of times. Each time the switch Sw is closed one pulse appears at each of the two outlets, the two pulses being separated by a given time interval depending upon the setting of R and C. The calibration time for the particular multivibrator scale is then determined by dividing the chronoscope time by the number of times the multivibrator push button was closed. This method is used in reverse when the multivibrator time interval is known and it is desired to calibrate the chronoscope.

The multivibrator was also calibrated against a Jackson oscillator by viewing the output pulses of the multivibrator on a calibrated cathode ray oscillograph screen when pulses from the oscillator were fed into the multivibrator. Since the oscillator generates a sine wave it was necessary to first pass the oscillator output through a square wave generator and then

[redacted]

through a differentiating circuit before feeding it to the multivibrator. The sweep frequency of the cathode ray oscillograph was set to one or two times the square wave generator frequency and then the pulse output of the multivibrator applied to the vertical plates of the oscillograph. The distance between the two pulses on the screen was then a measure of the time delay due to the multivibrator and consequently a calibration of the multivibrator. The chronoscope was calibrated as described above and the calibrations by stop watch and oscillator found to check within 2%.

DESCRIPTION OF ONE SHOT MULTIVIBRATOR USED FOR TIMING STANDARD

A cathode coupled one-shot multivibrator or flip-flop circuit was constructed on a metal chassis 7X7X2 inches to be used to calibrate the chronoscope as described above. The circuit shown in fig. 5 utilizes one double triode 6SN7 and two 6H6 double diode tubes, the power being obtained from an external power supply.

The input diode limiting circuit permits only positive pulses to reach the grid of V_1 while the two output diode limiting circuits in conjunction with the two RC differentiating circuits (100,000 ohm and .0001 μf) select the proper negative pulses for the output.

The circuit values are chosen so that the plate current of V_2 when it is conducting causes sufficient voltage drop in the V_1 - V_2 cathode resistance to keep V_1 cut-off, which is the stable condition of operation. The triggering pulse obtained either from the input external oscillator or by closing switch Sw is applied to the grid of V_1 turning it "on". The instantaneous drop in plate voltage of V_1 is then coupled through the variable coupling condenser C to the grid of V_2 cutting it "off". This plate drop of V_1 is also used to obtain the initial output pulse. Since V_2 is "cut-off", only the current from V_1 flows in the cathode resistance so that V_1 conducts and V_2 remains "off" until the condenser C has discharged sufficiently toward the 200 volt plate supply through the variable resistance R to allow the grid voltage of V_2 to come up to cut-off. When V_2 again starts to conduct, the operation instantly switches back to the stable condition with V_1 "cut-off" and V_2 conducting. The second output pulse is obtained from the decrease in plate voltage of V_2 when this action takes place. The time between the initiating pulse and the final pulse is determined by the value of RC.

[redacted]

MEASUREMENT OF FLAME SPEEDS

The measurement of flame speeds by utilizing the flame conductivity has been carried out in a reaction tube similar to that used in the determination of limits of inflammability, with exactly the same mixing system. (1) Due to the difficulty encountered with the spark ignition triggering the chronoscope circuit, hot wire ignition has been substituted.

A detailed diagram of the reaction tube with the necessary circuits for the hot wire ignition and triggering of the chronoscope are shown in fig. 6. Co-axial cable is used for the chronoscope leads with the outer conductor grounded. The power supply leads to the platinum plate electrodes and to the chronoscope are shielded wire, while the variac leads to the 110 volt supply and to the hot wire are a shielded twisted pair. Sw is a momentarily-closed push button switch used to close the ignition wire circuit when it is desired to ignite the charge.

Table 1 shows a selected number of sample measurements made with the chronoscope, covering a large range of pressures and flame speeds. More detailed work on flame speeds will follow in subsequent papers. These values are included solely to demonstrate the range of the instrument.

TABLE I

SAMPLE RESULTS OBTAINED WITH CHRONOSCOPE

Flame conductivity used to trigger instrument.
Distance between triggering electrodes = 20.385 cm.
Using hot wire ignition.

[redacted]

Sample	Total Pressure mm. Hg	Range R_2	Discriminator Switch R_1	Sensitivity P_1	Electrode Potential Volts	Meter Read X10^6 amps.	Time Sec. X 10^3	Flame Speed cm./sec.
3.30 % Echylene oxide in air	266	9	18	5	400	68	764	26.6
3.29 % n-Butane in air	136	8	16	5	120	95	396	51.4
3.32 % n-Butane in air	448	7	14	3	30	82	243	84.7
4.46 % n-Butane in air	94.8	8	16	4	5	135	230	88.5
8.44 % n-Butane in air	760	7	16	5	400	89	225	90.5
3.31 % n-Butane in air	158	7	12	3	5	165	64	318
2.17 % n-Butane in air	760	7	14	5	15	167	60	339
5.55 % n-Butane in oxygen	35	7	14	4	5	192	15	1350
3.70 % n-Butane in air	760	6	12	4	400	148	13.7	1490
5.55 % n-Butane in oxygen	44	6	14	4	5	186	3.6	5650

[redacted]

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1. Badin and Davidson, Technical Paper No. 5, 3/25/46.

2. For a general discussion of the circuits involved see such books as:

   Reich, J. H., Theory and Application of Electron Tubes (2nd edition only) McGraw-Hill Book Co. (1944).

   Muller, Garman and Droz, Experimental Electronics, Prentice-Hall, Inc. (1942).

3. For a discussion of Electrometer tubes and circuit considerations, with literature references see:

   Strong, Procedures in Experimental Physics, Prentice-Hall, Inc. (1941)

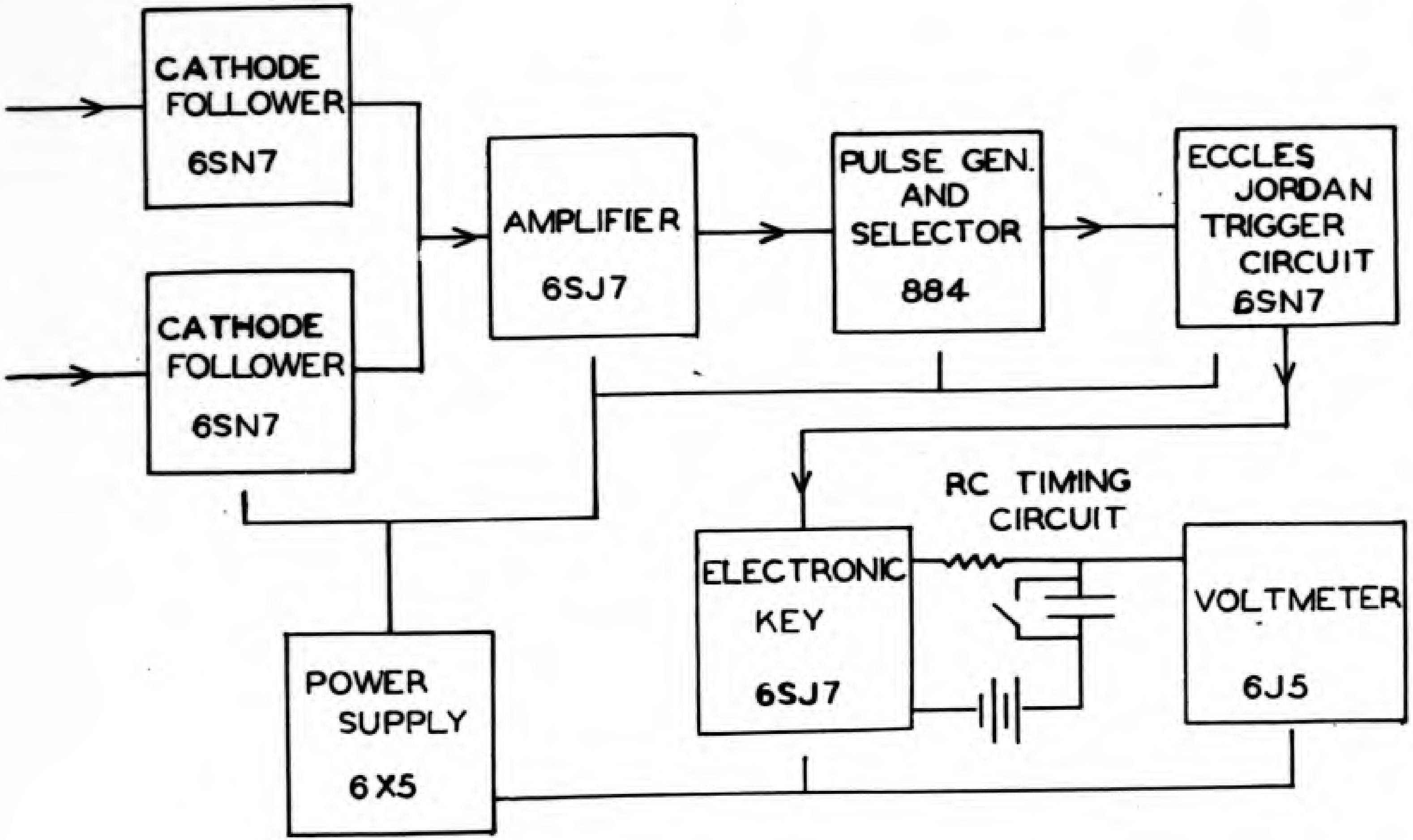

FIG. 1 BLOCK DIAGRAM OF CHRONOSCOPE

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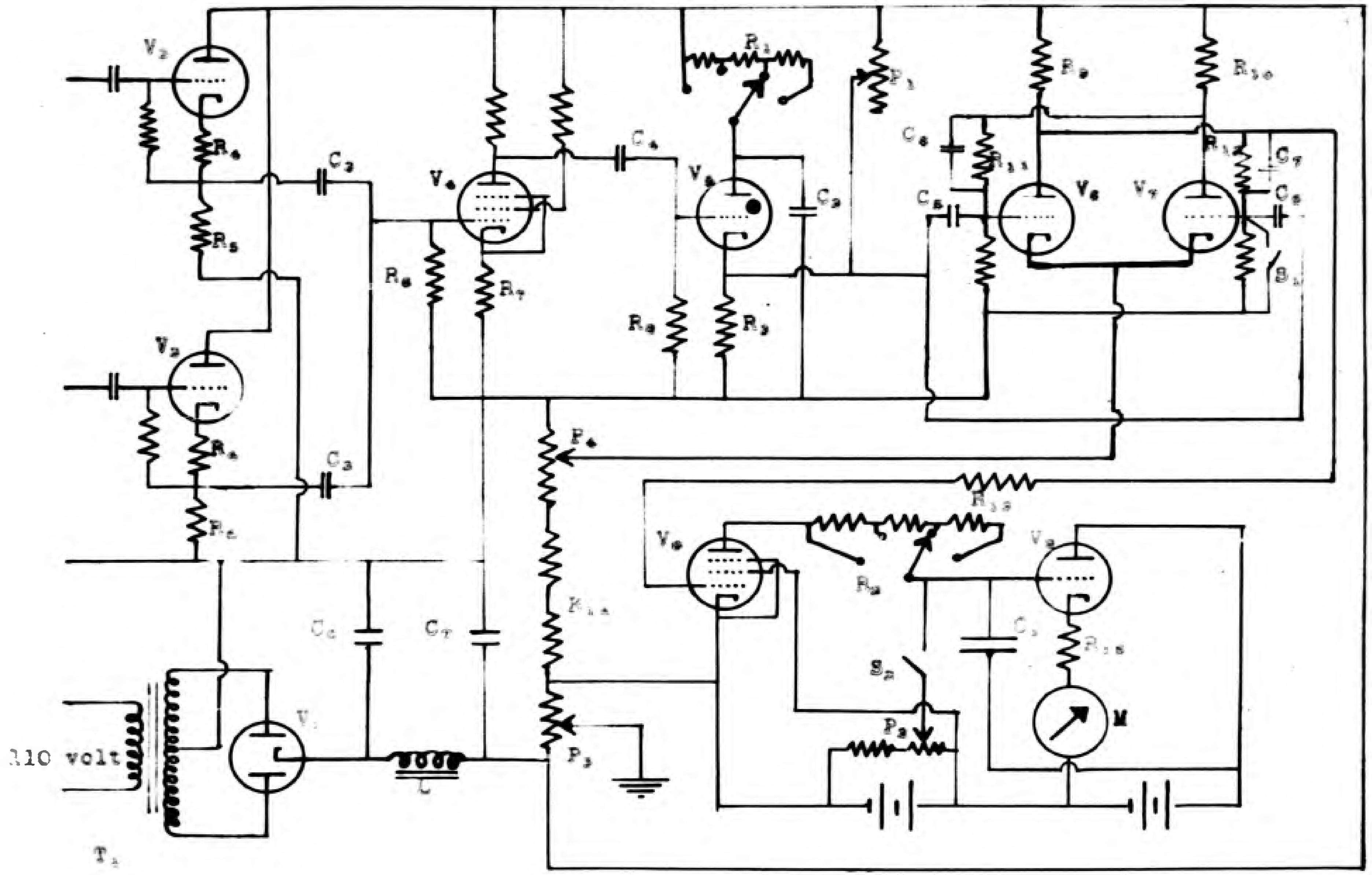

FIG. 2 SIMPLIFIED CHRONOSCOPE CIRCUIT

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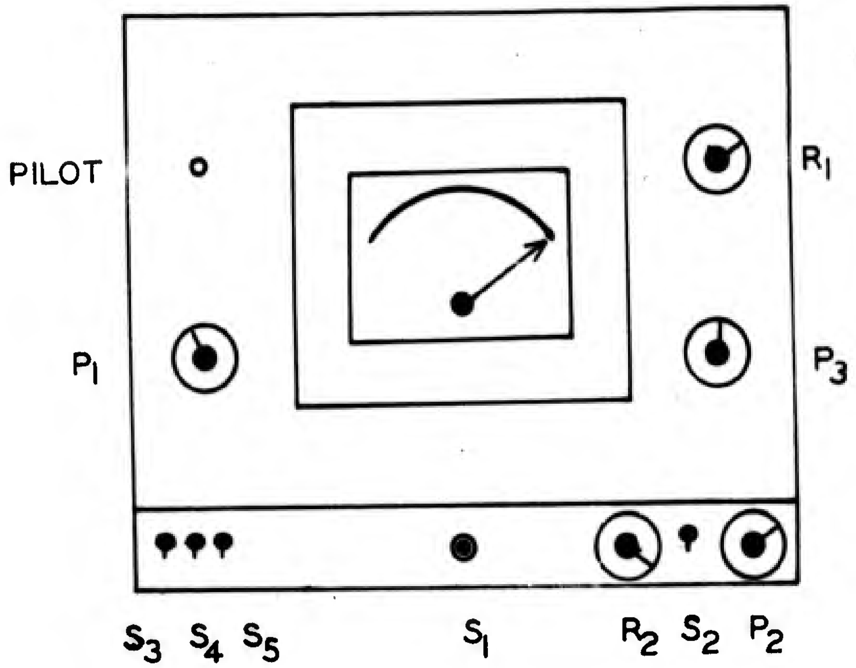
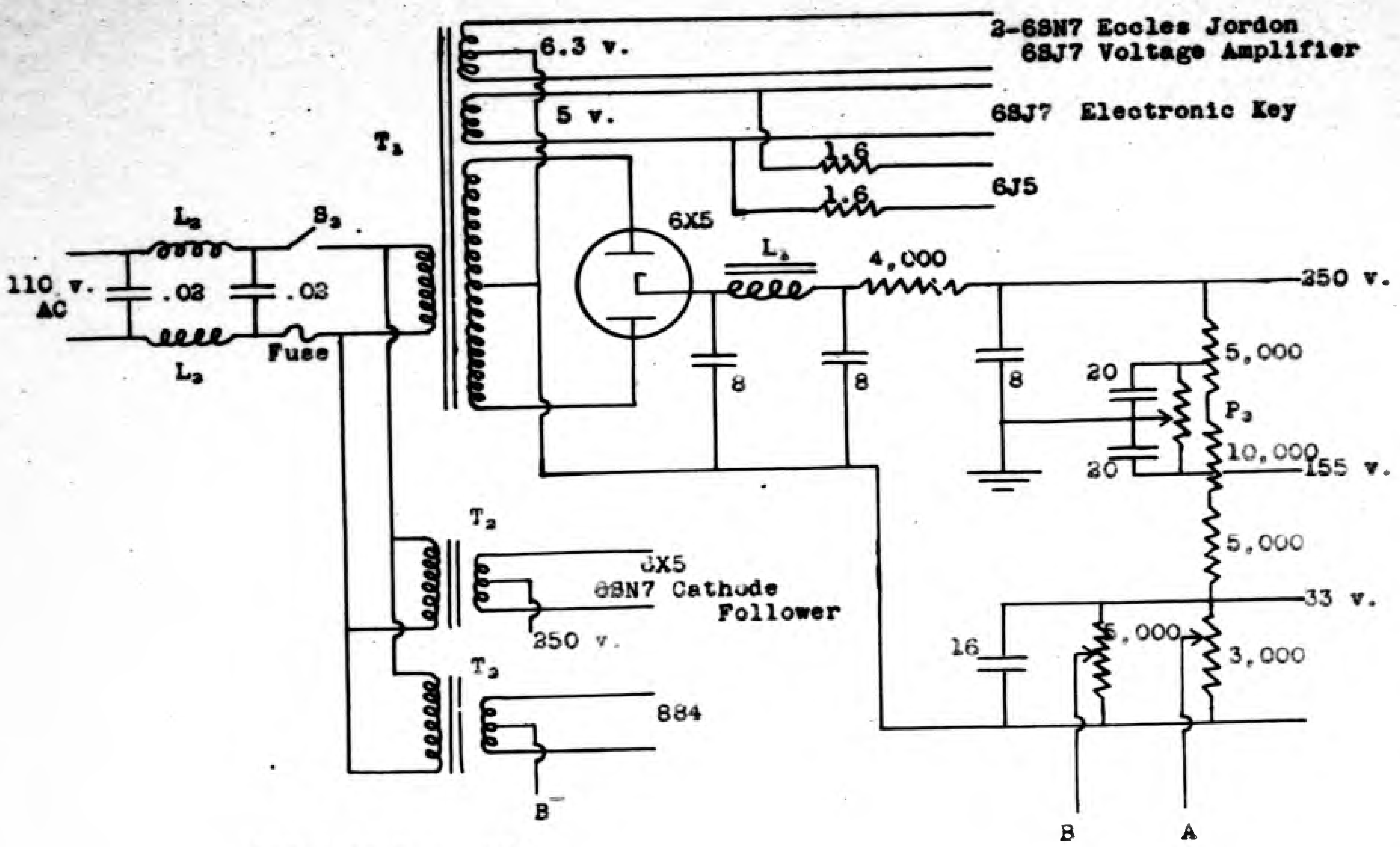
FIG. 3

ELECTRONIC CHRONOSCOPE
FRONT VIEW





Resistance in ohms
Capacity in microfarads

FIG. 4-A ELECTRONIC CHRONOSCOPE

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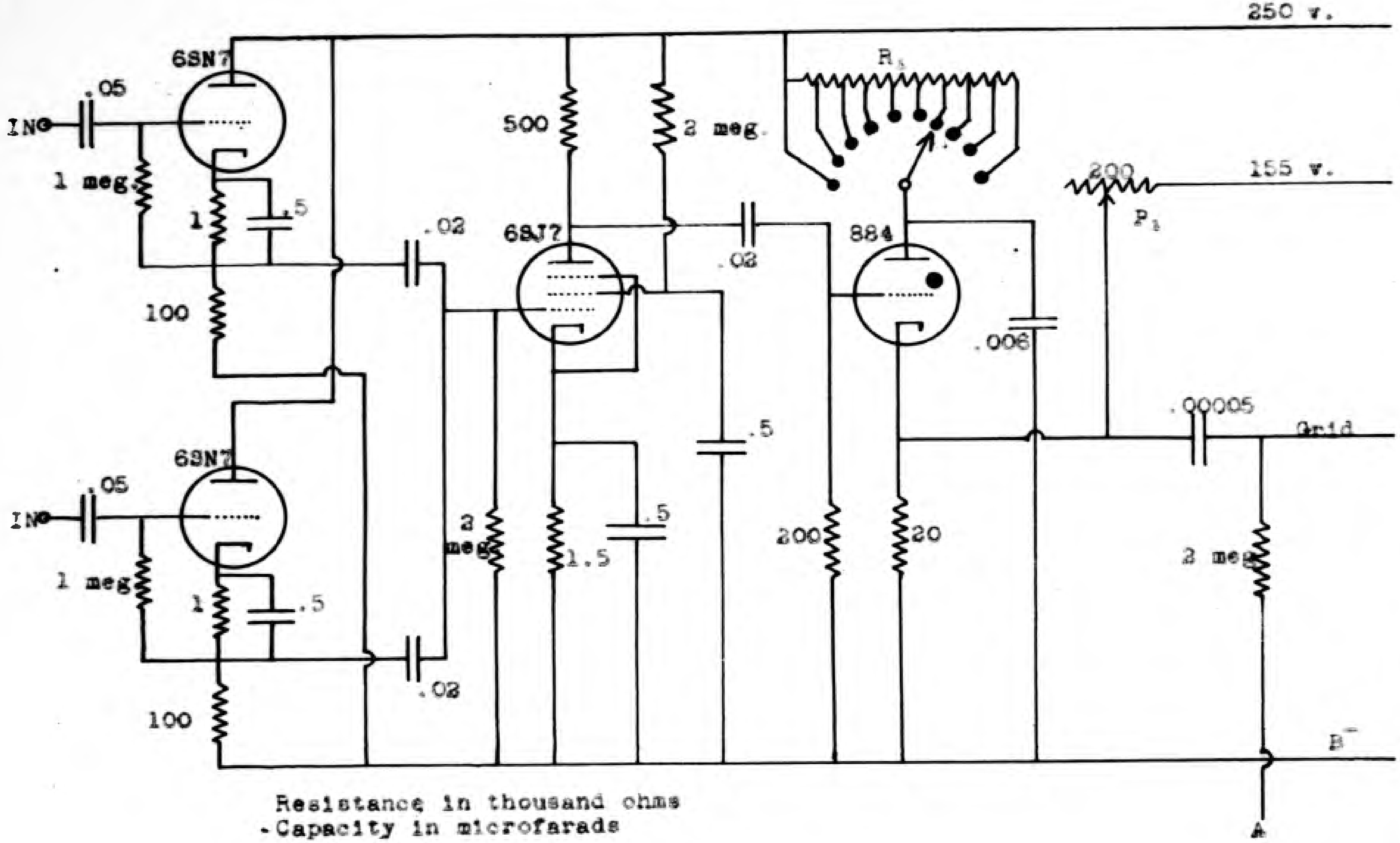
[redacted]



Resistance in thousand ohms
-Capacity in microfarads

FIG. 4-B

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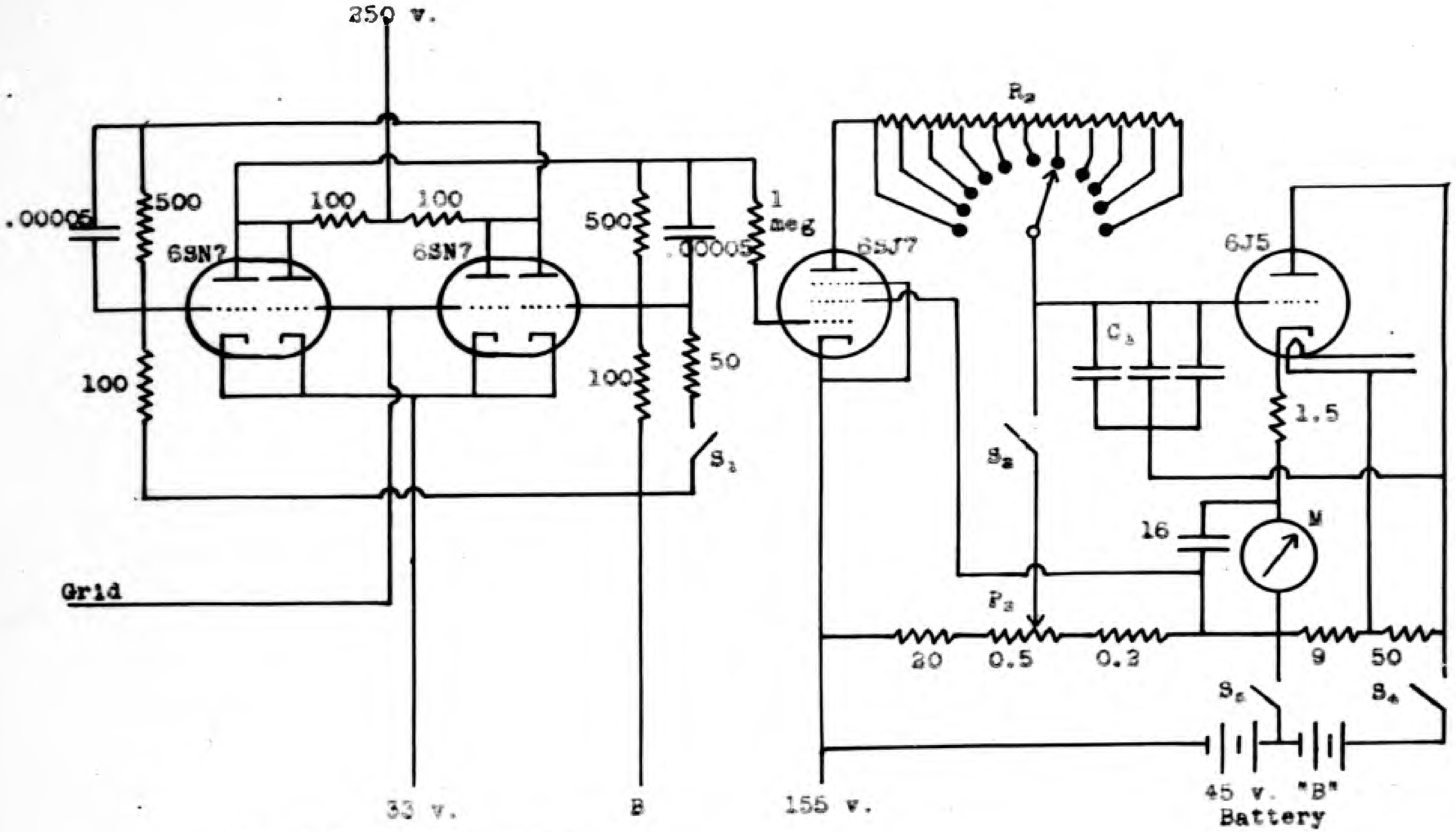


Resistance in thousand ohms
Capacity in microfarads

FIG. 4-C

[redacted]

LEGEND FOR FIGURE 4

L_1 - Choke, 10 henries 475 ohms: Thordarson T-13C27

L_2,L_3 - Chokes, 12 windings of No. 16 copper wire around 3/8 inch diameter condensers

T_1 - Power Transformer, 580 volts CT 50 ma., 5 volts at 3 amps., 6.3 volts at 2 amps. CT: Thordarson T-13R11

T_2,T_3 - Filament Transformers, 6.3 volts at 1 amp.: Thordarson T-19F80

R_1 - Bank of resistances mounted on 10 position selector switch. R=25, 7, 6, 4, 2, 0.4, 0.2, 0.07, 0.04, and 0.02 meg ohms.

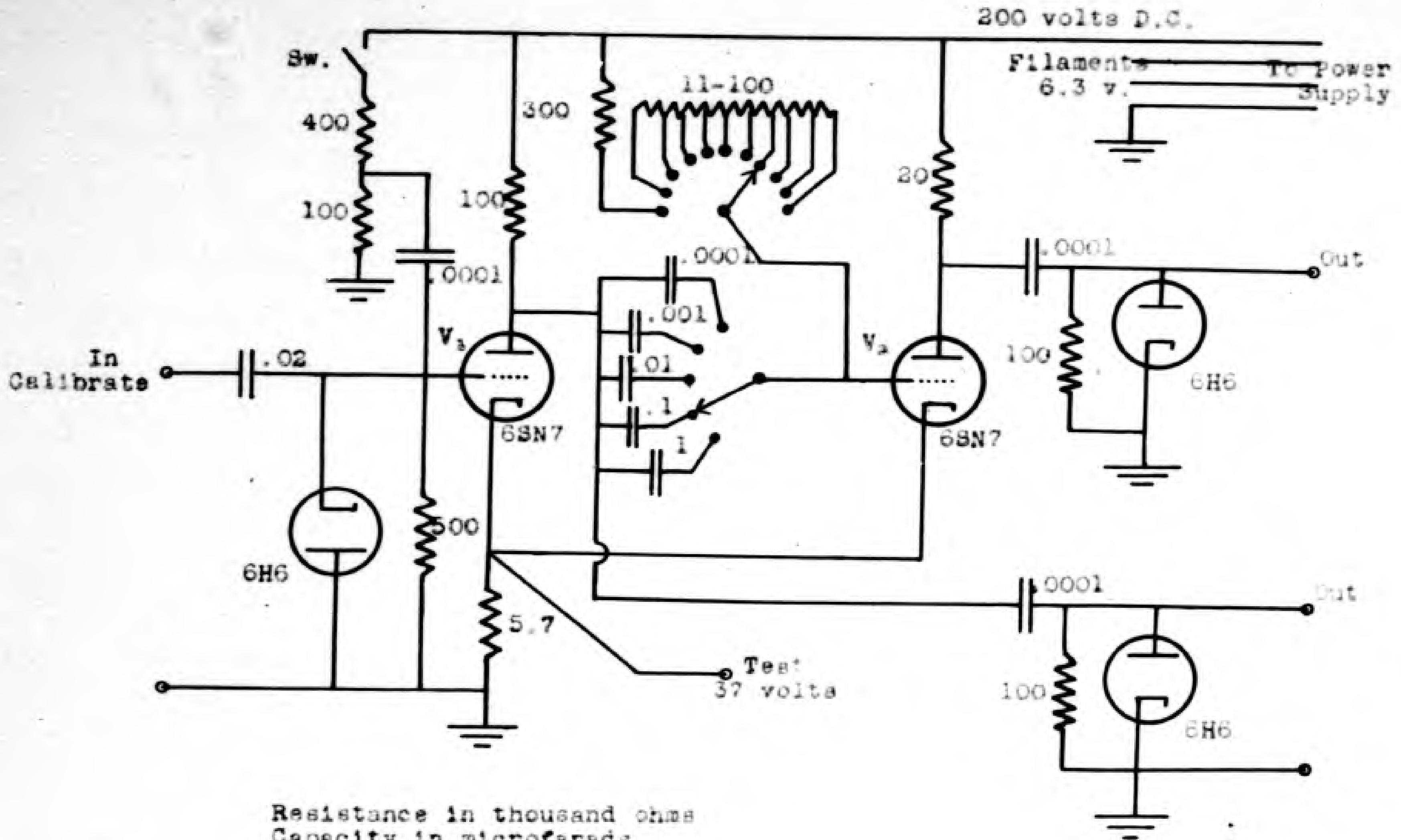
R_2 - Bank of resistances mounted on 11 position selector switch. R=1, 2, 2, 100, 200 thousand ohms. and 2.5, 2.5, 2.5, 25, and 25 meg ohms.

S_1,S_2 - Momentary push button switches

S_3,S_4,S_5-Toggle switches

C_1 - 3 Pyranol Capacitors, 1 microfarad, 500 volts D.C. General Electric, Cat. 23F115CG481190

M - D.C. Microammeter, Full scale 200 Microamperes Marion Electrical Instrument Co., Manchester, N. H.



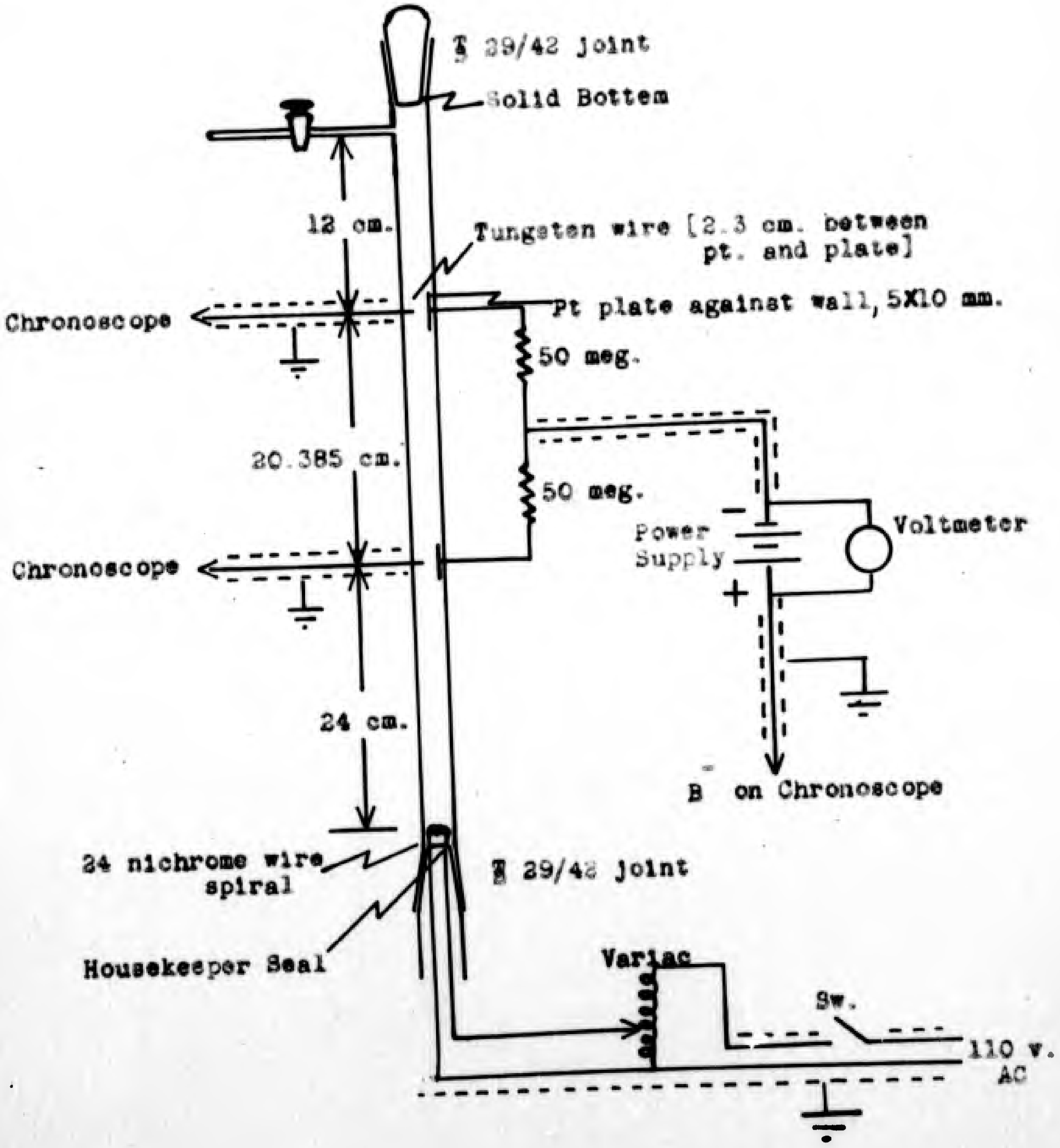
Resistance in thousand ohms
Capacity in microfarads

[redacted]

FIG. 5 ONE SHOT MULTIVIBRATOR FOR TIMING STANDARD

[redacted]

FIG. 6 REACTION TUBE AND AUXILIARY CIRCUITS



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COMBUSTION OF N-BUTANE-OXYGEN MIXTURES WITH ZINC DIMETHYL IGNITION

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Contract NOrd-7920, Task PRN-3

Technical Paper No. 24

February 1, 1947

SUMMARY

Combustion of n-butane-oxygen mixtures with ignition induced by the explosive reaction between zinc dimethyl and oxygen has been studied at a total pressure of 200 mm. and initial reactant temperature of 20°. The products predominating were carbon dioxide, water, carbon monoxide and hydrogen with some olefin and paraffin in mixtures rich in butane. Increase of the initial temperature to 100° resulted in a more violent reaction. In the slow oxidation region the hydrocarbon functioned as an inert diluent.

[redacted]

[redacted]

INTRODUCTION

In a previous study of the combustion of zinc dimethyl(1) it was found that the explosive oxidation occurred within well defined limits. It was of further interest to determine conditions under which zinc dimethyl would act to initiate the combustion of a hydrocarbon such as butane. Such spontaneously igniting mixtures ought to be of use in promoting stable combustion. Zinc dimethyl should provide free radicals for the hydrocarbon combustion. On the other hand, the endothermic cracking of hydrocarbon might well provide a "sink" for such radicals.

APPARATUS AND METHOD

The apparatus and method used were essentially those described in Technical Paper No. 18(1). A clean spherical reaction bulb of volume 148 ml. (6.7 cm. diameter) was used for each experiment. It was cleaned and dried in the usual manner. Zinc dimethyl vapor was first metered into the evacuated bulb and n-butane then added to the desired pressure. No reaction occurred between the n-butane and the zinc dimethyl vapor when they were mixed in this manner at 20°. Oxygen was then added up to the previously calculated pressure as was done in the previous cases(1).

Zinc dimethyl was prepared and purified as outlined in Technical Paper No. 18. Oxygen was obtained from a laboratory cylinder and passed through P_2O_5 before use; n-butane was used from a cylinder obtained from the Matheson Company.

Explosion of the reaction mixture occurred within 10 seconds after the admission of the oxygen unless the reaction mixture was below the explosion limit in which case a slow oxidation occurred. Pressure changes were followed on a mercury manometer. Combustion in most cases was accompanied by a brilliant flash.

Gaseous mixtures were analyzed by removing a gas sample with a Töpler pump and subsequent gas analysis. Carbon dioxide was analyzed for by absorption in 30% aqueous potassium hydroxide, olefins in very dilute (33% saturated) bromine water, oxygen by continued passage through Oxsorbent, carbon monoxide by Cosorbent, hydrogen by copper oxide combustion at 310°C and paraffins by copper oxide combustion at 570°C. Olefins have been reported as ethylene and paraffins as methane.

[redacted]

RESULTS AND DISCUSSION

Below the explosion limit zinc dimethyl reacts with air or oxygen at a measurable rate which may be followed by the negative pressure change. The reaction predominating in this slow oxidation region is believed to be

$$CH_3\text{-}Zn\text{-}CH_3+\tfrac{1}{2}O_2 \longrightarrow CH_3\text{-}Zn\text{-}OCH_3. \qquad (1)$$

Above the critical limit the oxidation is explosive and occurs with complete or partial rupture of the zinc dimethyl molecule. The products predominating are CO_2, H_2O, CO and H_2.

The flash accompanying combustion in the explosive region has been used as an "igniter" for n-butane combustion. Results at 20°C. with 25 mm. zinc dimethyl plus 175 mm. of varying ratios of butane and oxygen are given in Table I.

All of these mixtures exploded, though in the last there was no visible flash. In all but the first run, nearly all the oxygen was consumed. However in the first three runs, the pressure-change was negative, as it is with no butane present. Only when the ratio of butane to zinc dimethyl approached 1:1 or more (decreasing oxygen) did a positive pressure-change occur. Under these conditions (low oxygen) the product gases were mainly carbon monoxide and hydrogen as would be expected for incomplete combustion.

A second series of runs at 20°C (Table II) was made with oxygen pressure constant at 240 mm., and varying amounts of zinc dimethyl and butane totalling 60 mm. Earlier work(1) showed that with no butane present the explosive limit was reached at about 15 mm. of zinc dimethyl, roughly independent of the oxygen concentration when this was in excess. The transition from slow to explosive reaction is shown in Table II to occur at about the same pressure with butane present (12-14 mm. zinc dimethyl). Thus butane has no marked effect on the limit. However, in its presence the total pressure-change becomes positive since there is now a new reaction which can take place.

[redacted]

TABLE I

PRODUCTS FROM COMBUSTION OF N-BUTANE-OXYGEN WITH ZINC DIMETHYL IGNITION

(200 mm. total pressure)
(temperature 20°)

REACTANTS				PRODUCTS (VOLUME %)					
Pressure zinc dimethyl (mm.)	Pressure n-C_4H_{10} (mm.)	Pressure oxygen (mm.)	Change in pressure after explosion (mm.)	% CO_2	% O_2	% CO	% H_2	% $CH_2=CH_2$	% CH_4
25	0	175	-82	23	76	1	0	0	0
25	10	165	-79	53	18	5	24	0	0
25	20	155	-63	6	7	54	33	0	0
25	35	140	+185	1	2	47	50	0	0
25	50	125	+172	0	4	42	49	4	1
25	95	80	+53	0	10	36	38	7	9

[redacted]

TABLE II

TRANSITION FROM SLOW TO EXPLOSIVE OXIDATION WITH BUTANE-ZINC DIMETHYL-OXYGEN

(Total pressure 300 mm., Initial temperature 20°C)

Pressure zinc dimethyl (mm.)	Pressure n-butane (mm.)	Pressure oxygen (mm)	Type of oxidation	ΔP (mm.)	Rate $\frac{d(\Delta P)}{dt}$ max. (mm./sec.x10^2)
8	52	240	Slow	-15	38.
10	50	240	Slow	-17	46.
12	48	240	Slow	-20	80.
14	46	240	Explosive	+26	---
16	44	240	Explosive	+30	---
20	40	240	Explosive	+45	---

[redacted]

One experiment was carried out with hydrogen substituted for butane. For the mixture, 12 mm. zinc dimethyl--48 mm. n-butane--240 mm. oxygen, the rate is fairly rapid but just short of explosion. When hydrogen was substituted for butane, the rate was substantially decreased--hydrogen tends to inhibit, just as does helium when substituted for nitrogen (no butane present).(1)

A few runs were made at 100°C. In general the explosion limits were broadened and explosion was more violent. Thus in one case (12 mm. zinc dimethyl--18 mm. butane--270 mm. oxygen) the reaction bulb was shattered.

Although the experimental evidence is insufficient to fix the details of the induced oxidation of butane by that of zinc dimethyl, the over-all effect may be imagined to be as follows. Granting that the non-volatile compound, CH_3OZnCH_3, is a primary product, it may be assumed that this can dissociate to yield either CH_3 or CH_3O. The butane might then be converted into an alkyl radical by reaction with either of these radicals (R)--

$$R + C_4H_{10} \longrightarrow RH + C_4H_9.$$

The butyl radical should then combine readily with oxygen to yield the peroxide radical--

$$C_4H_9 + O_2 \longrightarrow C_4H_9O_2,$$

which would then set up the hydrocarbon oxidation chain.(2)

[redacted]

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   See also, Thompson and Kelland, J. Chem. Soc. (London) p. 746 (1942).

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[redacted]

LOW-PRESSURE FLAMES IN MIXTURES OF N-BUTANE, BUTADIENE-1,3, OR ETHYLENE OXIDE WITH OXYGEN.

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Contract NOrd-7920, Task PRN-3

Technical Paper No. 25

February 1, 1947

SUMMARY

Combustion of n-butane, butadiene-1,3 and ethylene oxide in sustained flames with oxygen has been studied in the pressure range below 20 mm. Burning velocities for butadiene-1,3 and oxygen at 18.1 mm. have been measured; burning velocity measurements based on flame areas are impossible much below this pressure due to the diffuse nature of the flame which increases with decrease in pressure. The effect of variables such as the rate of flow, effect of burner diameter and the type of fuel together with general characteristics of flames down to 4.7 mm. are reported.

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INTRODUCTION

A study of sustained combustion in the pressure range below 20 mm. has been undertaken with the ultimate end in view of obtaining stationary flames at pressures below 1 mm. These are of interest in themselves, as well as in their relation to high-altitude operations. In addition they offer a starting-point for the development of low-pressure sampling techniques.

Earlier work from this laboratory(1) was concerned with burning hydrocarbon-air mixtures at a relatively small orifice (6 to 8 mm.). Lowest pressures were of the order of 250 mm. These experiments have now been extended using somewhat larger burners (15 to 22 mm.) and substituting oxygen for air. In this way steady flames could be obtained down to about 5 mm.

APPARATUS AND METHOD

The apparatus used is diagrammed in Figure I. Oxygen was admitted at point A. A constant flow was maintained by using a diaphragm valve and a large water column C of adjustable height. Butadiene-1,3 or other fuel gas was admitted at B. The rate of flow of the gas was held constant by a diaphragm valve followed by a brass Sylphon bellows-type valve D. Using this system a perfectly steady flow of both oxygen and butadiene-1,3 could be obtained. Flowmeters E and F were of the type with removable glass capillaries, a different capillary being calibrated for each flow range. Water was used as the flowmeter liquid. Flowmeters were calibrated using wet test meters or, in the case of water soluble gases, direct displacement of mercury from a calibrated tube. Calibrations were carried out in the actual system; the connecting pyrex tubing was of such size that a zero pressure drop was observed in the static manometer H (fluid, water). All calibrations were made at 760 mm. and 25°.

In operation the gases were mixed at point G, particular care being exercized in making this joint so that the disturbance in the flow introduced would be a minimum. A short mixing tube with indentations between G and the throttling stopcocks K further premixed the gases. Stopcocks K were adjusted so that the reading

[redacted]

on manometer H was that observed during calibration conditions, gases above K being at atmospheric pressure and below K at the experimental pressure.

Burner lead tube M was of Pyrex graded to a quartz tube of the same size at point M'. The total length of M in the straight-run portion was 100 cm. The silica burner rim was ground with 1000 mesh carborundum powder. Ignition was effected by two tungsten electrodes sealed into the outer mantle so as to throw a spark across the burner when the switch was closed. The spark was obtained with an induction coil having 240 turns on the primary and 32,400 turns on the secondary operating with 12 volts d.c. on the primary side. In preliminary experiments it was found that, during ignition, the flame had a tendency to flash down the burner tube M and propagate through stopcocks K resulting in detonation and shattering of the apparatus on the atmospheric pressure side. A flash-back trap L, loosely packed with steel wool, was found to extinguish the flame before it could reach the throttling stopcocks and, thus, eliminated the danger of violent explosion.

Exhaust gases were passed through two traps T and T' (volume of each, 900 ml.) surrounded by Dewar flasks containing liquid nitrogen. These traps condensed out most of the gaseous products. A large 45 liter glass vessel R absorbed pressure fluctuations induced by operation of the manostat.

Pressures were measured near the combustion zone by a mercury manometer N or, more precisely, by a McLeod gauge O of small multiplying factor (average about 10-15) The pressure was maintained constant by a manostat system which allowed a small influx of air when the pressure dropped below the desired value. It consisted of a mercury manometer P with a fixed tungsten electrode and an adjustable glass-sheathed tungsten-tipped electrode which could be raised or lowered by a knob at Q. A fluctuation in the pressure either made or broke contact in the manostat system. The leads from the fixed and movable electrodes were suitably connected (as shown in Figure II, Technical Paper No. 4 (1)) to the solenoid operating on 120 volts A.C. Air was either admitted or closed off by means of a rubber-seated iron core. Two large Megavac pumps in parallel were operated continuously during an experiment.

[redacted]

The approximate ratio of the diameter of the pyrex jacket mantle to the burner diameter used was 2:1. All other glass tubing used was at least 16 mm. I.D.

In igniting the burner it was found that ignition below about 28 mm. pressure was not possible due to the weakened or discharge character of the spark below this pressure. Consequently oxygen at the desired rate was passed through the burner with a continuous spark and the butadiene-1,3 then increased in rate until a stable flame resulted. The pressure was then decreased and flows adjusted to the desired points. In determining the stable flame and flash back limits a constant pressure was maintained, the oxygen rate held constant and the gas rate either decreased very slowly or increased very slowly until blow-off or flash back was observed. During this procedure, the stopcocks at K were constantly adjusted so as to maintain the same reading on manometer H.

In determining burning velocities an image of the flame cone was projected and traced. A light-tight box fitted with a transparent glass screen at the end was mounted directly behind the flame. An 80 mm. diameter, 100 mm. focal length double convex lens was mounted in the box so that the flame was just outside the focus. In this way an inverted real image of the flame was cast on the screen and outlined on tracing paper. A beam of light was used to obtain a projection of the burner tube of known outside dimensions. By using an enlargement factor it was possible to determine the flame dimensions (both inner and outer cones). The cone area was obtained from the projection by calculating the lateral areas of frustums into which the projected image was divided. Burning velocities were calculated from the formula(2)

$$L = V/A$$

where

L = Linear burning velocity, cm. per sec.

V = Volume rate of flow corrected to the experimental pressure, cc. per sec.

A = Calculated area of cone, sq. cm.

[redacted]

RESULTS AND DISCUSSION

Comparison of the characteristics of n-butane, butadiene-1,3 and ethylene oxide flames with oxygen under identical conditions are shown in Figure II. These data were obtained at a constant flow of oxygen of 38.7 liters per minute at the experimental pressure. In the case of n-butane this corresponds to a linear feed velocity of 400. cm./sec. at the stoichiometric point (13.3%), for butadiene-1,3 410. cm./sec. at the stoichiometric point (15.4%), and 485. cm./sec. for ethylene oxide at the stoichiometric point (28.6%). In general, limits were broadened and a lower pressure could be attained in the order:--

Ethylene oxide—butadiene-1,3—n-butane

In Table I, data at chosen pressures are given for the combustion limits and for the minimum pressure at which a stable flame resulted under the operating conditions. It should be pointed out that, although neither n-butane nor ethylene oxide exhibited a flash-back region below 18 mm., butadiene-1,3 did, at the rates employed.

In Figure III the effect of increasing the volume rate of flow is shown for butadiene-1,3 oxygen mixtures. Figure III A at 19.4 liters per minute oxygen flow (corresponding to a linear feed velocity at the stoichiometric point of 205. cm./sec.) shows a very large flash back region at all pressures with a minimum for the stable flame at 8.5 mm. Similarly, Figure III B at 38.7 liters per minute oxygen flow (linear feed velocity) 410 cm./sec. at the stoichiometric point) had a minimum in the stable flame region of 7.0 mm.; at 48.4 liters per minute of oxygen, Figure III C, (linear feed velocity 510. cm./sec. at the stoichiometric point) 6.2 mm. was the minimum in the stable flame region. A further increase in flow rate to 58.1 liters/min. oxygen flow (linear feed velocity at the stoichiometric point 615. cm./sec.) did not bring about a further decrease in the minimum pressure, the limit being about 6.2 mm. From these data, it can be seen that a decrease in the depth to which the flash back region penetrates parallels an increase in flow rate.

[redacted]

TABLE I

COMBUSTION LIMITS FOR N-BUTANE, BUTADIENE-1,3 AND ETHYLENE OXIDE IN OXYGEN

(15.40 mm. quartz burner)

(38.7 l.p.m. O_2 flow at pressures indicated)

FUEL	PRESSURE (mm.)	LIMITS (Vol. % in O_2)	
		Lower	Upper
n-butane	15.0	4.0	17.4
	10.0	5.8	14.2
	8.7	minimum point	
butadiene-1,3	15.0	4.0	22.8
	10.0	5.0	17.7
	7.1	minimum point	
ethylene oxide	15.0	7.7	~45.
	10.0	9.7	35.5
	6.1	minimum point	

[redacted]

When the burner diameter was increased from 15.40 mm. to 22.10 mm. (Figure IV) for comparable rates of flow it can be seen that, although the minimum decreased from 7.0 mm. for the 15.40 mm. burner to 6.5 mm. for the 22.10 mm. burner, the area of the "flash-back region" increased tremendously. At this rate of flow no data could be obtained for a 30.15 mm. burner since the flame would not stabilize on the burner rim and flashed back at practically all compositions. However, when the feed rate was increased by a considerable factor (95.3 l.p.m. O_2 flow with feed velocity 255 cm./sec. at 13.0% butadiene-1,3 in O_2) very narrow limits at the pressure of 4.7 mm. just above the minimum were obtained. Complete data on larger size burners have not yet been obtained.

In this connection it is of interest to note some results reported in a captured German document(3), which Dr. W. R. Hawthorne of the British group kindly made available in translation. The authors, H. J. Hubner and H. G. Wolfhard, investigated (among other things) the stability of acetylene-air and acetylene-oxygen flames at low pressures as a function of flow rate and burner diameter. It was found that minimum pressures attainable were roughly inversely proportional to burner diameter, and that minimum linear flow rates were approximately constant. Lowest pressures reached were about 20 mm. for acetylene-air with a 35.4 mm. burner; 5 mm. for acetylene-oxygen with a 27.4 mm. burner; and 35.4 mm. burner; 5 mm. for acetylene-oxygen with a 27.4 mm. burner; and 35 mm. for propane-air with a 57 mm. burner (or 50 mm. pressure with a 36 mm. burner).

Reduction of pressure, in general, has the effect of broadening the combustion zone or flame front. Whereas, at atmospheric pressure the thickness of the flame front is of the order of 10^{-2}-10^{-3} mm.(4), pressures of the order of 1/100 of an atmosphere may cause the flame front to be so broadened as to have an apparent visible thickness of a few millimeters with resultant separation of the primary cone into an "inner" and "outer" cone both becoming increasingly diffuse with decreasing pressure. In addition the cone becomes more rounded with decrease in pressure. Measurements of the linear burning velocity depending on accurate surface measurements of cone areas, thus, become impossible at very low pressures. In Table II one set of data are presented to indicate the order of magnitude for burning velocities of an oxygen-butadiene mixture at 18.1 mm. pressure. This pressure

[redacted]

TABLE II

BURNING VELOCITIES OF BUTADIENE-1,3-OXYGEN

AT 18.1 mm. PRESSURE

(15.40 mm. I.D. quartz burner)
(Projection method)

C_4H_6-1,3 rate*	Oxygen rate*	Vol. % C_4H_6-1,3 in O_2	Inner Cone		Outer Cone	
			Area (cm^2)	Burning Velocity (cm./sec.)	Area ($cm.^2$)	Burning Velocity (cm./sec.)
2.54	39.0	6.1	1.91	363	3.11	223
3.10	39.0	7.4	1.59	442	2.38	295
3.53	39.0	8.3	Lower flash back limit			
8.63	39.0	18.1	Upper flash back limit			
8.67	39.0	18.2	2.23	356	3.27	243
9.44	39.0	19.5	2.47	327	3.73	206
10.76	39.0	21.6	2.77	299	4.72	175
11.58	39.0	22.9	3.68	229	4.98	169
12.30	39.0	23.9	4.88	175	7.32	117

* liters per minute at 18.1 mm. pressure.

[redacted]

represents approximately the limit at which any reproducibility for burning velocity determinations may be expected. Burning velocities have been calculated for both the "inner" and "outer" cones.

In the region 4 to 10 mm. and especially in rich mixtures, the flame overlapped the burner considerably and was very diffuse. Such a "rich" flame was also observed as separating into several diffuse but distinct colored zones. This has been diagrammed in Figure V. Spectroscopic observation of flames (see e.g. Plate I, Technical Paper No. 19(5)) have shown the violet to predominate in OH and the green in C_2 (and CH). At low pressures these zones seem to separate more or less distinctly and may be attributed to presence of excited radicals of the type mentioned above.. Such a colored flame was very pronounced for butadiene-1,3 and ethylene oxide and less pronounced for n-butane. The ethylene oxide flame in all cases had a distinct violet cast.

In connection with the flame just described, combustion products have been examined for aldehydes. The colored flame was maintained for 60 minutes during which time gaseous products were collected in the liquid nitrogen traps. Very little aldehyde was found (quantitative precipitation with 2.4 dinitrophenylhydrazine) for either n-butane, butadiene-1,3 or ethylene oxide. In the case of n-butane only 1 molecule of aldehyde (calculated as HCHO) survived for every 18,000 n-butane molecules entering. Under similar conditions no peroxides could be detected in the condensed gases.

The diffuse nature of the reaction zone at 10 mm. and below suggests that, if a factor of 100 in pressure reduction could be achieved ($\sim$0.1 mm.), reaction zones might be sufficiently broad so that a probe for molecular species either transient or stable might be made in the region preceding and throughout the flame front.

[redacted]

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(4) Lewis and v. Elbe, J. Chem. Phys. 2, 283 (1934).

(5) Technical Paper No. 19, "Emission Spectra from the Combustion of C_4 Hydrocarbons", February 1, 1947.

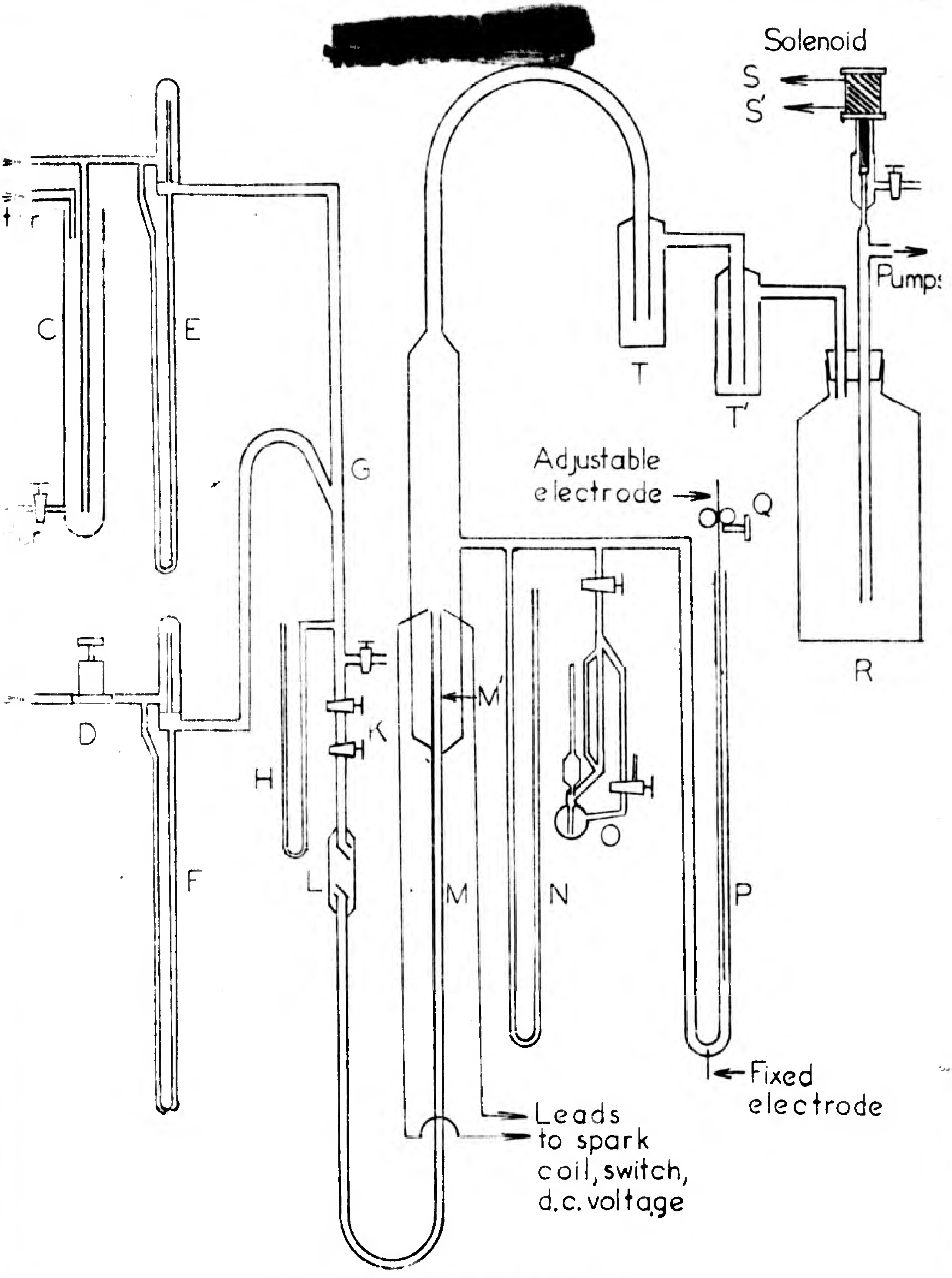
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FIGURE I APPARATUS

[redacted]

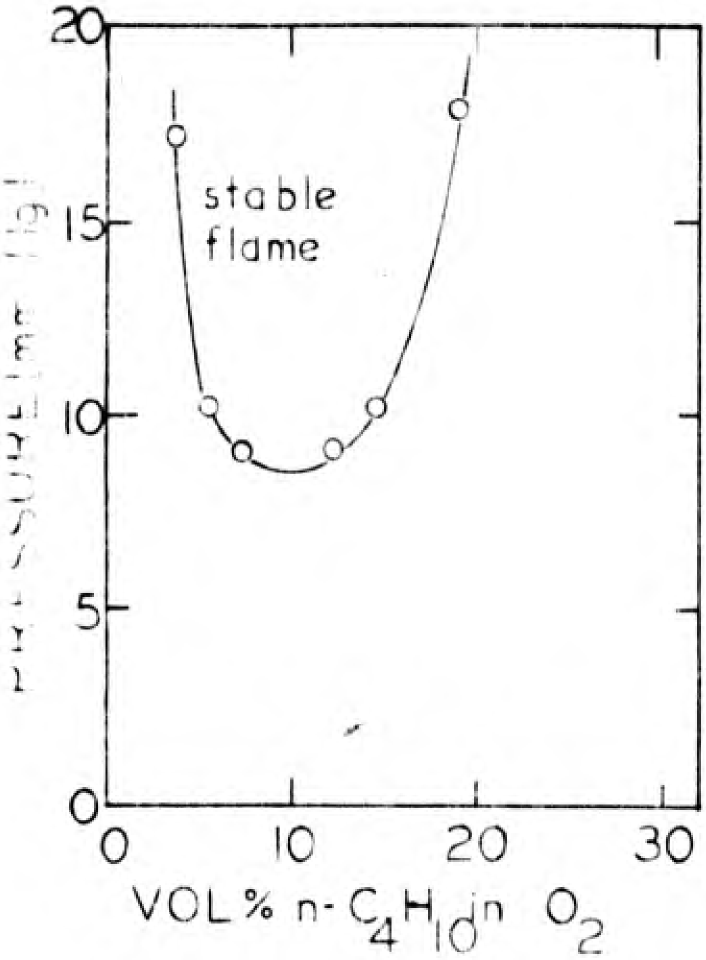


FIGURE IIA

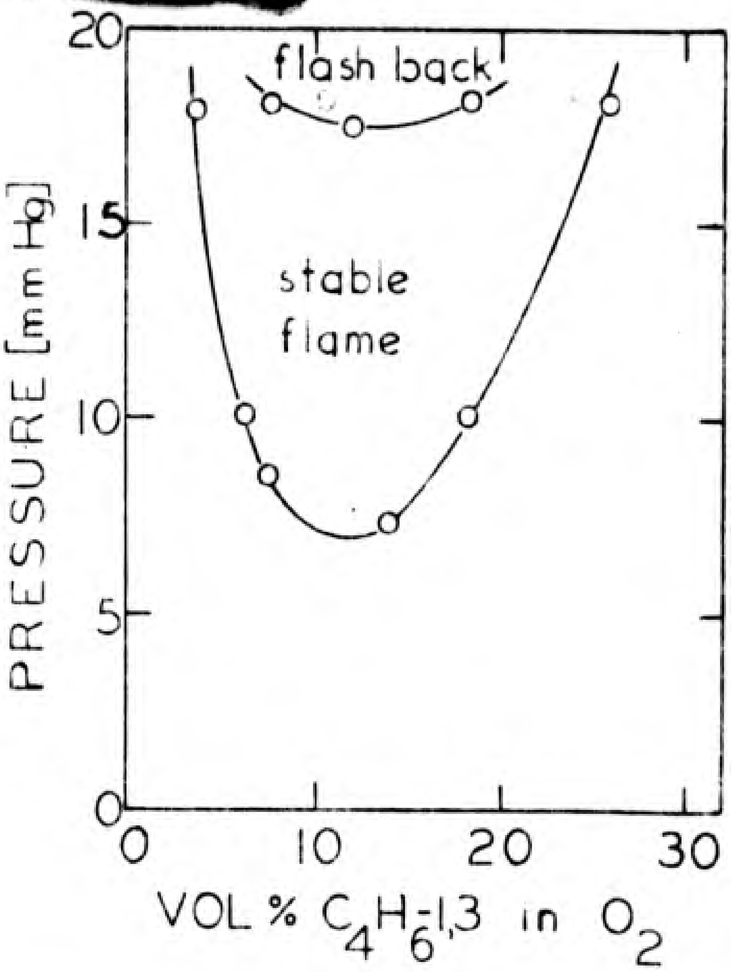


FIGURE IIB

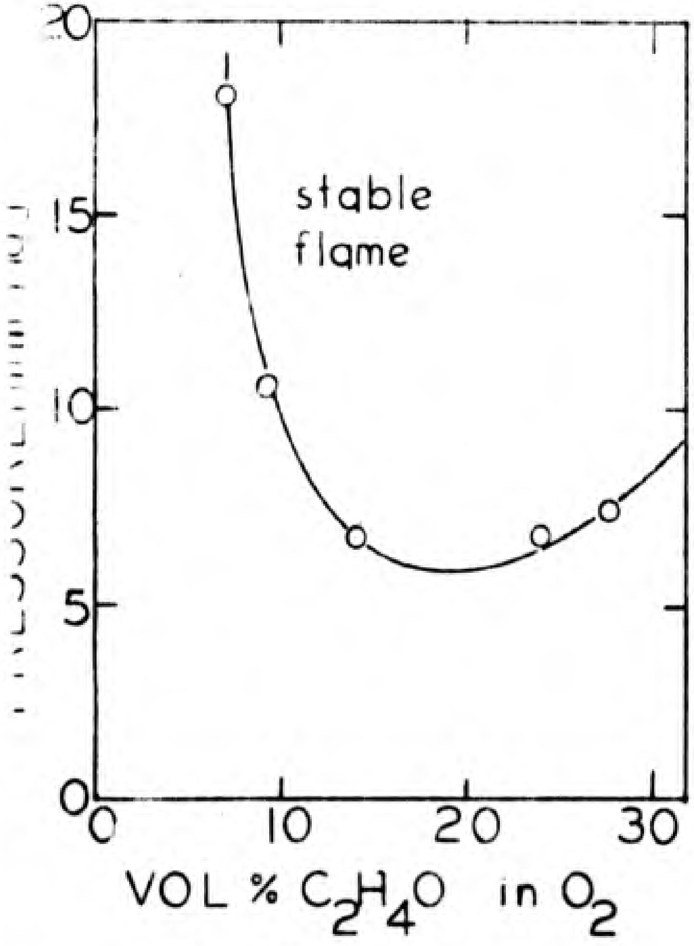


FIGURE IIC

FIGURE II

COMBUSTION OF n-BUTANE BUTADIENE-1,3 and ETHYLENE OXIDE in OXYGEN

15.40 mm quartz burner

38.7 liter per min of oxygen at indicated pressure

[redacted]

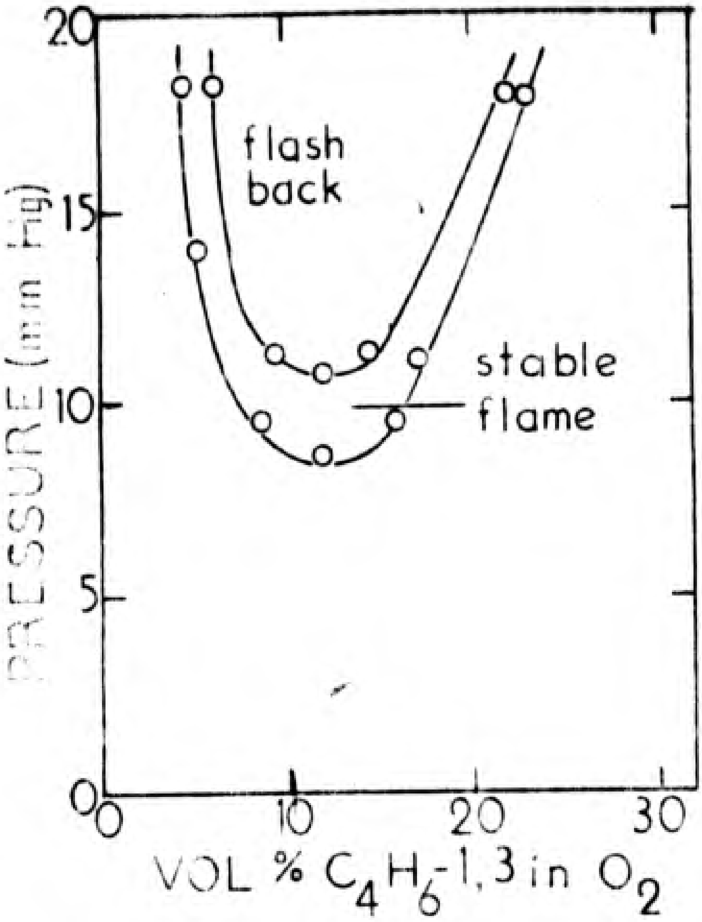


FIGURE III A

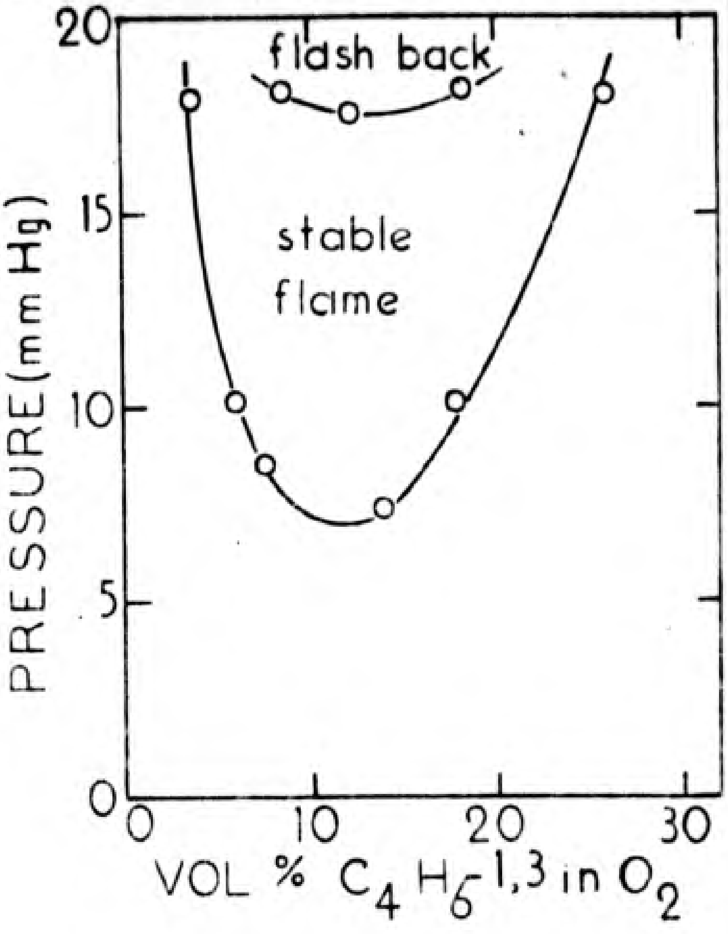


FIGURE III B

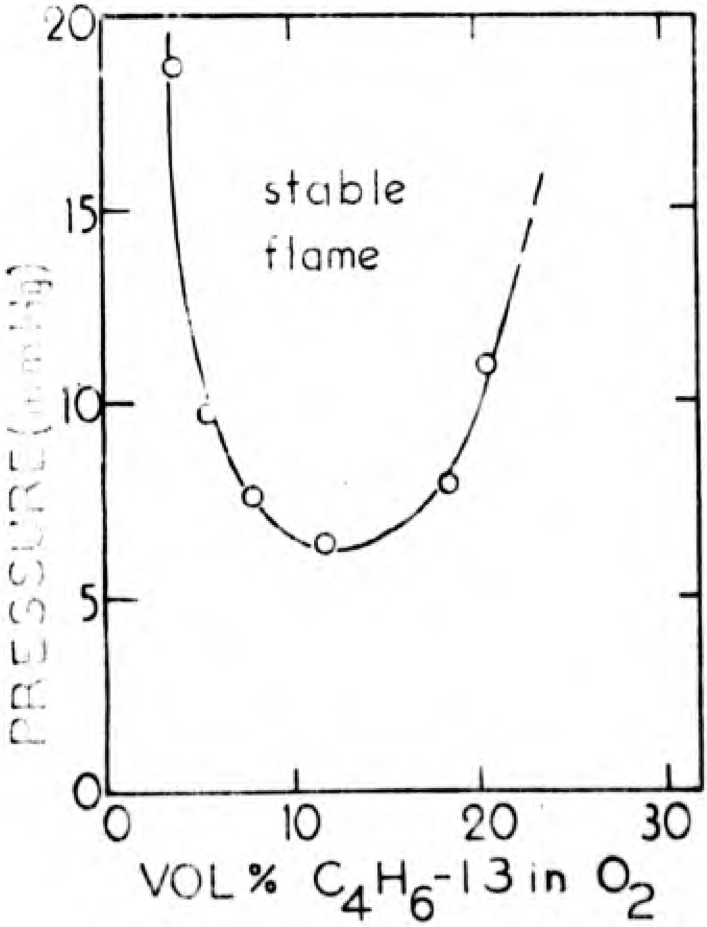


FIGURE IIIC

FIGURE III

BUTADIENE-1,3-OXYGEN
COMBUSTION

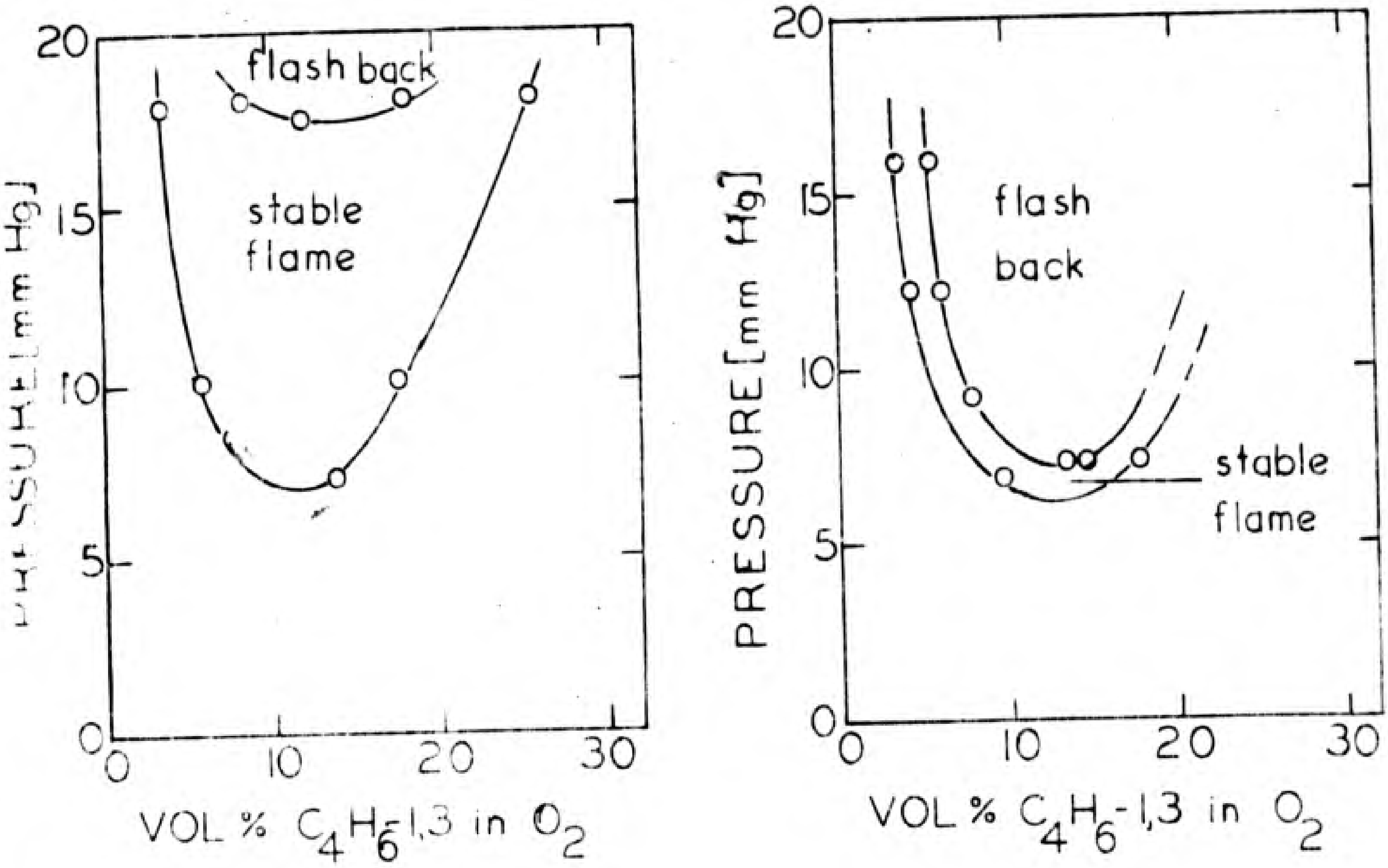
15.40mm quartz burner

FIGURE IIIA 19.4 liters per min of oxygen at indicated pressure

FIGURE IIIB 38.7 liters per min of oxygen at indicated pressure

FIGURE IIIC 48.4 liters per min of oxygen at indicated pressure

[redacted]



[15.40mm I.D. quartz burner]

[22.10mm I.D. quartz burner]

FIGURE IV EFFECT OF BURNER SIZE ON BUTADIENE-1,3 OXYGEN COMBUSTION [38.7 liters per min oxygen flow at indicated pressure]

[redacted]

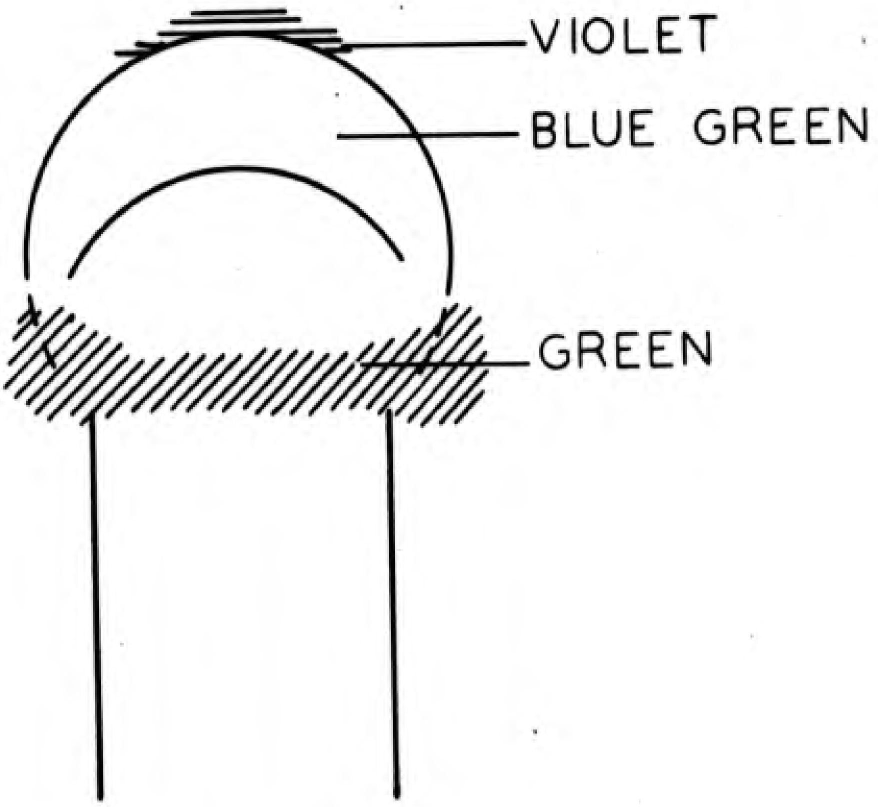


FIGURE V SCHEMATIC REPRESENTATION OF BUTADIENE OR ETHYLENE OXIDE FLAME AT 5-10 MM. WITH DEFICIENCY OF OXYGEN.