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COMBUSTION WITH OZONE-MODIFICATION OF FLAME SPEEDS C_2 HYDROCARBON-AIR MIXTURES

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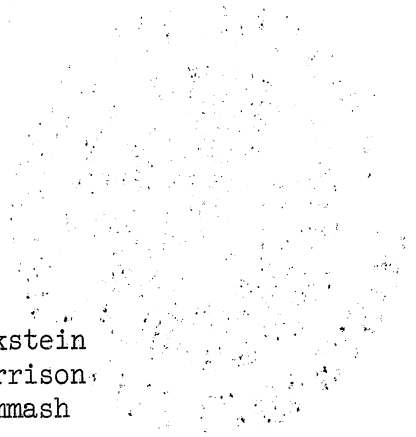

Martin E. Gluckstein
Richard B. Morrison
Tariq B. Khammash

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(4) Personal Authors:
Gluckstein, Martin E.
Morrison, Richard B.
Khammash, Tarif B.

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(12) Abstract: This report presents experimental data on the effect of ozonation of a portion of combustion air on the flame speeds of ethane, ethylene, and acetylene at atmospheric pressures and at brief analysis of the observed effects from the viewpoint of possible reaction mechanism and kinetics.

COMBUSTION WITH OZONE-MODIFICATION OF FLAME SPEEDS C_2 HYDROCARBON-AIR MIXTURES

by

Martin E. Gluckstein[1], Richard B. Morrison[2], and Tariq B. Khammash[3]
Aircraft Propulsion Laboratory
University of Michigan

This paper reports the effect of ozonized air on the combustion of ethane, ethylene and acetylene in a Bunsen burner. This work was undertaken to determine whether ozone introduced into a combustor would produce significant alterations of the combustion processes and the magnitude and direction of such changes, if any. Information of this type may prove useful in the evaluation of the relative importance of the various hydrodynamic and chemical parameters in the determination of flame structure and may have possible application in combustor development. Comparatively little information on the use of this simple additive can be found in the literature and the experimental data reported generally indicate that there is no effect.(2, 6) It is likely that the failure of these investigations to show any effect may have been due to the extremely low ozone concentrations used (less than 0.1%). The data reported in this paper were all obtained with ozone concentration of about 1% by weight.

To determine if the partial ozonization of the combustion air would have any effect on combustion, the flame speeds for the mixture burning with and without ozone were determined from experimental measurements. This method of evaluation was used because it provides a comparatively simple, rapid technique of obtaining information on overall flame behavior from readily obtained physical measurements.

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[1]Research Associate, Engineering Research Institute.
[2]Associate Professor of Aeronautical Engineering and Supervisor, Aircraft Propulsion Laboratory.
[3]Assistant in Research, Engineering Research Institute.

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The flame speed may be defined as the velocity of the unburned gas normal to the flame front. If the characteristic conical shaped Bunsen flame were a true cone, the flame speed would be given by the equation

$$V_f = \frac{Q_j}{A_j} \sin \alpha , \tag{1}$$

where V_f is the flame speed, Q_j the volumetric flow rate of the unburned gas, A_j the area of the jet, and α the semi-vertex angle of the cone. The use of this equation presumes that the incoming fuel-air mixture has a uniform velocity profile. Most flames, however, are not true cones and the use of Equation 1, is, at the best, a crude approximation. If the burner port is circular in cross section, the flame will be a surface of revolution and the flame speed can be calculated by the equation

$$V_f = \frac{Q_j}{A_f} , \tag{2}$$

where A_f is the flame area and the other terms are as before. The flame area was computed from measurements of a photograph of the flame by the equation

$$A_f = 2 \pi L \bar{x} , \tag{3}$$

where $\bar{x}$ is the centroid of the curve with respect to the axis of revolution (i.e., axis of the burner) and L is the length of the flame front, measured from the tip of the flame to its base.

The physical interpretation of flame speed in terms of flame mechanism is a matter of some conjecture. A complete physical description of the flame may be made from consideration of the general conservation equations. One finds, however, that the resultant set of differential equations for continuity of mass, momentum, and species and for energy conservation are not particularly amenable to mathematical manipulation. However, certain simplifying assumptions, consistent with known physical behavior, permit simplification of these equations. These simplified equations

usually express the flame speed in terms of transport phenomena and a term related to the chemical kinetics. The derivations of these equations have been given elsewhere and will not be considered here.(3, 4, 7) It is important for this work to bear in mind only the dependence of the flame speed on the chemical kinetics and transport processes involved in any particular system.

To determine the role ozone might play in causing variations in the flame speed of hydrocarbon-air mixtures, one should examine, briefly, some of the possible reaction mechanisms involved. Lewis and von Elbe and Jost have presented extensive material on these mechanisms of hydrocarbon combustion and Semenoff has given some of the reactions of the system O_2-O_3.(3, 4, 5)

The hydrocarbon oxidation reactions have been shown to proceed in a series of steps involving active species such as O, OH, H and various carbon containing radicals. Of particular importance in this application is the O which may be formed from O_3 as follows (5)

$$O_3 = O_2 + O . \qquad (A)$$

The O formed may then enter into direct reaction with oxidizable material, or react further with additional oxygen or ozone

$$O + O_3 = 2\ O_2^* ; \qquad (B)$$

$$O_2^* + O_3 = 2\ O_2 + O , \qquad (C)$$

or be deactivated by collision with N_2. The latter course is the most likely, since the reaction mixture is about 75% N_2.

In general then, the O_3 may be expected to perform the role of an O donor and consequently to accelerate the rate of reaction for those steps where O enters in the formation of combustion products. If these steps are rate controlling, then the overall reaction rate for the combustion process will be accelerated and hence the flame speed increased.

A further contribution of the O_3 could be due to the heat release associated with the overall reaction

$$O_3 = \frac{3}{2} O_2 . \qquad (D)$$

However, the ratio of the heat release due to this reaction to that of the overall combustion reaction is about 1% and, consequently, this heat release should play a minor role.

In this work no attempt was made to verify the mechanisms by which ozone may affect the flame speed, but simple considerations such as those given above are helpful in the development of the experimental programs and in the interpretation of the results.

To ascertain the effect of ozone on the flame speed, the fuel-air-ozone mixture was burned in a specially designed stainless steel Bunsen burner. A cross sectional view of this burner is shown in Figure 1. Two inlets are provided, one for the fuel-air and another for the ozonized air. Mixing of the two streams occurs in the entrance section. after which the mixture passes through an inlet nozzle and smoothing screen to the burner lip. An overall schematic diagram of the equipment is shown in Figure 2. Rotometers were used throughout for metering.

The experimental technique utilized was quite simple. A rich mixture of fuel and air was prepared and stored in pressure tanks. This mixture was first metered through the control panel and then allowed to enter the burner mixing inlet. Air, from a high pressure system, was dried by passage through a dry ice-acetone trap and then metered through a Welsbach model T-23 ozone generator to the mixing zone. By the use of this technique, it was possible to compute the overall mixture ratio from the flow rates of the air and fuel-air streams. Ignition was accomplished by means of an electric spark from a high voltage transformer.

In the usual operating procedure, the flame was ignited and the flow rates were adjusted and permitted to stabilize. Normally, the ozone generator was off during the ignition process, i.e., there was flow through it to dilute the fuel-air mixture but the power was off. After the flow rates were allowed to stabilize, two photographs of the flame burning in the absence of ozone were taken. Ozone was then supplied to the burner by simply turning on the power. In this way the total flow of gases remained constant but a portion of the air was ozonized. After allowing a few minutes for mixing and stabilization of O_3 production, a photograph of the flame burning with ozone was taken on the same plate as the second photograph of the flame without ozone. This was done without changing camera focus or setting. The use of this technique permitted ready referencing of the two flames for later flame speed computations. (The photographic procedure was occasionally reversed for convenience.)

Ozone analysis was not made for each run. It was shown by iodometric titration for O_3, that the output of the generator was reasonably constant over the flow range used providing it was operated at constant pressure and primary voltage.

In examining the flame photographs it was possible to tell immediately from the double exposure if any change had occurred and usually the larger of the two areas could be determined visually. A number of these photographs for different gases are shown in Figures 3-12.

Of particular interest in these flames was the transition from button shape to the cone shape when ozone was added or eliminated and the fact that the behavior of the ethane (Figures 3-6) was the reverse of that of the ethylene, (Figures 7-10), and the acetylene (Figures 11, 12). This shows that the flame speed is reduced for the ethylene-air and acetylene-air mixtures and increased for the ethane-air mixtures. A resume of these and other data, together with the computed flame speed values is given in Table I.

TABLE I

FLAME SPEED VARIATION FOR C_2 FUELS
(Ozone Content Approximately 1%)

Fuel	Nozzle Size inches	Flame Speed feet per second		Fuel-Air Ratio (By Weight)
		No Ozone	Ozone	
C_2H_4	1/4	2.036	1.822	.0555
	1/4	1.877	1.805	.0572
	1/4	2.018	1.871	.0582
	1/4	1.904	1.451	.0591
	1/4	1.932	1.749	.0577
	1/4	1.823	1.812	.0583
	1/4	1.956	1.525	.0633
	1/4	2.133	1.879	.0542
	1/4	2.004	1.688	.0586
	1/4	2.075	1.971	.0554
C_2H_6	3/8	1.360	1.478	.0407
	3/8	1.438	1.466	.0391
	3/8	1.389	1.466	.0387
	3/8	1.211	1.291	.0424
	1/4	1.344	1.602	.0308
	1/4	1.166	1.113	.0406
	1/4	1.145	1.276	.0421
	1/4	1.361	1.747	.0390
C_2H_2	1/8	3.233	2.396	.0932
	1/8	3.657	2.908	.0595
	3/16	2.311	1.843	.0709
	3/16	2.508	2.079	.0734

Examination of the data presented in Table I indicates that the flame speeds of ethylene and acetylene were decreased when ozone was present while that of ethane increased. These data were not sufficiently well grouped to permit a general correlation of the observed facts, except in the qualitative sense. The large variations in the flame speed shown in Table I occurred in those runs in which there was considerable alteration in the flame shape. The small variations were for runs in which the flame shape was not significantly changed. It was observed that the addition or removal of ozone from an otherwise stable flame often induced oscillations, blow-off or flash-back. Also, rich flames appeared to be more susceptible

to instabilities than lean ones. For a plausible explanation of the observed increase in the flame speed of the ethane-air mixtures the reader is referred again to the oxidation reactions and the ozone decomposition reactions previously given.

Variations in the distance between the lip of the burner and the lower edge of the flame when ozone was added or removed indicate that the rate of heat release was changed. For ethane-air flames this alteration was in the direction of increased rate of reaction.

The decrease in the flame speed observed in the case of ethylene-air and acetylene-air mixtures cannot be analyzed on the same basis. To explain the possible cause of this effect, one should consider the reactions of multiple carbon to carbon bonds.(1) For ethylene these reactions proceed as follows:

$$C_2H_4 \xrightarrow{O_3} H_2C\underset{\underset{O-O-}{|}}{-O-C}H_2 \xrightarrow{H_2O} 2HC\lesssim^{H}_{O} + H_2O_2 \qquad \text{(E)}$$

Since these reactions occur at room temperature, it would be expected that they took place in the mixing zone. Formaldehyde, which is a partial oxidation product of the hydrocarbon, was formed. Because of the physical construction of the equipment, reaction (E) occurred non-adiabatically and the heat of reaction dissipated. This reduced the net heat release available by about 2.5%. Moreover, the fuel was no longer ethylene but a mixture of formaldehyde and ethylene and the combination of these two effects served to reduce the flame speed.

The same type of explanation should be applicable to a higher degree to acetylene flames. This was indeed the case, for in many runs after the addition of ozone, the flame became so diffuse that satisfactory photographs could not be taken.

Within the limits of the experimental techniques employed, it can be stated with certainty that ozone, in a concentration of about 1% may increase the flame speed of ethane-air mixtures and decrease the flame speeds of ethylene or acetylene mixtures, and that large changes in the flame speed are associated with abrupt changes in the flame shape. While there is not available at this time sufficient general

information for a rigorous mathematical development, it is felt that the evidence is consistent with the hypothesis advanced in this paper.

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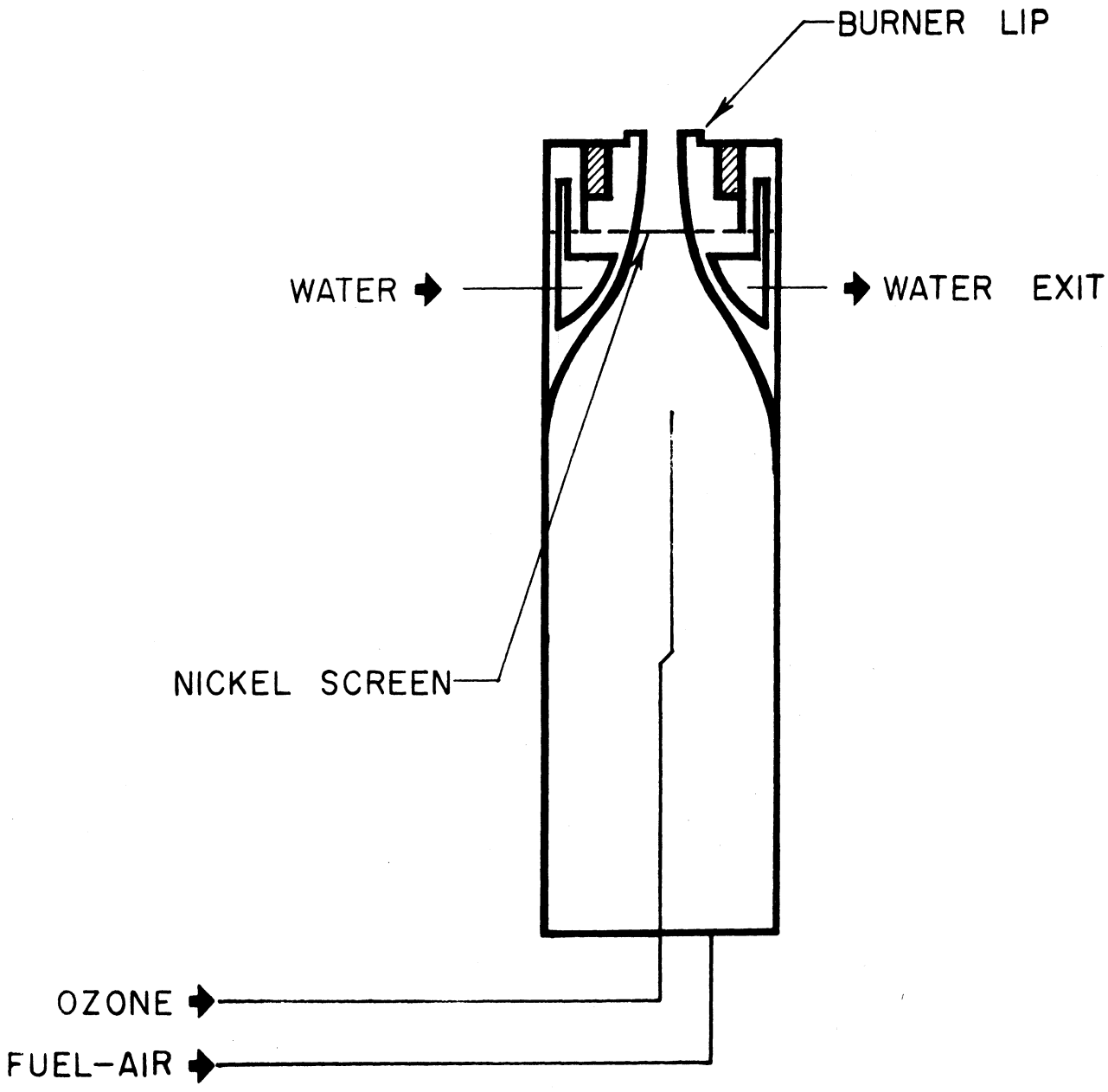

Figure 1. Cross-sectional view of burner

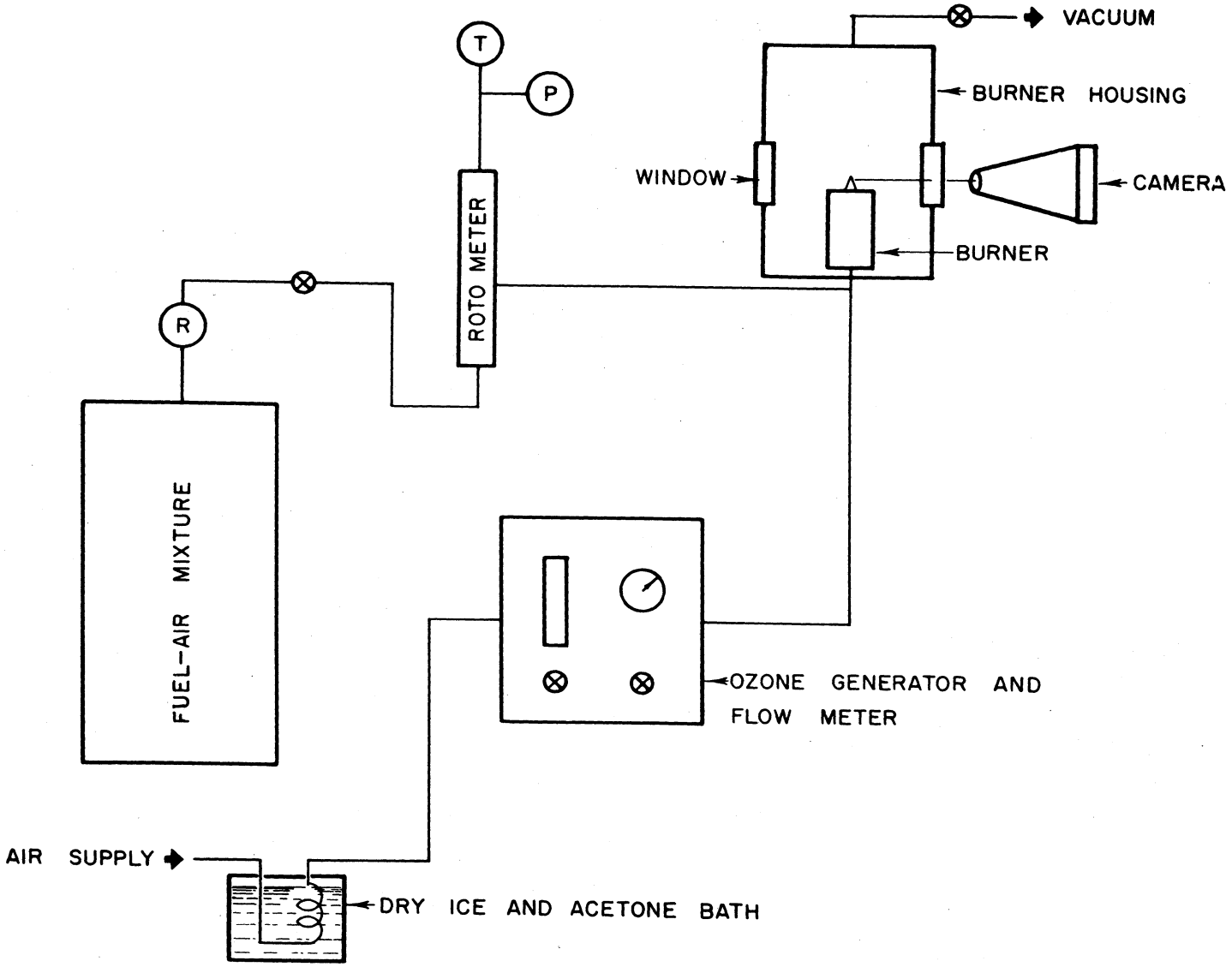

Figure 2. Schematic diagram of equipment

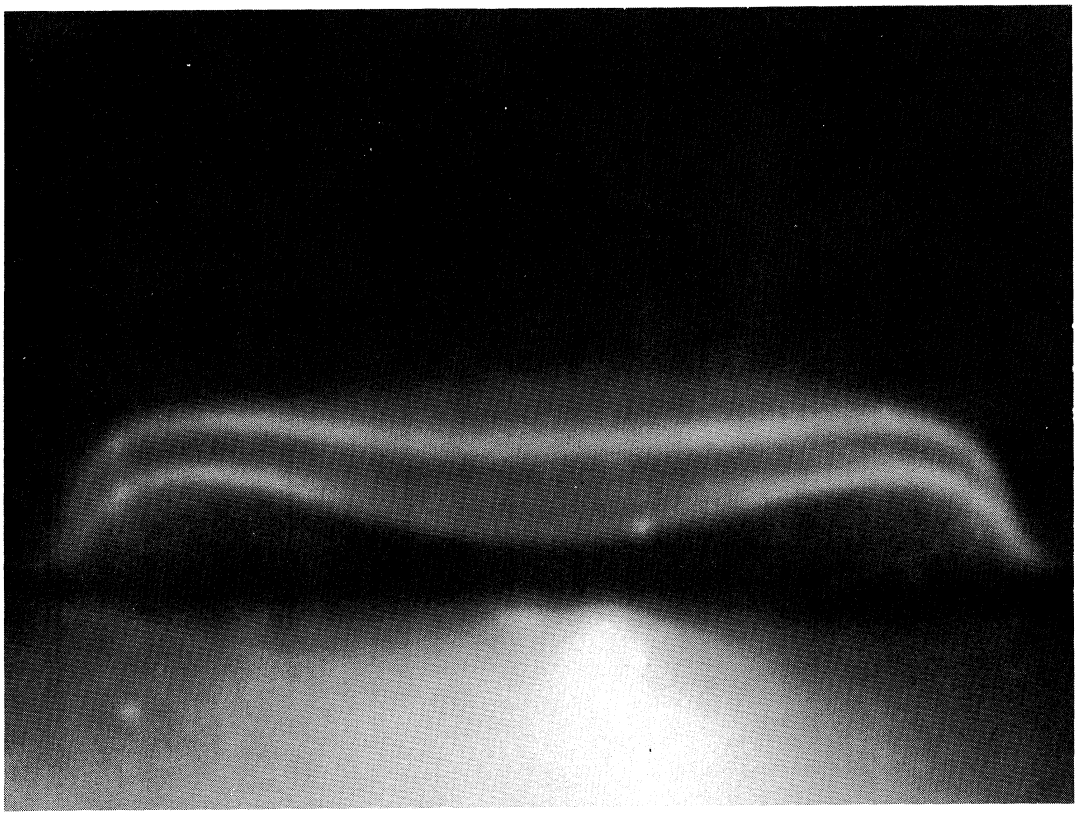

Figure 3. Ethane flame - ozone present in lower flame

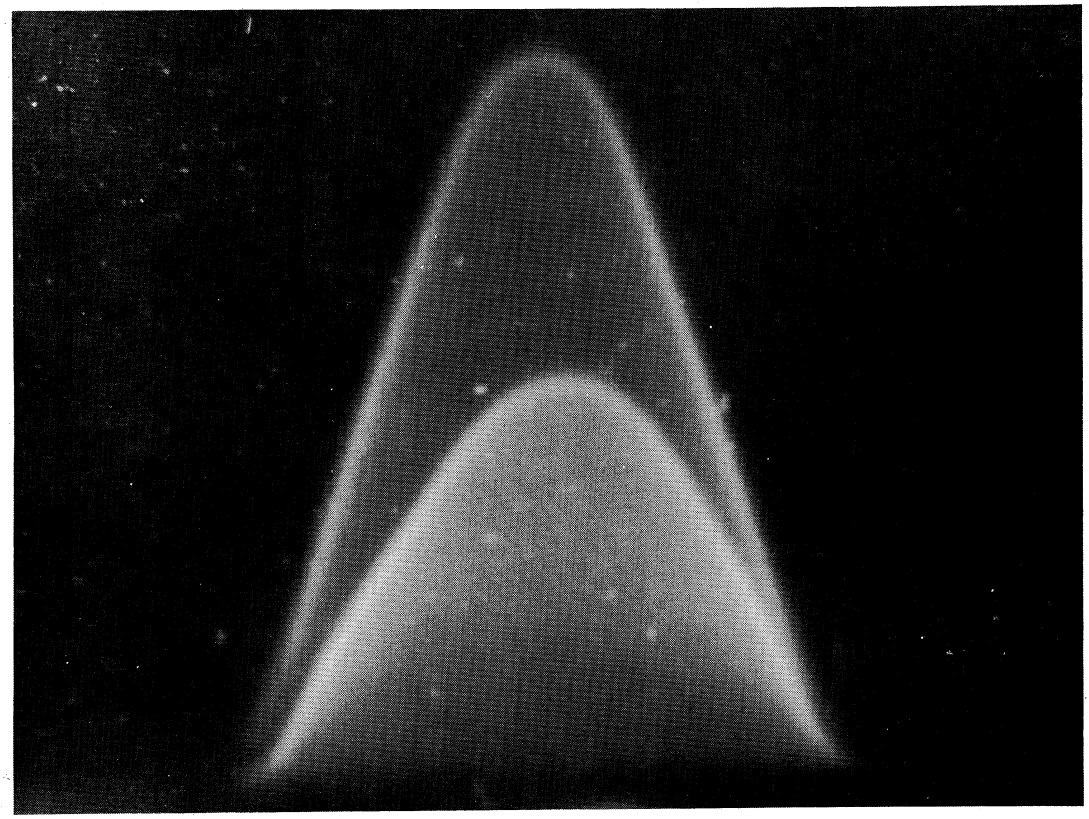

Figure 4. Ethane flame - ozone present in lower flame

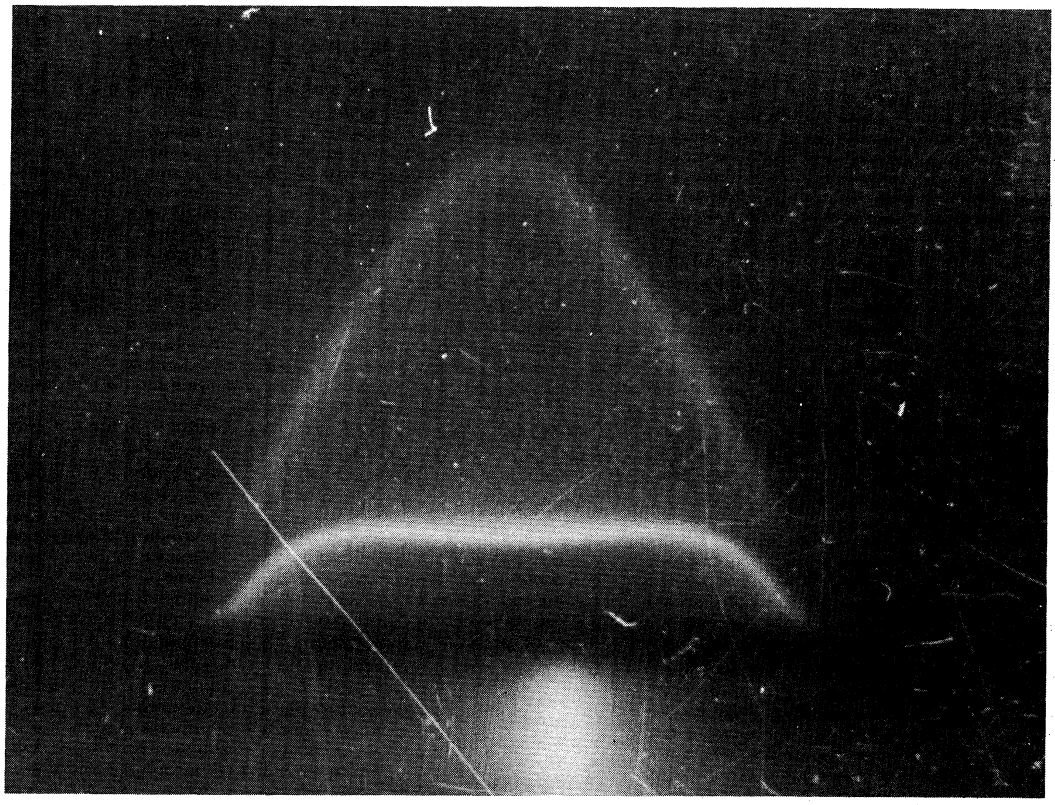

Figure 5. Ethane flame - ozone present in lower flame

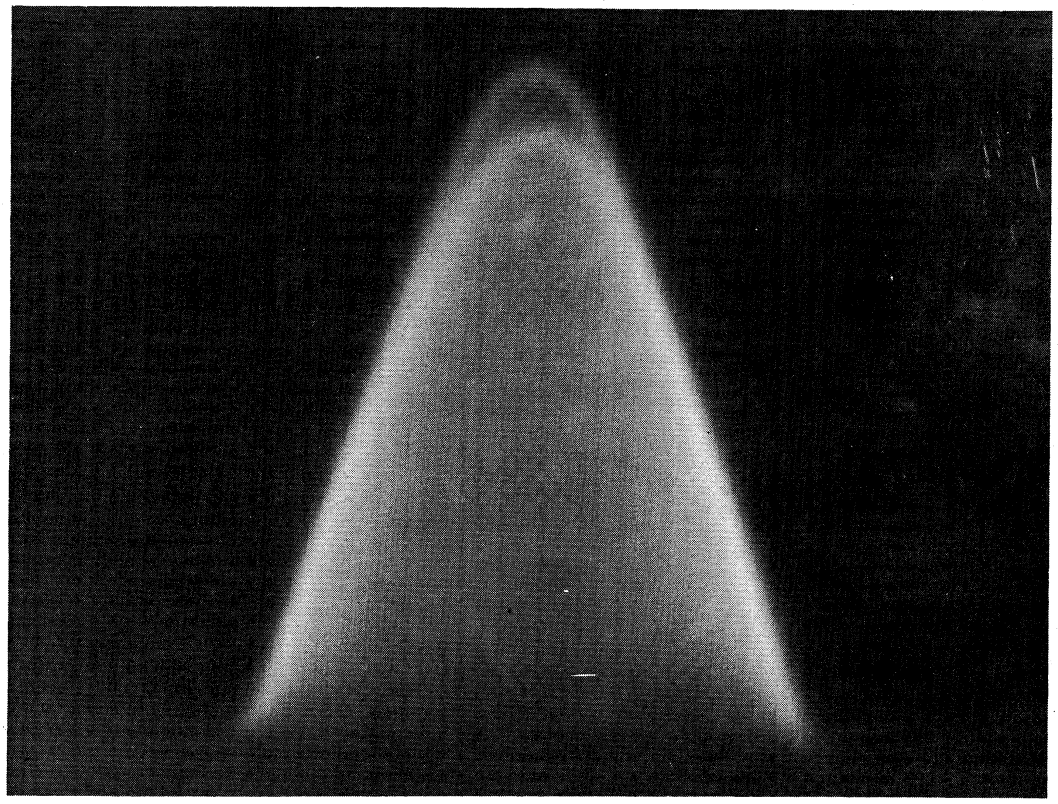

Figure 6. Ethane flame - ozone present in lower flame

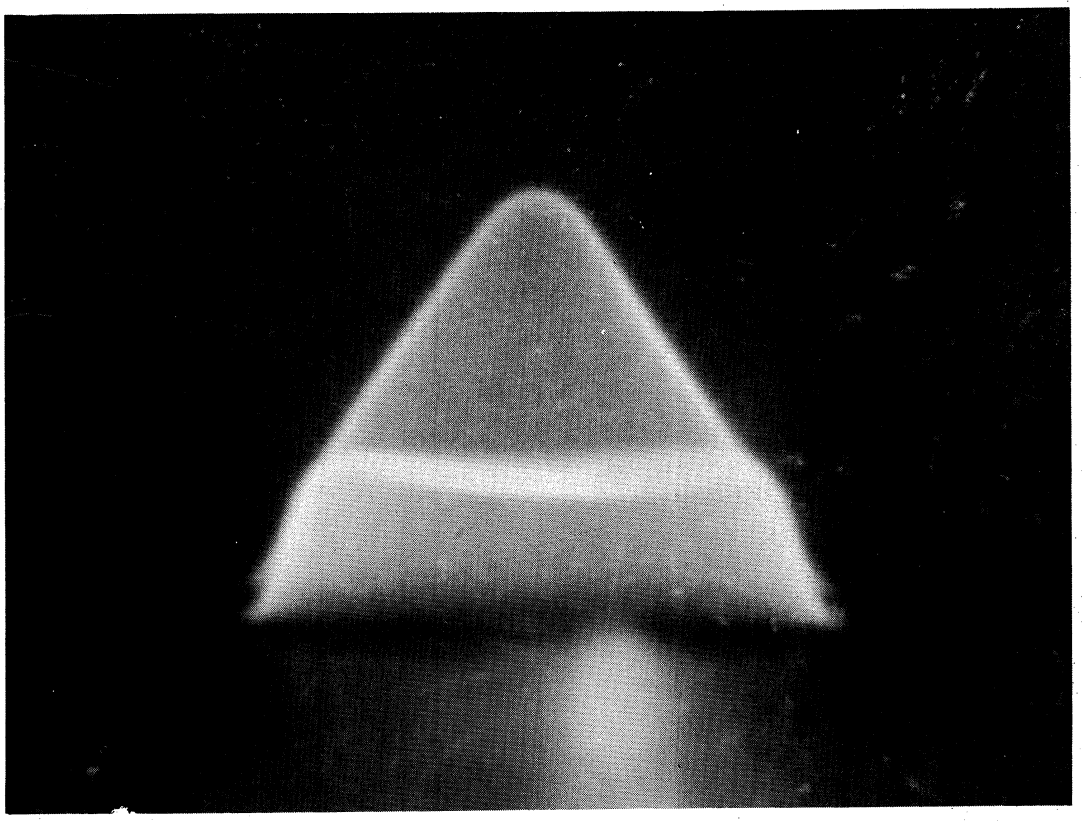

Figure 7. Ethylene flame - ozone present in upper flame

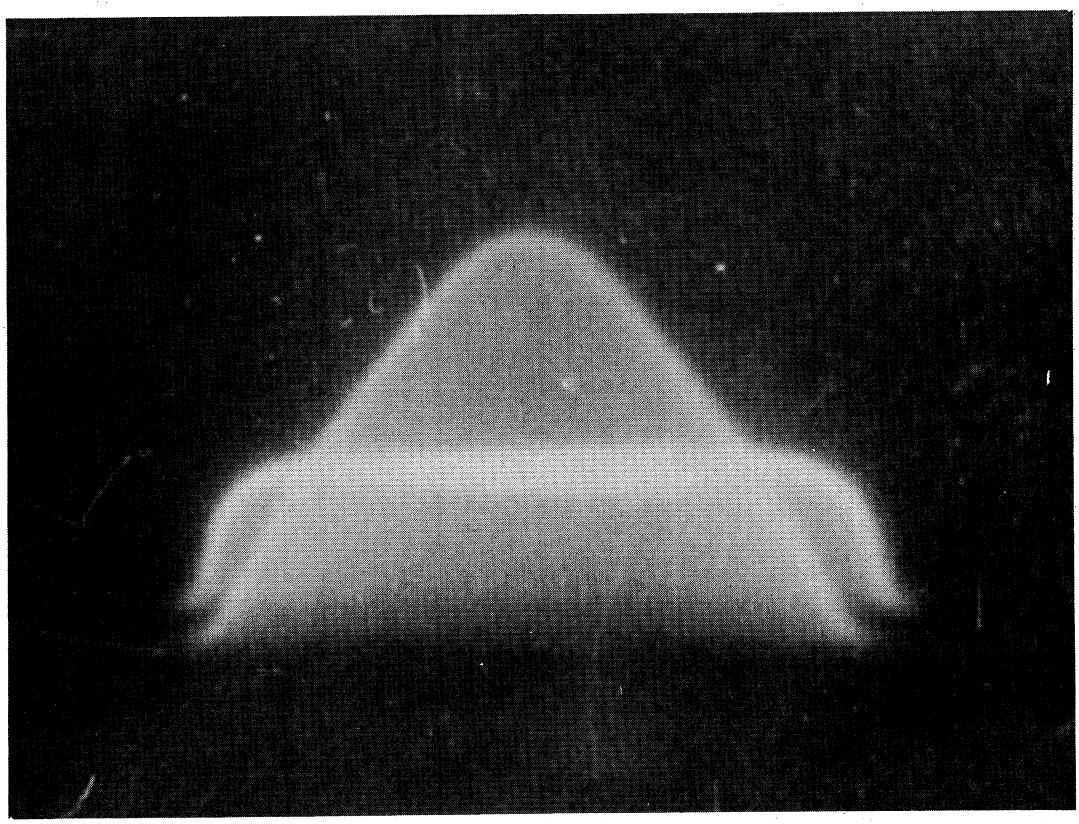

Figure 8. Ethylene flame - ozone present in upper flame

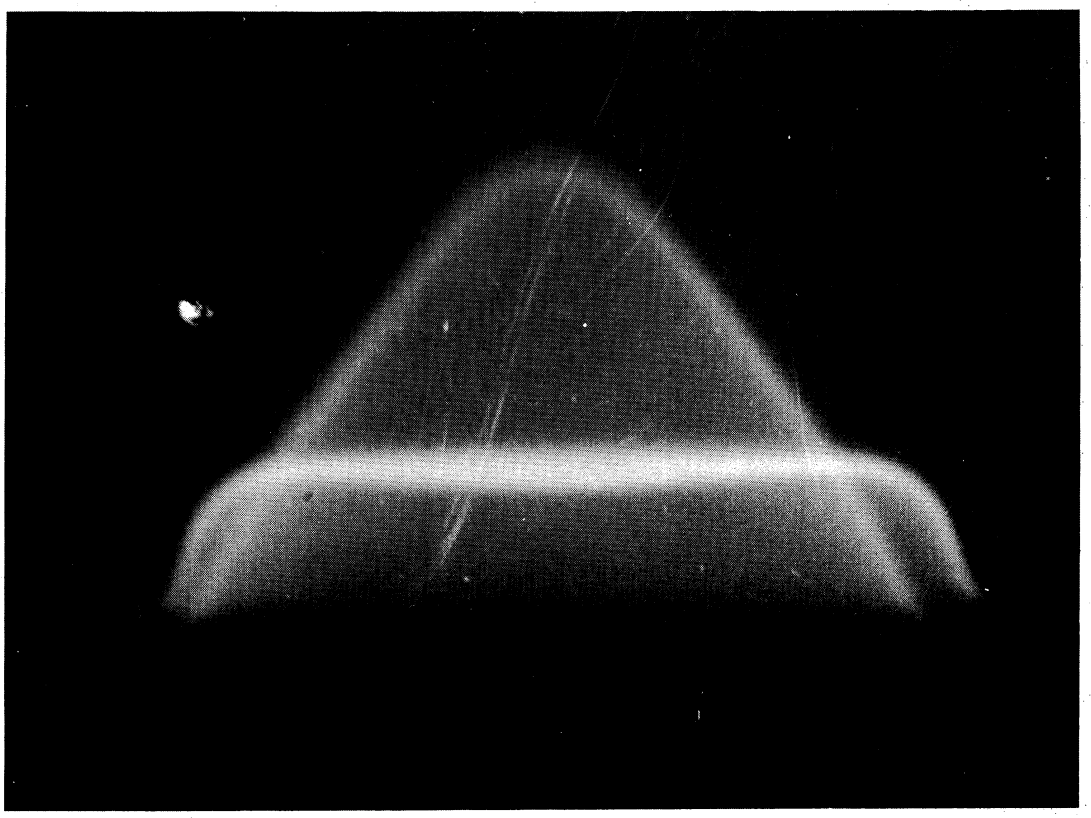

Figure 9. Ethylene flame - ozone present in upper flame

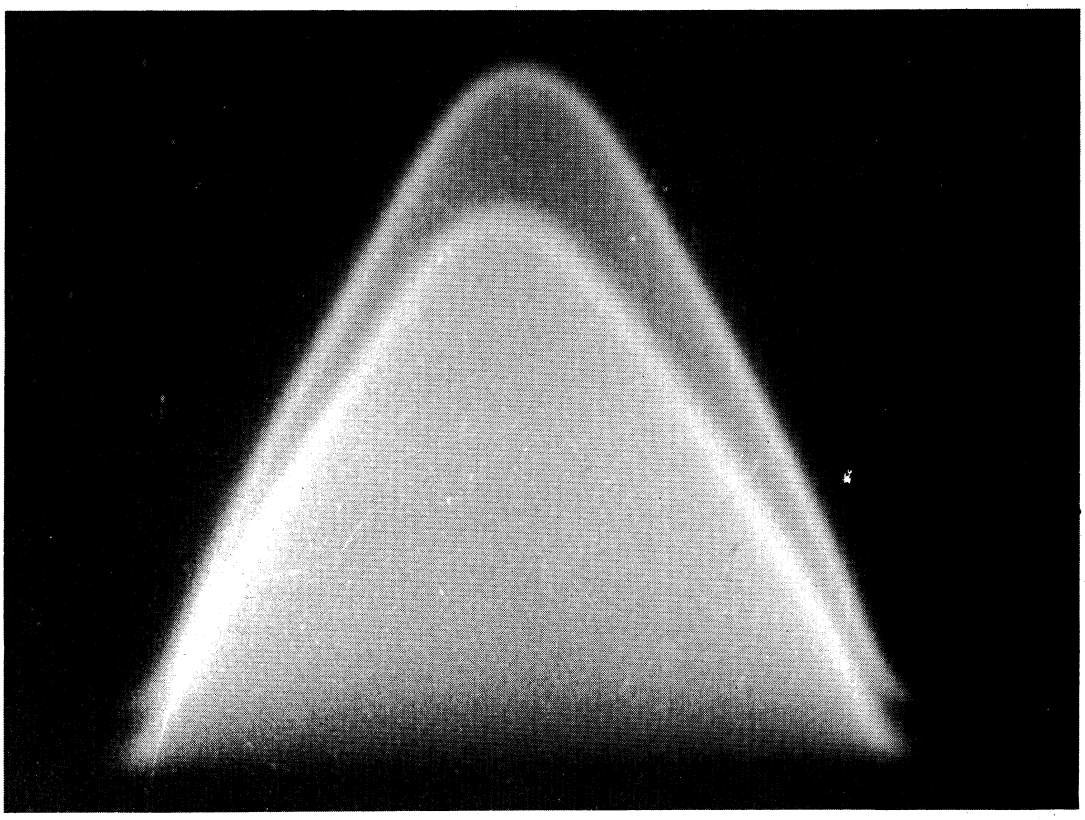

Figure 10. Ethylene flame - ozone present in upper flame

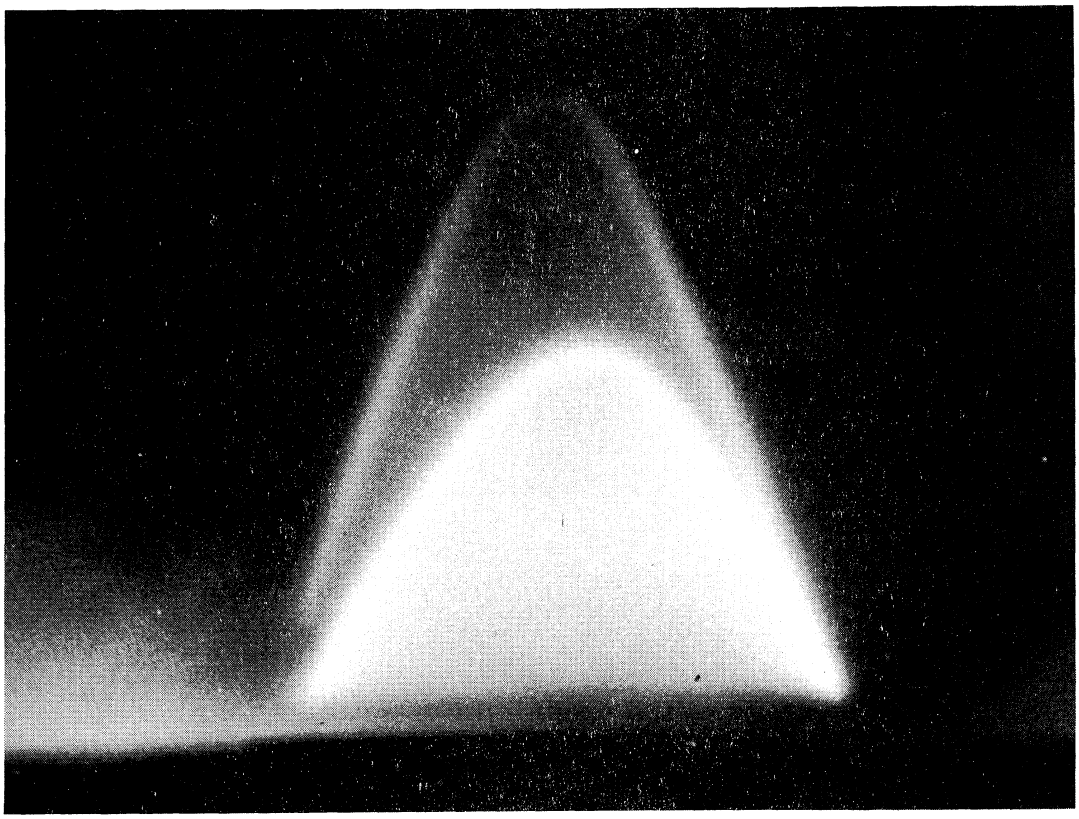

Figure 11. Acetylene flame - ozone present in lower flame

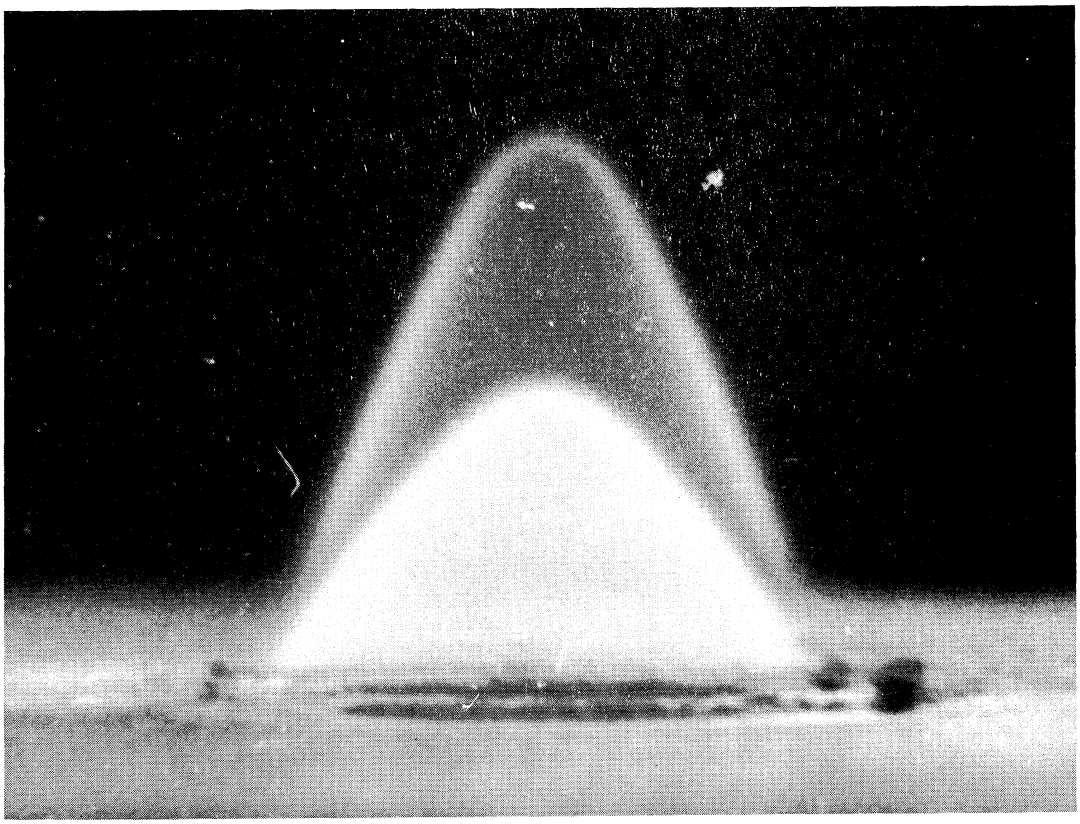

Figure 12. Acetylene flame - ozone present in upper flame