THE PHOTOGRAPHIC STUDY OF THE PHENOMENA
FOLLOWING FLAME PROPAGATION

by

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Prof. A. L. Merrill
Secretary of the Faculty
Massachusetts Institute of Technology
Cambridge, Mass.

Dear Prof. Merrill,

In partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering Practice, I am submitting herewith a thesis: 'The Photographic Study of the Phenomena Following Flame Propagation.'

Sincerely yours,
The Author wishes to express his grateful appreciation of the invaluable suggestions and very friendly co-operation of Professor Hoyt C. Hottel and of Mr. Victor C. Smith of the Department of Fuel and Gas Engineering.
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OBJECT

The object of this research is the photographic study of the phenomena following flame propagation, as occurring in an internal combustion engine under detonating and non-detonating conditions.

SUMMARY

Experimental apparatus has been designed and constructed for the photographic study of flame propagation and the phenomena following it. Results have been obtained which demonstrate the feasibility of the apparatus.
INTRODUCTION AND REVIEW OF LITERATURE

Flame has been a thing of wonder to man ever since the extremely remote era when he first became familiar with it. Alchemists, seeing magic everywhere, tried to unlock the great mystery of fire. Today, hundreds of research workers are studying flame in its many varieties and aspects and by widely diverse methods of investigation.

The study of flame propagation in combustible gas mixtures was instigated in the nineteenth century for the purpose of finding means of preventing explosions in mines. Much valuable information was obtained by scientists in England and France, one practical result being the invention of the well-known miners' safety lamp by Sir Humphrey Davy. Modern work on the subject really dates from the epochal discovery in 1881 by Berthelot and Vielle (3) of what they called the detonation wave. This phenomenon is a flame propagation at a very much higher speed than that of the ordinary burning gas jet. In 1883, Mallard and LeChatelier (36) showed that under certain conditions a gaseous explosion passes through well defined stages, commencing with a comparatively slow flame propa-

Note: Numbers in parentheses refer to bibliography at the end of the thesis.
gation of uniform velocity which suddenly becomes accelerating and culminates in the extremely high velocity flame known as detonation. Mallard and LeChatelier originated the method of photographing the flame through a slit onto a moving plate. Modern apparatus is but a development and refinement of theirs.

In recent years when cylinder knocking seemed to place a limit on the compression ratio and therefore the efficiency of internal combustion engines, the study of flame propagation received fresh impetus. Several anti-knock compounds have been discovered and are being used, but the cause of knock has not yet been determined or described satisfactorily. Several theories have been ventured but none is completely acceptable and there is still a general lack of agreement on the subject.

At one time it seemed probable that the two phenomena of knock and the detonation wave were identical. Indeed, it is perfectly true that the two often occur together, but recent work has apparently demonstrated that this is not always the case and that they are simply frequently associated in the same combustion. In other words, a detonation wave may be built up without the occurrence of the knock.

There exist several theories of the mechanism of the combustion of hydrocarbon-air mixtures. One of
the most widely known is the peroxide theory (9) (20) which considers that the first reaction is the formation of an alkyl peroxide, subsequently giving aldehydes and water as decomposition products. A similar theory (4) (7) states that the first change is the addition of oxygen to the hydrogen atoms of the hydrocarbon to form hydroxyl groups. Another is the theory of primary dehydrogenation (34) which is that there occurs a direct combination of oxygen with those atoms of hydrogen which are most easily split off from the hydrocarbon molecule, the initial products being unsaturated hydrocarbons, containing one or more double bonds, and water. The proponents of each of these and other theories have published data substantiating their own and proving false the others; so there is a wide difference of opinion as to the true mechanism of the gaseous combustion reaction.

Nearly all of the students of the problem, however, agree substantially on the effect of antiknock substances, as being a negative catalysis or inhibition of the oxygenation of the hydrocarbon molecules (20) (34). In order to understand why this slowing of the hydrocarbon oxidation is thought to result in the elimination of knock, it is necessary to consider some of the opinions as to the fundamental difference between knocking and non-knocking combustion.
Brown and Watkins (8) published their belief that the knock is caused by heterogenous (liquid and gas phase) reactions on heated surfaces and that autoignition of unburned mixture adiabatically compressed against the hot surfaces was the mechanism. Maxwell and Wheeler (37) give a very clear and concise expression to the idea, "In a pinking explosion, such as those of pentane-air mixtures at high initial pressures, combustion is not completed in the flame front and is not continuous behind the flame. It would seem as though some additional impetus were required to cause the completion of the reactions. When this impetus is given; for example, by the production of a shock wave when the accelerating, vibrating flame is arrested at the end of the cylinder, the combustion is completed almost instantaneously throughout the cylinder, with a consequent increase in pressure. This subsequent energy release may maintain the shock wave, thereby producing effects similar to those of a 'detonation wave'.

"In a non-pinking explosion, such as those of benzene-air mixtures, the combustion reactions are continuous and long-continued behind the flame front. Even when conditions are such that the initial flame can commence to vibrate and accelerate, its subsequent arrest does not lead to any violent after-effects as the energy available is not sufficient."
Layng and Youker (51), from a study of the effect of antiknock compounds on the slow oxidation of hydrocarbons, conclude that, "for a compound to have properties to be classed as a suitable antiknock, it must be an inhibitor of gas-phase oxidation and an accelerator of liquid-phase oxidation. Compounds which fail to approach lead tetraethyl but which have some effect as antiknocks appear to have their effect only in one of the phases present in the gas engine at the temperatures tested."

Tizard and Pye (48) point out that the ignition temperature of the hydrocarbon has a marked relation to its knocking qualities. The ignition temperatures of the paraffin series of hydrocarbons diminish steadily as their molecular weights increase and it is a fact that the higher members knock more readily than the lower ones. This appears to substantiate the theory that hot surfaces increase knock. Carbonized cylinders dissipate less heat to the outside, are overheated, and the knock results.

Egerton and Gates (21) believe that antiknock compounds function in the initial stages of the explosion as negative catalysts, forming peroxides which mutually decompose organic peroxides formed as the first stage of hydrocarbon oxidation. Also they have found that antiknocks do not affect detonation. Laffitte and Dumanois
similarly find that the velocity of propagation is unaffected by the presence of antiknocks.

Brown (8) has published an extensive bibliography to show that, while the detonation wave and knocking are similar in that an increase in initial pressure stimulates both, and the addition of diluents represses both; on the other hand, an increase in initial temperature decreases the tendency to initiate the detonation wave but increases the tendency to knock, and also that surface conditions have no effect on the velocity of detonation waves but have a pronounced effect on knock.

It would appear to be the consensus of many investigators that engine knock is not only emphatically non-identical with the detonation wave, but is not even invariably associated with it. The salient point is that it is not the passage of the detonation wave that determines whether there will be knock or not, but that the occurrence or non-occurrence of this phenomenon is dependent upon the condition of the gas behind the flame front. If combustion is incomplete behind the flame it appears that knock occurs; if the combustion is uniform there is no knock, although the velocity of the flame is unaltered.

The study of this relation between knock and the phenomena following flame propagation is the object of the present research, of which this thesis is the preliminary part.
EXPERIMENTAL APPARATUS

The experimental apparatus is comprised of three main groups: the bomb or explosion vessel, the carburetor or apparatus for preparation of fuel-air mixtures, and the camera or photographic apparatus. In the laboratory, the bomb is mounted upon a small table between the carburetor on one side and the camera on the other. This arrangement is shown in the photographs following this page.

**Explosion Vessel**

The explosion vessel was designed to approximate the detonation conditions found in an internal combustion engine cylinder as closely as possible, while avoiding factors which are functions merely of shape or mechanical requirements but which impose complications upon the flame propagation. This simplification is best accomplished by a spherical bomb with central ignition. Figure I (following page 9) illustrates the design and dimensions of the bomb constructed according to this principle.
Experimental Apparatus
Experimental Apparatus
The bomb consists of two similar hemispheres, prepared as follows. Two castings were made of 'semi-steel' which is a type of cast iron possessing better finishing properties than the ordinary gray iron castings. These were machined on the inside to give a sphere when the two sections are joined six inches in diameter, with a shell of one-quarter inch thickness. At the center of each hemisphere there was machined out a raised, circular elevation, two and one-half inches in diameter and at the edges one-half inch above the outer surface of the shell. This provides horizontal, plane surfaces for clamping the halves of the sphere together. The bomb rests on a bar of mild steel, nine inches long, three inches wide, and one inch thick. Bolts pass between this bar and a similar one resting on the bomb's upper flat surface. These bolts also secure the bomb to the table top. At the center of each bar there is a hole bored one and one-half inches in diameter to give clearance to spark plug and valve, respectively. The spark plug is tapped into the center of the upper hemisphere, the valve in the lower.

In the preliminary design of the bomb, it was intended to use a quartz or glass annular ring set into the horizontal mid-circumference of the bomb as a window through which to photograph the flame movement. This was later found to be impracticable, and another form of
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Spun Copper Steam Jacket

Window Slot for Photograph.

Bomb Material Cast "Semi-Steel"
window was devised. The rim of each hemisphere was machined on the outer surface to give, when the bomb is assembled, a band one-half inch wide and inset one-sixteenth of an inch. The two halves were fitted together with a male and female groove joint to insure tightness. A slit one-sixteenth inch wide was cut at the juncture of the hemispheres for a length of about one-third of the circumference. This is covered by a strip of transparent Cellophane which is held by a band of spring brass tightly in place against the set-in portion of the bomb. This set-in area is highly polished to permit the Cellophane to fit snugly. The brass band is tightened by bolts through angle sections attached to its ends. Cellophane is obtainable in a wide range of thicknesses and it has been found that very thin grades are amply strong to withstand the initial pressures of as high as five or six atmospheres used in these experiments. It is possible to use a thickness, still remarkable for its transparency, heavy enough to resist bursting under the pressures reached during the explosions, but this is unnecessary since by the time the explosion has reached the walls, the photographic record is complete.

To obtain initial temperatures similar to those in actual engine cylinders, the bomb has been steam-jacketed. A spun copper hemisphere was soldered to each half at the central raised surface and just above the edge of the
polished part around the rim. Low pressure steam is admitted separately to each jacket.

For ignition, a standard spark plug with extended electrodes is screwed into the central tap in the upper half of the bomb. The electrode extensions were spot-welded to the ends of the original spark points. The orifice of the plug is closed by a mica disc secured by lacquer. This was done to avoid distortion of the explosion flame through inequalities of vessel shape. For a similar reason, the lower inch of each electrode was reduced in diameter by etching with concentrated nitric acid.

The port for admission of explosive mixture and also for exhaustion of products of combustion is attached by means of the tap in the center of the lower hemisphere. A nipple, especially designed with a central bore of only one-sixteenth inch to make its effect on the sphere volume small, and reducing the diameter from that of the bomb tap to one-eighth inch pipe thread, forms the connection between the bomb and a one-eighth inch right-angle needle valve. Attached to the other side of this valve by a space nipple is a tee connection to a calibrated Bourdon gage reading from zero to one hundred pounds per square inch gage pressure. Beyond this gage connection, another tee leads to similar needle
valves, one connected by seamless tubing to the carburizer, the other to a water vacuum pump.

Apparatus for Preparation of Fuel-Air Mixtures

The carburizer is a system for vaporizing a measured amount of fuel with a measured amount of air and supplying the mixture to the bomb. Figure II (following this page) is a diagram of the arrangement of the various parts of the system but is not drawn to scale.

Air is measured in three calibrated vessels, so arranged with stopcocks that each is independent of the others. The air is drawn in by draining off water to a twelve liter aspirator bottle below the apparatus, and is forced out by applying ten pounds per square inch air pressure at the mouth of the bottle. The first measuring vessel is a copper cylinder with conical ends designed to furnish a basic amount of air, corresponding to approximately eighty per cent of the theoretical requirement for combustion of the amount of fuel used. The second vessel is a glass cylindrical burette with calibration to permit the addition of any part of its volume of air (within one-tenth of one per cent) to the basic volume from the copper container. Use of the entire volume of this cylinder in conjunction with the
APPARATUS FOR PREPARATION OF FUEL-AIR MIXTURE

FIGURE II
basic volume gives approximately the theoretical air requirement. Up to one hundred and twenty per cent of theoretical air is obtained by adding a measured part of the volume of another glass cylinder similar to the first.

The fuel to be used is measured in a calibrated bulb attached to the vaporizer. In the case of heptane, the volume used is 1.208 cubic centimeters. By reversing a three-way stopcock, the measured fuel is dropped to the bottom of a small vaporizer bulb. The measured air is slowly bubbled through the fuel, vaporizing it completely.

The vaporized mixture is collected in a twelve liter aspirator bottle over saturated zinc sulphate solution. The level of this solution is lowered by gravity and raised by air pressure, as in the case of the air measuring vessels. The vaporized fuel-air mixture from this collecting bottle is carried to the bomb by a hand pump that has been fitted with an additional valve on the outlet end to insure prompt closing and a snug piston lubricated with glycerine. Care was taken to eliminate rubber from all connections between the vaporizer and the bomb in order to avoid possible loss of hydrocarbon. This was also the reason for using glycerine to lubricate the pump and soap-glycerine paste for stopcock lubricant.
Photographic Apparatus

The photographic apparatus is of the type usual for flame propagation study, consisting of a film drum revolved at high speed upon which is recorded a slit image of the flame in the bomb, together with a time record from a tuning fork arrangement. The optical system is shown in Figure III and the wiring diagram in Figure IV, both following this page.

The drum, four inches in diameter, is rotated by a friction drive from an electric motor. By moving the friction contacts, a wide variation of speed is available, from the slowest when one contact is near the center of the disc attached to the motor shaft and the other at the rim of the similar disc on the drum spindle, through the entire range on up to the highest speed at the reverse arrangements of the contacts.

As the drum revolves, it receives through a slit the image of the explosion flame, the image broadening as the flame progresses towards the wall of the bomb. The picture produced is in the form of a wedge, the initial spark as the point and the rate of divergence of the sides being relative to the velocity of the flame movement. The true velocity is given by the accompanying time record which appears at the side of the film.
ELECTRICAL SYSTEM
OF CAMERA
FIGURE IV
The source of the time record is a lamp giving an intense light concentrated in a very small area, approximating a point. This beam is focussed by a lens on parallel vanes attached to the prongs of a tuning fork. Each vane contains a slit, and when the fork is at the condition of rest these slits are made to coincide. When the fork vibrates, the beam of light focussed on the vanes passes through the slits and is condensed by a lens onto the film drum, with a period one-half that of the fork. This beam, before reaching the lens, must pass through a slit shutter which opens only at the time of explosion.

The electric wiring of the photographic apparatus is arranged to open the time recorder shutter for only a single revolution of the drum and to synchronize the time record with the explosion. Figure IV shows an argon arc Point-o-Lite bulb which operates through the switch (a) on 110 volt direct current. An alternate lamp for this purpose is one using 3.5 volts and 11 amperes through a transformer on the 110 volt alternating current, but this lamp is not shown on the diagram. Switch (b) operates the tuning fork vibrator on two dry cells. When the double pole switch (cd) is closed, the motor runs and the direct current circuit is also complete, with the exception of the contact on the end of the drum spindle shown in the upper middle of the diagram. This
contact is made by a trigger mechanism which is pulled just after the main camera shutter is opened. Closing this contact causes the electro-magnetic coil to pull down the little arm, held in place normally by a spring, which opens the slit shutter on the time recording system. The contact arrangement on the drum spindle leaves the line closed and the shutter open throughout only one revolution. The core of the electro-magnet is a part of the primary circuit of the spark coil. When the shutter arm is pulled down, the circuit is completed, firing the spark in the bomb and initiating the explosion. In this way the time record is synchronized with the explosion.
RESULTS AND DISCUSSION

The chief result of this thesis is the experimental apparatus, the design and construction of which has been described on preceding pages.

Several photographs of flame propagation have been taken. These show the feasibility of the apparatus, but they also indicate the need for considerable practice in the technique of flame photography. Changes in the apparatus may be necessary to obtain improved results.

Limitation of time has made it impossible to carry on the extended study which this problem merits. It is hoped that the work will be continued and the results presented subsequently in a Doctor's thesis.

A print of a typical negative appears on the following page. This represents two propagations in similar heptane-air mixtures. In one of them (A) the cellophane window burst, causing the sudden flash extending beyond the walls of the bomb.
ADDED NOTE

March 10, 1931

Work on this problem has been continued and is still in progress. Numerous changes have been made in the apparatus, the most important being the use of an especially designed lens with an aperture ratio of f/1.75, which was adopted after the trial of several other types.

Several series of photographs have been taken in the study of various phases of the investigation. In most of these, the velocity of propagation can be obtained by measurement of the flame front. With certain mixtures a sudden, bright intensity of light is initiated at the center of the bomb just before the flame front reaches the walls. The composition at which this phenomenon first appears varies with the initial pressure.

This information is given to show that the photographs included in this thesis are to be considered merely as first attempts, and that reference should be made to the later work for the real results of the research.
CONCLUSIONS

The apparatus is satisfactory for the study of detonation phenomena over a wide range of conditions similar to those found in the cylinders of internal combustion engines.

RECOMMENDATIONS FOR FUTURE WORK

Future research should include the following studies:

1. Comparison of a fuel possessing extreme and reproducible knocking properties, such as heptane, with a non-knocking fuel such as iso-octane.
2. Comparison of lean and rich fuel mixtures.
3. Comparison of high and low compression ratios.
4. Effect of variation of temperature of walls.
5. Effect of substitution of other inert gases for the nitrogen of the air.
6. Effect and comparison of various antiknocks.
APPENDIX A

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APPENDIX B

Calculation of Fuel Mixtures

Using normal heptane, the proportions for theoretical combustion with air are represented by the following equation:

\[ C_7H_{16} + 11 O_2 + 41.4 N_2 = 7 CO_2 + 8 H_2O + 41.4 N_2. \]

The heptane used in the present experiments was measured in a bulb calibrated to deliver 1.208 cubic centimeters of heptane.

\[ 1.208 \text{ cc. heptane.} \]
\[ \times 0.683 \text{ grams per cc. density of heptane.} \]
\[ = 0.825 \text{ grams heptane used.} \]

Molecular weight of heptane = 100.

\[ 0.00825 \text{ mol heptane used.} \]
\[ \times 52.4 \text{ mols air required for 1 mol of heptane.} \]
\[ = 0.432 \text{ mol air required for theoretical combustion.} \]
\[ 0.432 \times 22,400 \times \left( \frac{273 \times 23}{273} \right) = 10,840 \text{ cc. dry air.} \]

Vapor pressure of water at 23° C. = 22 mm. Hg.

Volume of saturated air required =
\[ 10,840 \times \frac{760}{760 - 22} = 11,160 \text{ cc. at 23° C.} \]