EFFECT OF INHIBITORS ON HYDROCARBON OXIDATION

by

Francis M. Pierce

B.S., Northeastern University (1960)

Submitted in Partial Fulfillment
of the Requirements for the
Degree of Master of Science

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

June, 1961
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Submitted to the Department of Chemical Engineering on May 19, 1961, in partial fulfillment of the requirements for the degree of Master of Science.

ABSTRACT

This thesis is a critical review of the literature published since 1950, on the effect of inhibitors on hydrocarbon oxidation. The various theories of inhibition and evidence supporting each theory have been included. When possible, conclusions justifying the theory have been given. The actual review has divided inhibition into three classes: 1) homogeneous inhibition of flame and explosion phenomena, 2) homogeneous inhibition of low temperature oxidation, and 3) heterogeneous inhibition. Investigators have studied inhibition under a number of conditions so care must be exercised in attempting to correlate the work of different authors. In this thesis most results have been put on a common basis to facilitate interpretation, however, the various conditions under which a particular experiment was conducted should be carefully noted.

Homogeneous additives have been subdivided into two classes, first, those substances which are inert and inhibit by a more or less mechanical process, and second, those substances which exhibit specific chemical inhibition. Most of the work on flame and explosion phenomena has been concerned with the effect of additives on flame velocity and explosion limits. There are little published data on the products or reaction intermediates, due mainly to the difficulties involved in obtaining this information. Results of this type are most desirable since they give better insight into reaction mechanisms.

Results of low temperature oxidation are more complete, however, correlation is hindered due to the differences in kinetic mechanisms between low and high temperature oxidation. Data on heterogeneous additives are even more scattered. Most of the published results merely give empirical generalizations on the effects of these inhibitors. Much work is necessary before any theories may be seriously considered.

Thesis Supervisor: Professor C. N. Satterfield
Title: Professor of Chemical Engineering
May 17, 1961

Professor Philip Franklin  
Secretary of the Faculty  
Massachusetts Institute of Technology  
Cambridge 39, Massachusetts

Dear Professor Franklin:

I am submitting to you my thesis entitled "Effect of Inhibitors on Hydrocarbon Oxidation". This thesis is submitted in partial fulfillment of the requirements of the degree of Master of Science in Chemical Engineering.

Very truly yours,
Signature Redacted

Francis M. Pierce
The author wishes to express his sincere appreciation to Professor C. N. Satterfield for his assistance with this work.
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I. SUMMARY

This thesis is a critical review of the literature published since 1950, on the effect of inhibitors on hydrocarbon oxidation. The various theories of inhibition and evidence supporting each theory have been included. When possible, conclusions justifying the theory have been given. The actual review has divided inhibition into three classes: 1) homogeneous inhibition of flame and explosion phenomena, 2) homogeneous inhibition of low temperature oxidation, and 3) heterogeneous inhibition. Investigators have studied inhibition under a number of conditions so care must be exercised in attempting to correlate the work of different authors.

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II. Effect of Inhibitors on Hydrocarbon Oxidation

A. Introduction

At present, much work is being done on oxidation kinetics, both flame and explosion phenomena and low temperature oxidation. Investigators have studied the effect of many additives in various oxidation systems and results are published in the literature, however, no review article has been published recently. It is the purpose of this thesis to review the literature and correlate the work of various authors on the effects of inhibitors on hydrocarbon oxidation.

The effect of inhibitors is of interest because of the large amount of work now being done with oxidation processes. It is also desirable to know which inhibitors may most effectively be used as fire extinguishers.

This report contains essentially three divisions: 1. effect of homogeneous additives on flame and explosion phenomena, 2. effect of homogeneous additives on oxidation kinetics, and 3. effect of heterogeneous additives. In general, it covers the theories of inhibition of oxidation processes. To accomplish this, a thorough review of the literature published since 1950 was undertaken. The various theories of inhibition and evidence supporting each theory are given. When possible, conclusions justifying the theory have been drawn.
B. Flame and Explosion Phenomena

1. Procedure

Most authors studying the effect of inhibitors on hydrocarbon oxidation, report the percent inhibitor necessary to prevent the propagation of a flame ignited by a spark or other method, in a standard combustion chamber. The "standard" chamber is a glass tube not less than 2 in. diameter nor less than 4½ ft. long. Changes in the dimensions of the combustion chamber prevent the correlation of work of many investigators because of the change in the wall effects in the "non-standard" chamber. The flame may be ignited at any point in the chamber, however, most authors use either an upward or downward propagating flame. Here again, correlation is hindered because of the different characteristics of the upward propagating flame and the downward propagating flame.

In making a run, the investigator fills the combustion tube with a known ratio of fuel-oxidant-inhibitor mixture, and either a flame or spark initiates a flame. The propagation of the flame is observed, usually visually. Various inhibitor concentrations are run, until the concentration required to prevent flame propagation is found.

Most of the articles reviewed present the percent inhibitor necessary to prevent flame propagation as a volume percent based on the oxidant. Other units have been used, but, for the purposes of this report, they have been converted to the above basis.
It has been observed that inhibitor concentrations less than required to prevent flame propagation decrease the flame velocity. It is desirable to investigate these effects separately, hence the effect of inhibitors on flame velocity will be treated first.

2. Flame Velocity

There are three generally accepted theories on the mechanism of inhibition of hydrocarbon oxidation: 1. influence on heat conduction or radical diffusion, 2. influence on flame temperature, and 3. influence on the chemical reactions occurring in the flame. (4) Each of these will be considered separately.

The influence of certain additives on heat conduction and radical diffusion can best be demonstrated by considering the effect of nitrogen and carbon dioxide on flames. (5) Their effect is studied by observation of the change of velocity of propagation with increased amounts of additive (Fig. 1). Three types of curves are obtained:

1. Lean flames -- small amounts of additives have little effect, but as the amount is increased, a decrease in velocity is noted.

2. Near stoichiometric flames -- no segmentation of the curve is noted, i.e., addition of inhibitor causes a sharp drop in velocity.

3. Rich flames -- small amounts of additives cause a sharp velocity drop, while larger amounts show little effect.
FIGURE 1 (6)

EFFECT OF INERT DILUENTS
ON BURNING VELOCITIES OF ETHANE-AIR FLAMES
FIXED RATIO ETHANE-AIR

Nitrogen Inhibited
Lean Flame
Rich Flame
Carbon Dioxide Inhibited
Rich Flame

Moles Inert/Mole Oxygen
Nitrogen and carbon dioxide exhibit similar behavior in their effect on flame velocity; however, the ability of carbon dioxide to decrease flame speed is greater than nitrogen. The greater heat capacity of carbon dioxide is probably responsible for this condition. This would decrease the flame temperature, thereby causing a decrease in the reaction rate and a corresponding decrease in flame velocity. Carbon dioxide may also affect the CO-CO$_2$ equilibrium in the flame, and some of its inhibition effect may be chemical in nature. More detail will be given to this mechanism later. (7)

The addition of methyl bromide to a flame has a more pronounced effect on the flame velocity than either nitrogen or carbon dioxide. (Fig. 2). Since the difference in heat capacity of methyl bromide and carbon dioxide is not great enough to explain the much higher effectiveness of methyl bromide, its inhibition action must be chemical in nature (8). The chemical nature of methyl bromide inhibition is also indicated from studies of effects other than flame velocity, and these will be discussed later.

Since flame velocity is some function of enthalpy difference between products and reactants, it would be expected that increasing the concentration of methyl bromide would change the products of combustion. Data on hydrogen-air-methyl bromide flames presented by Burdon and co-workers show that the products do change with change in the percent inhibitor (Table I). It is reasonable to extend these results to hydrocarbon flames.
FIGURE 2

EFFECT OF NEUTRAL PROBABLE
ON BURNING VELOCITY OF METHANE-AIR FLAMES

--- Lean Flame
--- Stoichiometric Flame
--- Rich Flame

Flame Velocity, cm/sec

Mol. Percent CH4/Ar
TABLE I (10)

PRODUCTS OF VARIOUS HYDROGEN--AIR--METHYL BROMIDE FLAMES

<table>
<thead>
<tr>
<th>Reactants, Percent</th>
<th>Products, Percent</th>
<th>Temp, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃Br</td>
<td>H₂</td>
<td>O₂</td>
</tr>
<tr>
<td>4.02</td>
<td>6.5</td>
<td>18.8</td>
</tr>
<tr>
<td>8.00</td>
<td>4.3</td>
<td>18.4</td>
</tr>
<tr>
<td>13.5</td>
<td>5.27</td>
<td>17.0</td>
</tr>
</tbody>
</table>
Simmons and Wolfhard report that methyl bromide has a less pronounced effect on lean methane-air flames than on stoichiometric or rich flames. This behavior is expected since there are fewer effective collisions taking place between the fuel and inhibitor in lean flames than in rich flames. Here again it is indicated that the effect of methyl bromide on flames is chemical in nature (11).

3. Explosion Limits

Egerton and Pouling claim that the main criterion for flame propagation is sufficient heat release to provide free radicals for reaction (12). The amount of heat release is directly proportional to the flame temperature; hence they define a "limit temperature" as that temperature required to provide sufficient free radicals to sustain a flame. Their work concerns mainly the effect of halogenated hydrocarbons, e.g., methyl bromide, as inhibitors. The work of Bendon and coworkers indicates that the addition of small amounts of inhibitors only slightly affects the adiabatic flame temperature (13). This is an expected result since the flame temperature depends on the heat of formation of the products and the heat capacity of the flame gases. A small amount of inhibitor would thus have a negligible effect on these figures, which are on the order of ten kilocalories.

Using the fact that the flame temperature is not appreciably changed, Egerton and Pouling have come to the conclusion that the limit temperature must be raised with the addition of small amounts of inhibitors (14). This flame limit temperature can be considered
analogous to the induction period in low temperature oxidation. Molecular collisions are occurring; however, those with the inhibitor are not at a high enough energy level to cause reaction. When the temperature is raised, a point is reached where the collisions with the inhibitor do react, and a flame is propagated.

Downing and coworkers in their work with inhibitors have stated that there seems to be a relation between the heat of combustion of the reactants and the percent inhibitor necessary to prevent flame propagation (15). Investigation of the data of various authors indicates that this relationship does exist for methyl bromide and Freon 12 (Fig. 3). Plotting the heat of combustion of the fuel, in kilocalories per gram, against the percent inhibitor required for extinction, gives straight lines for saturated hydrocarbons. It is not possible to include hydrogen or unsaturated compounds in this plot because of the reactivity of halogens with them. The plot gives straight parallel lines for methyl bromide and Freon 12, with lower inhibitor concentrations required as the heat of combustion increases. It is also noted that methyl bromide is a more efficient inhibitor of combustion reactions.

The heat of combustion inhibitor concentrations plots are in general agreement with the theory of Egerton and Pouling presented earlier, i.e., there must be sufficient heat release to provide free radicals for flame propagation (16). Thus, a fuel with a high heat of combustion requires a greater heat release in an uninhibited reaction
FIGURE 3 (17)(18)(19)(20)

EFFECT OF HEAT OF COMBUSTION ON INHIBITOR CONCENTRATION REQUIRED TO PREVENT FLAME PROPAGATION

Fraction Inhibitor for Extinction

POLYOL

Methyl Ester
than does a fuel with a lower heat of combustion. The fuel with a high heat of combustion is, therefore, more sensitive to the addition of inhibitor than the fuel with a low heat of combustion.

Simmons and Wolfhard present a comparative study of the effect of methyl bromide and bromine on methane and ethane flames (21). They found that the peak concentration of bromine necessary to prevent flame propagation occurs with stoichiometric flames, while the peak for methyl bromide occurs near the lean limit. The peak concentration of methyl bromide necessary to prevent propagation is almost twice that required for bromine (Fig. 4). From these data it is obvious that the bromine radical is acting as an inhibitor while the methyl radical acts as additional fuel in the flame. Making correction for the additional fuel and defining $\bar{L}$ as the ratio of available oxygen to oxygen required at stoichiometry gives curves which are almost coincident (Fig. 5). This is the most convincing evidence indicating that it is the halogen radical which inhibits the combustion reaction. The data of Simmons and Wolfhard also show that ethane requires a greater percent inhibitor for extinction than methane. This agrees with the observation of Downing on the effect of heat of combustion.

The lack of sufficient information on reaction intermediates and products makes it difficult to postulate a specific mechanism by which inhibitors react in combustion. It has been demonstrated that halogen acids, $HX$, inhibit combustion reactions, probably by a chemical mechanism. Halogenated hydrocarbons, $RX$, may react with hydrogen radicals present in the flame to give $HX$, as:

$$H + RX \rightarrow HX + R^*$$
FIGURE 1 (22)

EFFECT OF METHYL BROMIDE AND BROMINE ON FLAME PROPAGATION LIMITS OF METHANE-AIR FLAMES

--- Methyl Bromide
--- Bromine

Mole Percent Methyl Bromide

Mole Percent Bromine

Percent Oxidant in Mixture

0 4 8 12 16 12 15 12

4 8 12 16 12 15 12
FIGURE 6

EFFECT OF METHYL BROMIDE AND DIBROMINE ON FLAME PROPAGATION LIMITS
OF METHANE-AIR AND ETHANE-AIR FLAMES
RECTIFIED CURVES

Mole percent by vol. or % mole percent, Cl₂ Br₂

L, Available oxygen/oxygen at stoichiometry

0.0  1.0  2.0  0.5  1.0  2.0

CH₂ Br
CH₂ Br
CH₂ Br
CH₂ Br
The effective concentration of the inhibitor is thus increased since HX may further react to inhibit combustion. This is a plausible explanation of the greater effectiveness of halogenated hydrocarbons (22).

Much work is being done to determine reaction intermediates and products. As more data are available, our understanding of specific inhibition mechanisms will be greatly increased.
C. Oxidation Kinetics

1. Procedure

There is no "standard" procedure for studying the effects of inhibitors on oxidation kinetics. Investigators use different equipment; one may use a spherical batch reactor, another a well-stirred reactor, and still another may use a continuous tubular reactor. Each of these vessels has its advantages for studying a particular reaction, however, correlation is difficult because of the lack of information on the wall effects of various reactors.

In general, there are two effects observed when an inhibitor is added to an oxidation process:

1. The induction period is increased.
2. The products of reaction are changed.

It is now accepted that hydrocarbon oxidation reactions proceed by a chain mechanism, i.e., the reaction is started by a chain-initiating step, followed by a long series of chain-propagating steps, which give the majority of products, and finally a chain-ending step by which the reaction is stopped. The induction period is the time required to give enough high energy collisions to start the chain-initiating reaction.

The effect of the inhibitor on the induction period may be due to the absorption of some of the energy necessary for the chain-initiating step. The inhibitor can affect the products by providing a new chain-ending mechanism. This new chain-ending mechanism will have a different energy distribution and thus change the reaction kinetics.
2. Observations

One of the most striking examples of an inhibitor is the behavior of propene in the oxidation of hydrocarbons. At first, it would seem that there is no mechanism by which propene could be an inhibitor, since it in itself is a reactive hydrocarbon. Rice has shown that propene inhibits the oxidation of propane, butane, ethylene oxide and other organic oxidation processes. This work indicates that the propene reacts as a third body to remove radicals, and forms the allyl radical. The allyl radical combines with itself to form the diallyl radical, which is resonance stabilized and, therefore, unreactive. The propene function is then to remove active radicals and substitute relatively inactive species.

Reid has studied the specific effects of propene on the oxidation of propane. His results indicate that the addition of propene to the propane oxidation system decreases the induction period while the rate of the major portion of the reaction is unchanged. This appears contradictory since propene has been established as an inhibitor in propane oxidation by Rice. It is probable, however, that the decreased induction period is a result of the reaction of propene with oxygen as:

\[ \text{C}_3\text{H}_6 + \text{O}_2 \rightarrow \text{C}_3\text{H}_5^+ + \text{HO}_2^+ \]

This reaction would occur before the attack on propane and hence the induction period would be decreased.

Propene had a marked effect on the products obtained from the propane oxidation. Increasing the concentration of propene led to increased yields of aldehydes, and decreased yield of hydrogen peroxide.
Although the yield of hydrogen peroxide decreased, the yield of water and peroxide remained essentially constant. Apparently the propene inhibits the decomposition of aldehydes while accelerating the decomposition of hydrogen peroxide.(25)

Aliphatic amines are efficient inhibitors of hydrocarbon oxidation, however, there has been some difficulty in studying the effect of amines, because they produce complex reactions at the temperatures required for hydrocarbon oxidation. Waddington has studied the effect of amines on diethyl ether-oxygen cool flames. Diethyl ether oxidizes readily around 180°C, and thus the inhibition mechanism of the amine is not obscured by side reactions.(26)

The effect of ethylamine on ignition delay of diethyl ether-oxygen at 193°C is shown in Figure 6. When the amine concentration is less than six percent, ignition is delayed, while above six percent, ignition is prevented. Other work by Waddington indicates that as the temperature is raised, the effect of the amine is decreased. Secondary amines are more powerful than primary amines, while tertiary amines have little effect. For example, the inhibition caused by secondary amines does not decrease so rapidly with temperature as do primary amines, and tertiary amine concentrations above ten percent have little effect on ignition delay.

It has been postulated that the oxidation of diethyl ether proceeds by the following chain reaction:(27)

I. \( \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + \text{O}_2 \rightarrow \text{C}_2\text{H}_5\text{O}^\cdot \text{CHCH}_3 + \text{HO}_2^\cdot \)  
II. \( \text{C}_2\text{H}_5\text{O}^\cdot \text{CHCH}_3 + \text{O}_2 \rightarrow \text{C}_2\text{H}_5\text{O}(\cdot \text{OO})\text{CHCH}_3 \)
Figure 6 (28)

Ignition Delay for a Diethyl Ether-Oxygen-Ethylamine Mixture

75% Oxygen, 25% Diethyl Ether, at 193°C
The addition of an amine to the above reaction scheme may interfere in any of the three reactions. Since there are few reactions of Type I compared to those of Types II and III, it is unlikely that small concentrations of amine would interfere with this reaction. Hence, the amine must be competing with oxygen in reaction II as:

\[
\text{IIa. } C_2H_5OC_2H_5 + C_2H_5NH_2 \rightarrow C_2H_5OC_2H_5 + C_2H_5NH^+.
\]

It is not clear where hydrogen abstraction from the amine takes place, however, there seems to be little difference in inhibitory power on the basis of length of the hydrocarbon chain.\(^{(29)}\) Also, secondary amines which have only one hydrogen connected to the nitrogen are more effective inhibitors, while tertiary amines with no hydrogen attached directly to the nitrogen seem to have little effect on the oxidation process.\(^{(30)}\)

Thus the inhibition by amines seems to depend on the ease with which hydrogen can be abstracted from the molecule. The activation energy of this step must be lower than the normal sequence, and the radical thus formed must be less reactive.

One of the most recent studies of the effect of inhibitors on induction period concerns the effect of inorganic lead compounds.\(^{(31)}\) Tetraethyl lead is a well known anti-knock compound, but its actual mechanism is not well understood. There are several conflicting theories on its effect:

1. Tetraethyl lead is a positive catalyst,--it is an inhibitor.\(^{(32)}\)
2. The organic part of the molecule is responsible for its action,--the metallic portion is responsible.\(^{(33)}\)
3. The reaction is homogeneous,--it is heterogeneous.\(^{(34)}\)
Walsh has postulated that tetraethyl lead acts as an inhibitor by removing \( \text{HO}_2 \) radicals on the surface of \( \text{PbO} \) molecules formed in the flame, however, this theory has been challenged by others. Investigation of the effect of coating a reaction vessel with lead oxide has been studied to determine its effectiveness as an inhibitor. \(^{(35)}\)

The oxidation of \( n \)-butane with air was studied in an uncoated glass tube and one coated with lead tetraoxide, \( \text{Pb}_4\text{O}_4 \), lead chloride, \( \text{PbCl}_2 \), and lead oxide, \( \text{PbO} \). In the uncoated vessel it was found that two cool flames were produced at 300°C, 100 mm total pressure. The first of these occurred after an induction period of 65 sec. and the second after 90 sec. The reaction was completely inhibited in the coated vessels, the rate of pressure change being less than 0.01 mm/min. Raising the temperature to 350°C and the pressure to 200 mm gave a single cool flame. In the uncoated vessel an induction period of 1 sec. was observed; the \( \text{Pb}_4\text{O}_4 \) and \( \text{PbCl}_2 \) coated vessels gave induction periods of 3 sec.; and the \( \text{PbO} \) coated vessel gave an induction period of 130 sec. A plot of cool flame propagation limits is presented in Figure 7. This figure gives the lower limit of the cool flame region, therefore, there is very slow reaction found below these temperatures. \(^{(36)}\)

It is clear from these data that lead oxide is the most effective inhibitor of this group. Similar results for hydrogen and methane have also been reported. Hughes and coworkers, however, found that \( \text{PbO} \) is a positive catalyst for the oxidation of \( n \)-hexane. \(^{(27)}\)

The results obtained with hydrogen, methane, and \( n \)-butane support Walsh's theory on the removal of \( \text{HO}_2 \) radicals by \( \text{PbO} \), but the lack of correlation with \( n \)-hexane causes doubts of this mechanism.
FIGURE 7 (38)

EFFECT OF LEAD SALT ON
COOL FLAME LIMITS OF
n-Butane-Air Mixtures

Total Pressure, mm. Hg
D. Heterogeneous Additives

1. Procedure

There has been little work done on the effect of heterogeneous additives on oxidation processes. Investigators realize that wall effects play an important role in oxidation kinetics, but the exact nature of the mechanism is perhaps the least understood factor in kinetics. There has been no "standard" procedure developed to study the effect of heterogeneous additives. Some authors use apparatus which they have on hand, and develop empirical relations on the effect of the additive. Others investigate a specific effect of the additive. It has not been possible to successfully correlate the work found in the literature because of these difficulties.

2. Observations

Palmer has investigated the effect of wire gauzes on flame propagation.(12) The apparatus used was a standard combustion chamber used to study flame properties, i.e., a glass tube 2½ in. diameter, and 4½ ft. long. The tube was cut into two sections, the shorter was 23 in. long. The wire gauze was sandwiched between the two sections. Provision was made to allow the flame to be ignited from either end. Several runs were made with each mesh size, at various flame velocities. The data are then presented graphically (Fig. 8), indicating at what flame speed the wire gauze prevented further flame propagation. Several mesh sizes and materials were used.
When the flame was arrested by the gauze, little damage was done to the mesh. If the flame passed through the gauze, little damage resulted to coarse gauze, however, the fine gauzes were destroyed and those of intermediate coarseness were often split. The destruction of the gauze was usually accompanied by the emission of light from the molten metal.

The data indicate that for each set of experimental conditions, there was a certain critical velocity below which the flame propagated through the gauze and above which it was arrested. When the logarithm of flame velocity is plotted against the logarithm of mesh width, a straight line can be drawn to separate the values for which the gauze quenched the flame and the values for which the flame propagated through the gauze. The critical flame velocity may be calculated from an equation of the form:

\[ V_c = \frac{C}{m^n} \]

where: \( V_c \) is the critical value of the flame velocity
\( m \) is the mesh width
\( C \), and \( n \) are constants

For the plot for propane flames, the values of \( C \) and \( n \) are 30 and 1.00, respectively. Results of several experiments indicate that the most important single factor in quenching is the speed with which the flame approaches the gauze.

If it is assumed that the gauze quenches the flame by removing sufficient heat to drop the temperature below that critical for reaction, an equation of the form given above can be derived. By taking a thickness, \( x \), in the flame, the total amount of heat removed from this volume
by a unit area of gauze is:

\[ q = hA\Delta T(x/V_c) \]

where:
- \( q \) is the total heat absorbed per unit area of gauze
- \( h \) is the heat transfer coefficient
- \( A \) is the area of the gauze
- \( \Delta T \) is the temperature difference between the flame and gauze
- \( V_c \) is the critical flame velocity

The value of \( h \) is given by the Nusselt number: \( \text{Nu} \)

\[ \text{Nu} = hD/k = \text{constant} \]

thus, \( q = k\text{Nu}A\Delta T/D(x/V_c) \)

or, \( V_c = k\text{Nu}A\Delta Tx/qD \)

or, \( V_c = K'/D \)

Where \( D \) is the effective diameter of the wire gauze.

It is probable in view of the above development that the effectiveness of wire gauzes depends on their ability to abstract heat from the flame. There may be other mechanisms, but these are not obvious from the work of Palmer.

Dufraisse and German have studied the effect of several powders on the flames of hydrogen, illuminating gas, methane, and carbon monoxide. They felt that in their work, the small quantities of material used probably had little effect on the cooling or dilution of the flame. They found that those substances most sensitive to heat (e.g., sodium and potassium chlorates) acted as positive catalysts for flames of illuminating gas and hydrogen, while inhibiting flames of methane and carbon monoxide. Those substances less sensitive to heat (e.g., sodium and potassium nitrates) extinguished all of the flames.
<table>
<thead>
<tr>
<th>Additive</th>
<th>Hydrogen</th>
<th>Illuminating Gas</th>
<th>Methane</th>
<th>Carbon Monoxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaHCO₃</td>
<td>0.70</td>
<td>0.45</td>
<td>0.10</td>
<td>0.30</td>
</tr>
<tr>
<td>KHCO₃</td>
<td>0.25</td>
<td>0.10</td>
<td>----</td>
<td>0.03</td>
</tr>
<tr>
<td>KClO₃</td>
<td>**</td>
<td>**</td>
<td>0.05</td>
<td>0.005</td>
</tr>
<tr>
<td>NaClO₃</td>
<td>**</td>
<td>**</td>
<td>0.15</td>
<td>0.05</td>
</tr>
<tr>
<td>KClO₄</td>
<td>**</td>
<td>**</td>
<td>0.08</td>
<td>0.03</td>
</tr>
<tr>
<td>KNO₃</td>
<td>0.45</td>
<td>01.0</td>
<td>0.015</td>
<td>0.008</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>0.55</td>
<td>0.25</td>
<td>0.05</td>
<td>0.04</td>
</tr>
</tbody>
</table>

For those flames marked **, the additive acts as a positive catalyst.
tested. Those substances which decomposed into inerts (e.g. $2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$) were poor inhibitors, their action probably depending on the dilution of the flame.

The results were interpreted by the authors to mean that there is some specific antioxidant catalysis reaction taking place with those substances which extinguish the flame. This conclusion cannot be justified solely on the basis of the data given. The authors have given no indication of the particle size of the powders used. It is possible that any of these results can be readily explained as merely a surface effect, that is, the removal of free radicals on the surface of the particles. This mechanism is apparently favored in the work of Laffitte.

Recently Laffitte and Bouchet have investigated the suppression of detonations by means of fine powders. In their first series of experiments, they allowed the flame to propagate through a tube in which they placed a small quantity of the finely powdered inhibitor. They found that, using potassium oxalate of 25 μ particle size, the flame could be suppressed in the pre-detonation period, when its velocity was less than 450 meters per second.

The most probable reason that the detonation could not be suppressed is that the powder was incompletely mixed in the flame. At low flame speeds, the shock wave proceeds the flame front by a sufficient distance to mix the pile of dust with the combustion gases. As the speed of the flame increases, the distance between the shock wave and the flame front decreases, thereby, preventing complete
mixing of the particles with the combustion gases. (45)

To overcome this difficulty in the next series of experiments, the dust was dropped into the combustion tube and a cloud formed as the particles were under the influence of gravity. Using silica and potassium chloride, it was found that the minimum quantity of material required is inversely proportional to the surface area of the particles. Table III shows the minimum quantity of material required to extinguish a detonation. Comparing this to the work of Dufraisse, (Table II) it appears that the order of increasing effectiveness for suppression of a detonation is totally different from that of a non-detonating flame.

Since this work does not readily correlate with the results obtained by Dufraisse, it is obvious that his conclusion that suppression is related to antioxidant catalysis does not give a complete explanation of the phenomena of suppression by fine powders. Work presently being done by Laffitte concerns the relation between suppression properties and the thermal energy developed in the flame. This may give a more satisfactory explanation of the mechanism actually controlling.
TABLE III (46)

EFFECT OF VARIOUS POWDERS ON METHANE DETONATIONS

<table>
<thead>
<tr>
<th>Additive</th>
<th>Grams Required for Extinction</th>
<th>Total Surface Area, cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>0.825</td>
<td>3,260</td>
</tr>
<tr>
<td>KCl</td>
<td>2.150</td>
<td>6,000</td>
</tr>
<tr>
<td>KHCO₃</td>
<td>0.835</td>
<td>3,470</td>
</tr>
<tr>
<td>K₂C₂O₄</td>
<td>0.920</td>
<td>4,800</td>
</tr>
<tr>
<td>K₂C₄H₄O₆</td>
<td>0.460</td>
<td>3,520</td>
</tr>
<tr>
<td>Na₂C₂H₄O₆</td>
<td>0.930</td>
<td>6,900</td>
</tr>
</tbody>
</table>

All additives are of the same particle size, 10-20 μ.
III. Appendix

Literature Citations


(6) Ibid. 181.

(7) Ibid. 183.


(29) Ibid. 169.

(30) Ibid. 167.


(36) Ibid. 73.


(40) Ibid. 497.


(43) Ibid. 1223.


(45) Ibid. 505.

(46) Ibid. 506.